AEROSOL RESEARCH BRANCH, ANNUAL REPORT FY 1976/76A

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U S. Environmental Protection Agency, have been grouped into nine series These nine broad categories were established to facilitate further development and application of environmental technology Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials Problems are assessed for their long- and short-term influences Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments

AEROSOL RESEARCH BRANCH
ANNUAL REPORT FY 1976/76A

Edited by
William E. Wilson and Christine Danskin
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The research program of the Aerosol Research Branch includes research grants and contracts at institutions in many parts of the United States, in addition to an intramural program. The purpose of these projects is to study the chemical and physical properties of aerosols, identify the mechanisms of aerosol formation and removal, and conduct experiments to measure these rates.

The results of the research are being used (1) to establish the contribution of the various sources to the ambient atmospheric aerosol loading, (2) to characterize urban, natural, and primary and secondary aerosols, (3) to develop quantitative descriptions of the generation and removal rates associated with each major aerosol source and sink, (4) to quantify the effects of aerosol on atmospheric chemical reactions, and (5) as a scientific basis for recommending regulatory actions concerned with air quality improvements.

In addition to base funding through EPA's Office of Research and Development, the Aerosol Research Branch (ARB) also receives funds from the Federal Interagency Energy/Environment Research and Development Program. This program is coordinated by the Office of Energy, Minerals, and Industry, Dr. Steven Gage, Deputy Assistant Administrator. The tasks conducted by ARB under this program relate to the transport and fate of pollutants associated with energy sources.

Tasks funded by the Energy/Environment program are not described in this report but are listed by title and principal investigator. The FY 1976/76A annual report of the energy program is found in EPA Report 600/7-77-076.

CONTENTS

5. Technique Development

Appendices

ABBREVIATED FUNCTIONAL STATEMENTS

The Environmental Sciences Research Laboratory (ESRL) conducts research programs in the physical sciences to detect, define, and quantify the effects of air pollution on urban, regional, and global atmospheres, and the subsequent impact on air and water quality and land use. ESRL is responsible for the planning, implementation, and management of research and development programs designed to quantitate the relationships between emissions of pollutants from all types of sources, air quality, and atmospheric effects. ESRL also plans, implements, and manages a research and development program to provide needed techniques and instrumentation for the measurement and characterization of pollutants in the ambient air and in the emissions from all types of sources. ESRL's research and development program consists of grants, contracts, and in-house work.

The Atmospheric Chemistry and Physics Division (ACPD) conducts research programs (1) to characterize the chemical and physical properties of ambient air pollutants and (2) to relate quantitatively the chemical and physical properties of emissions from mobile, stationary, and natural sources to the effects on air and water quality and land use. ACPD also develops techniques and instrumentation for the measurement and characterization of gaseous and aerosol pollutants.

The Aerosol Research Branch (ARB) studies the chemical and physical properties of aerosols, identifies the mechanisms of aerosol formation and removal, and conducts experiments to measure these rates. The properties of atmospheric aerosols are related to health and welfare effects for the purpose of selective control of pollutant sources.

ACKNOWLEDGEMENTS

1. INTRODUCTION

The Aerosol Research Branch (ARB), as part of the Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency, administers an extramural research program consisting of grants and contracts at institutions in many parts of the United States. In addition to the extramural program, ARB conducts a modest in-house program. Since the major responsibility of ARB is to conduct an extramural research program, the in-house program is designed to support the extramural program. It has three major functions: 1) to provide rapid-response capability to respond to agency needs, 2) to test out concepts prior to establishing extramural programs, and 3) to maintain the scientific competence of the EPA project officers. It is considered extremely important that the scientific competence and reputation of ARB's project officers be such that grant and contract principal investigators consider them as scientific peers rather than funding clerks.

This progress report presents results of tasks active during fiscal years 1976 and 1976A. The reports have been classified into projects as shown in the Summary of Aerosol Research Branch Fiscal 1976 Program by Project. ARB tasks funded through the Federal Interagency Energy/Environment Research and Development Program are listed by Title and Principal Investigators in the Appendix. The Appendix also includes a Publications, Presentations, and Thesis Listing. The Publications List includes only EPA funded research authored by the investigators funded through the Aerosol Research Branch. Following the listing is an Authors Index. To find a particular author's work in the Publications List first find the author's name in the Index and then turn to the Publications List.

2. SUMMARY OF AEROSOL RESEARCH BRANCH
FISCAL YEAR 1976 PROGRAM BY PROJECT

Project MISTT   (Midwest Interstate Sulfur Transformation and Transport)

A study of pollutant transformations and removal during atmospheric transport over various scale lengths.
Urban scale (50 km): Tracer and portable chamber studies.
Power plant plumes (250 km): Aircraft measurements.
Urban plumes (500 km): Aircraft and ground measurements.
Blobs (2000 km): Weather Service visibility reports and a ground network of 14 stations extending from eastern Kansas to New England.
Model Development and Data Analysis.

Funded by the Federal Interagency Energy/Environment Research and Development Program through USEPA, ORD, OEMI. Program Element 1NE625.

Auto-Exhaust Catalyst Program

Determination of chemical and physical properties of sulfuric acid aerosol produced by automobile catalysts.

Funded by USEPA, ORD, OHEE. Program Element 1AA601.

Atmospheric Processes and Effects

Aerosol Formation, Growth and Removal. Identification of physical and chemical mechanisms for aerosols processes in the atmosphere, measurement of important rate constants, and development of models for formation, growth and removal of atmospheric aerosols.

Aerosol Characterization and Sources. The utilization of physical properties, elemental and chemical analyses, and microscopy for the characterization of atmospheric aerosols and the use of this information to determine the primary and secondary source contributions to urban pollution.

Visibility and Radiation Effects. Measurement of pertinent aerosol properties and determination of relationships between concentration, composition, size and effects.

Heterogeneous Reactions. Measurement of the rates and mechanisms of reactions involving gases with surfaces or condensed phases.

Technique Development. Development of new instruments or techniques required for the aerosol research program.

Funded by USEPA, ORD, OALWU. Program Element 1AA603 and 1AD712.

A. ATMOSPHERIC PROCESSES AND EFFECTS

1. Aerosol Formation, Growth, and Removal. Identification of physical and chemical mechanisms for aerosols processes in the atmosphere, measurement of important rate constants, and development of models for formation, growth and removal of atmospheric aerosols.

1. Task Title: Formation of Atmospheric Aerosols - Parametric Measurement of Submicron Atmospheric Aerosols

2. Objective:

    To develop and validate a method for calculating the submicron size distribution of atmospheric aerosols from three integral measurements on the aerosol, namely, concentration nuclei count, electric charger current, and the response of an integrating nephelometer.

3. Institution: University of Minnesota, Minneapolis, Minnesota
    Investigator: K.T. Whitby

4. EPA Project Officer: W.E. Wilson

5. Progress:

    Studies by G.M. Sverdrup were conducted in order to determine how many aerosol parameters must be measured to adequately specify the number, surface, and volume weightings of a submicron atmospheric aerosol size distribution. A constraint placed upon the instrumentation was that all instruments must operate in a continuous mode. This eliminated the need for bag samples in order to accommodate instruments' long sampling periods.

    A minimum of three instruments (e.g., condensation nuclei counter, aerosol charger, and nephelometer) are necessary to obtain significant information about the entire submicron size spectrum. Figure 1 shows the sensitivities of the three instruments as a function of particle size for a family of size distributions. The areas under the three curves are equal to the total number concentration (N), the total current from the charged aerosol (I) and the aerosol light scattering coefficient (bsp). The nuclei counter and aerosol charger sensitivities were experimentally determined. The nephelometer sensitivity was calculated from Mie theory.

    The submicron size distribution was determined by calculating the expected values of N, I, and bsp, using a bimodal log-normal size distribution model. Three of the log-normal function parameters were held fixed while the other three were varied. The difference between the theoretical and measured values of N, I, and bsp were minimized until these differences were within the instrument uncertainty for all three instruments.

    Figure 2 shows plots of a comparison between the size distributions obtained from the minimization procedure and the measured size. The difference in total number concentration is zero due to the minimization. The difference in total surface concentration is 0.4%, in total volume 13%. These differences are due to instrument uncertainty.

6. Publications, Presentations, Theses:

    1. Sverdrup, G.M. Parametric Measurement of Submicron Atmospheric Aerosols. Ph.D. Thesis. Submitted to: Mechanical Engineering Department, University of Minnesota. November 1976.

7. Plans:

1. The procedures developed in this task will be applied to data acquired during the 1976 summer MISTT projects. The results will be compared with actual size distributions measured with the Minnesota Aerosol Analyzing System.
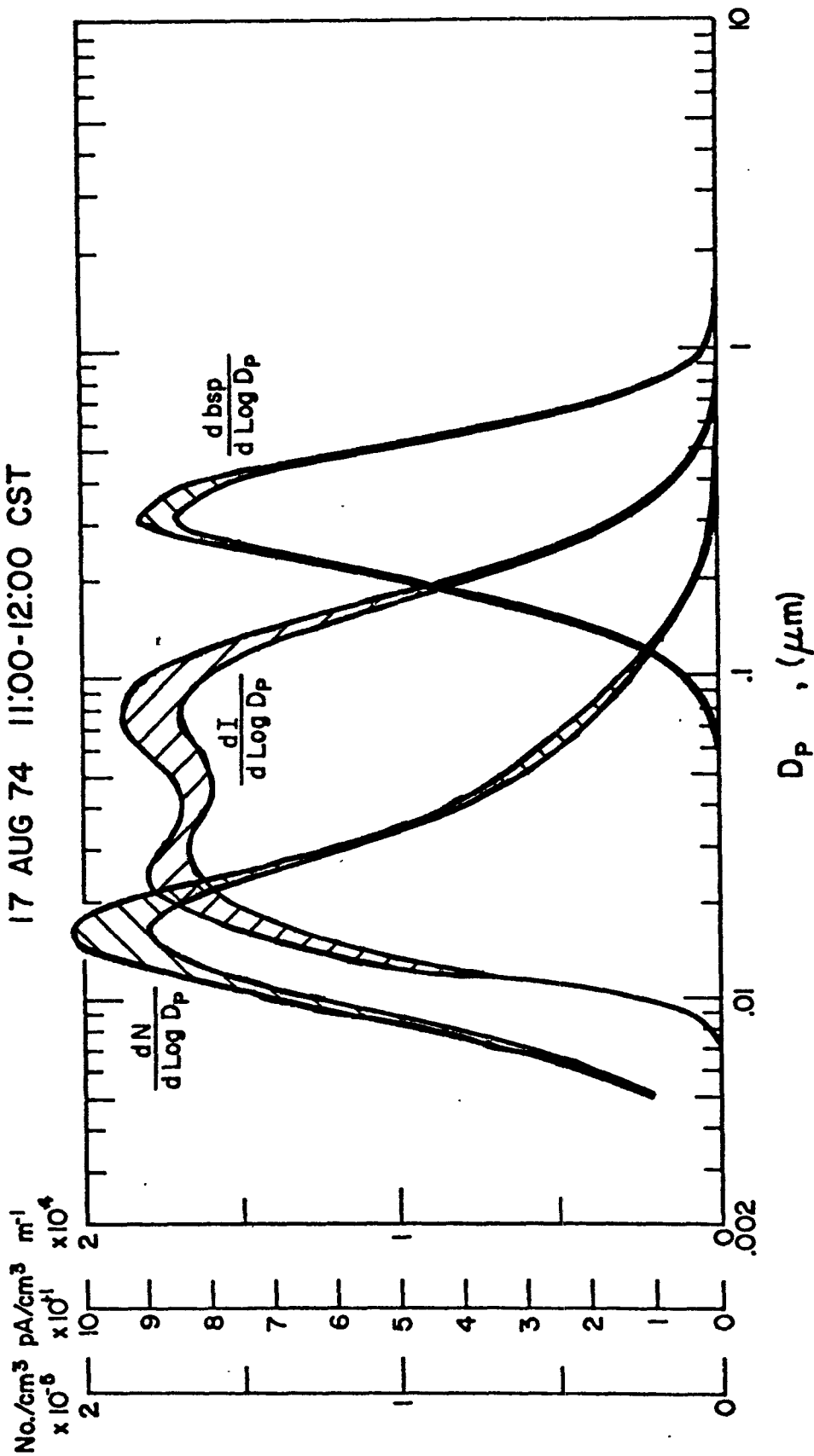
Figure 1. The sensitivity of a condensation nuclei counter (N), an aerosol charger (I), and an integrating nephelometer (bsp) as a function of particle size for a family of typical aerosol size distributions.
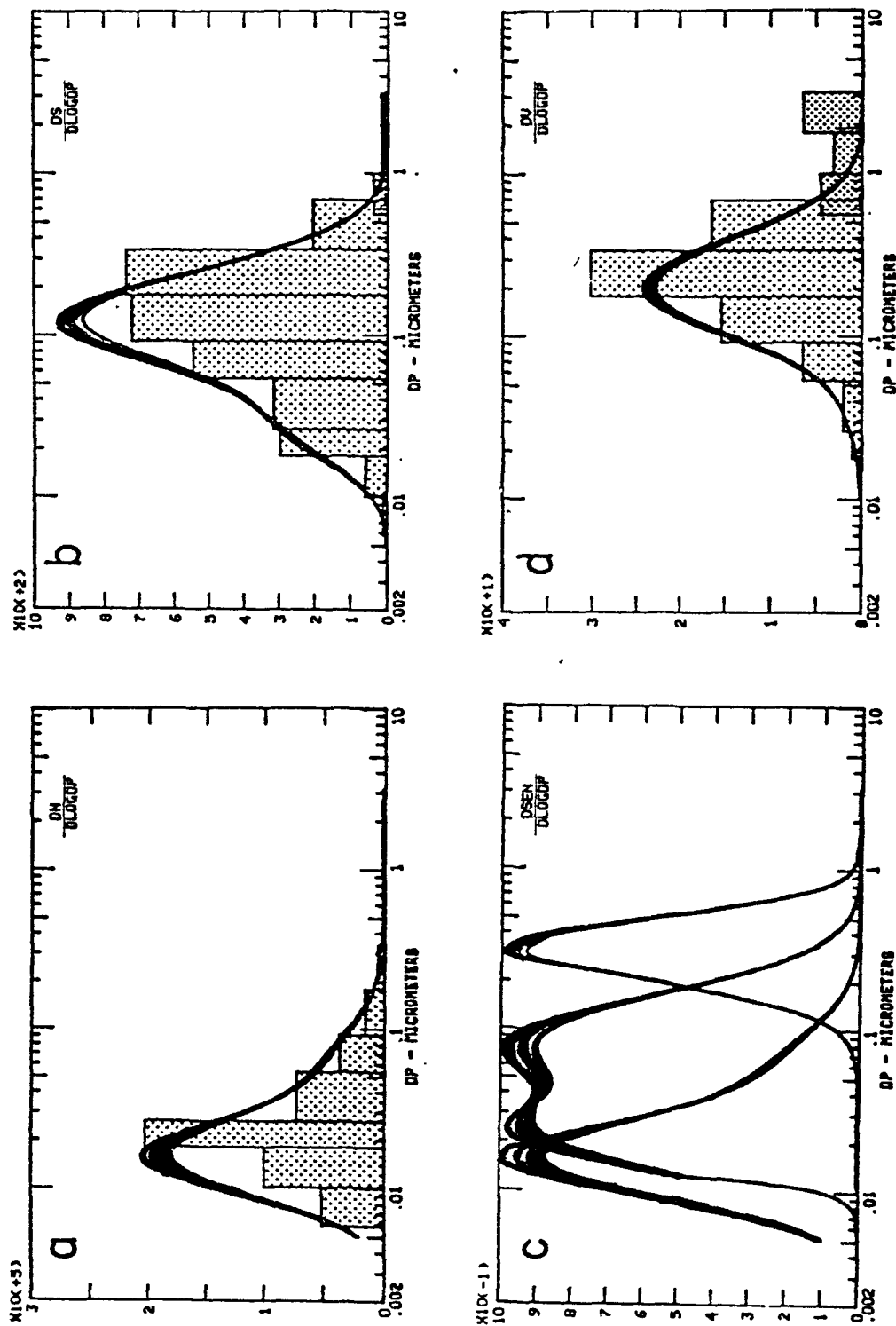
Figure 2. A comparison between the parametric measurement determined by a computer minimization routine and the direct size distribution measurement for three size distribution weightings.

1. Task Title: Investigate the Atmospheric Contribution of Biogenic
                Sulfur to the Urban Load of Sulfur Aerosols

2. Objective:

   To investigate the atmospheric contribution of biogenic sulfur
   to the urban load of sulfur aerosols.

3. Institution: Hitchcock Associates
   Investigator: Diane Hitchcock

4. EPA Project Officer: L.L. Spiller

5. Progress:

   The existence of "natural" biogenic sulfur contributions to the
   atmosphere has been recognized for some time, but estimates of the
   strength of these natural sources or their distribution is virtually
   unknown. Little useful information exists for assessing the claim
   that biogenic S sources can contribute significantly to the load of
   gaseous or particulate S in urban sites, or to the non-urban load
   ("background" level).

   Many biological processes produce volatile sulfur compounds, and
   may be responsible for biogenic S emission. The most important of
   these processes appears to be the metabolism of the bacterial sulfate
   reducers--chiefly of the species Desulfovibrio desulfuricans. These
   organisms are obligate anaerobes and inhabit aquatic environments
   where oxygen is absent. They use dissolved sulfate as a source of
   oxygen in the oxidation of available organic matter, producing H_2S
   as a metabolic by-product.

   H_2S production by bacterial sulfate reducers may proceed at an
   extremely rapid rate under suitable conditions. Field studies and
   laboratory experiments show that rates of 50 to 100 metric tons per
   km^2 per yr may be common in suitable habitats. But no quantitative
   data exist, and very few measurements have been made of atmospheric
   sulfides near sites where sulfate reduction is active.

   Included are preliminary results of a field study designed to
   survey the distribution of atmospheric biogenic sulfur compounds near
   sites where they are produced.

   Atmospheric reactive sulfides and sulfur dioxide were measured in
   a tidal marsh near Morehead City, North Carolina. $AgNO_3$ and LiOH
   impregnated millipore filters were used for collecting the samples,
   and analyzing for elemental S by means of X-ray fluorescence spectro-
   scopy. Sample collection intervals of 12, 6, and 4 hours were synchro-
   nized with tidal movements in order to observe the relationship between
   exposure of the heavily organic H_2S-rich muds at low tide, and the level
   of sulfide in the atmosphere. Similarly synchronized 12 and 6-hour
   samples were collected at a control site, a two-story building roof top
   on the shore of Bogue Sound, approximately 1.5 miles from the marsh site.

Sulfide levels in the marsh averaged 4.6 ppb over the 13-day field study. A strong dependence on the tidal cycle was revealed by the 4-hour samples taken at successive high and low tides. Sulfide was rarely detected during high tide, and did not exceed 2 ppb. Low-tide levels ranged from 2 to 57 ppb and averaged 10 ppb. The highest levels were observed at night when local wind movements were minimal. At night, the 10-tide sulfide levels averaged 5.5 m sec^{-1}. Attempts to detect sulfides in the air at the control site were generally unsuccessful. Of 26 12-hour samples, only 4 showed detectable levels of sulfides, and these did not exceed 1.5 ppb. (Fig. 1)

A second set of measurements was made in November to determine whether biogenic S is present in the atmosphere at sites where no H_2S-rich muds are exposed during the tidal cycle, but where reducing sediments occur under water. Measurements were made for 24 and 6-hour intervals at 3 sites, 25 to 30 miles from any sources of anthropogenic SO_2. One of these sites is at the Coast Guard Station at Bogue Inlet on Bogue Banks, and the others are a few miles north on White Oak River. Sulfide-rich muds occur at both the latter sites, but are never exposed by the tide. No sulfide-rich muds occur near the Coast Guard site, but some exist inside the sound. (Water from the sound passes through the inlet four times daily, and it may contain H_2S derived from bottom sediments). The results showed higher levels of atmospheric sulfur than originally anticipated, with sulfide levels ranging from 0.5 to nearly 5 ppb; SO_2 ranged from below detection limits to over 20 ppb. The means were 1.5 to 1.9 ppb sulfide: 4.5 to 4.8 ppb SO_2. Wind speeds were usually very high, and temperatures abnormally cold for this time of year. The atmospheric S is biogenic, and we infer that it is derived from the marine muds near the monitoring sites, although fresh-water swamps in surrounding woods cannot be ruled out.

6. Publications, Presentation, and Theses: None.

7. Plans:

1. This survey will be repeated and extended with the following changes in measurement procedures:
a) sulfide measurements with durations from one to two hours; b) measurements of SO_2 by means of a Meloy #FA-285 at best possible sensitivity (1 ppb), with short integration time (2 sec.); c) measurement of ozone and possibly other potential oxidizers.

2. Studies will be conducted at the same sites as in 1976 and at a new site. The new site will be a brackish water site further inland, with little tidal flushing and less sea water sulfate.

16

NIGHT

14

LOW TIDE

12

HIGH TIDE

10

8

DAY

6

4

2
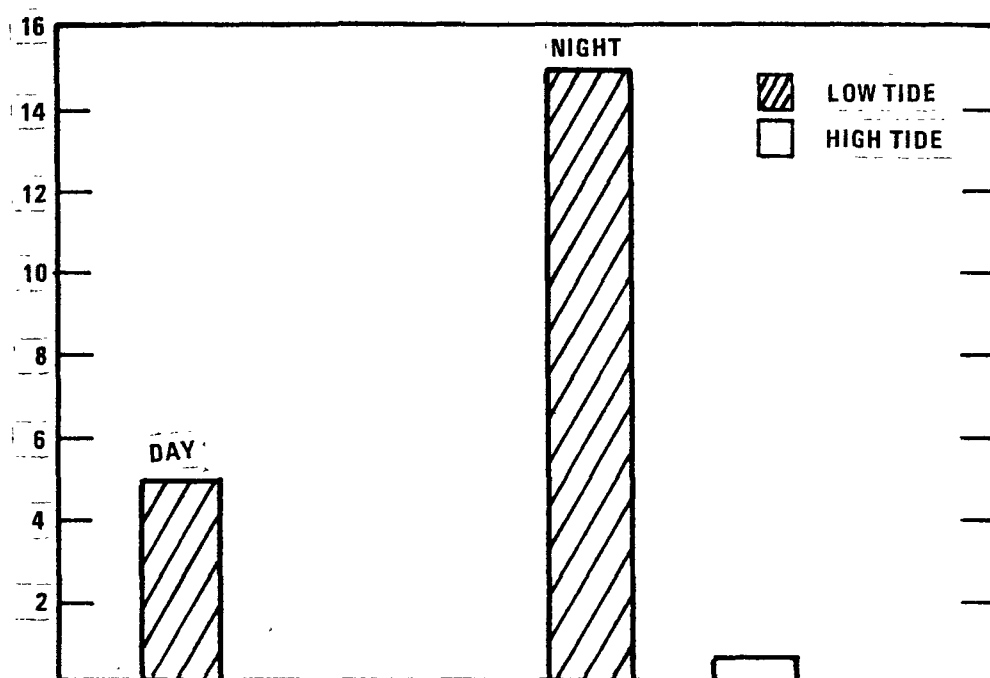
Figure 1. (Note – These numbers are 5 ppp, 0,15 ppb and 1.4 ppb)

1. <u>Task Title</u>: Experimental Study of Aerosol Formation Mechanisms in a Controlled Atmosphere.

2. <u>Objective</u>:

   To conduct experiments in a large outdoor chamber to obtain data for modeling purposes on aerosol formation mechanisms from chemical systems containing sulfur.

3. <u>Institution</u>: University of North Carolina at Chapel Hill, Chapel Hill, North Carolina
   <u>Investigator</u>: D.L. Fox

4. <u>EPA Project Officer</u>: J.L. Durham

5. <u>Progress</u>:

   An investigation of photochemical systems containing hydrocarbons, oxides of nitrogen, and sulfur dioxide has been conducted with the use of a long-path infrared (LPIR) -fourier transform spectrometer (FTS). This instrument has been successfully operated in situ in the outdoor chamber and has provided the analytical capability to measure gas phase product concentrations of some species not ordinarily measured in smog chamber experiments (e.g., formic acid and peroxyacyl nitrate). In propylene, NO_x, and SO_2 systems, SO_2 oxidation increases during the NO-NO_2 crossover region; the same region where modeling predicts an increased flux of free radicals to be present. Computer modeling of these systems has been improved by knowledge of the product concentrations measured through the course of an experiment by the LPIR-FTS system.

   In the presence of sunlight, sulfur dioxide in ambient air will be oxidized to form sulfuric acid aerosol. One mechanism in this conversion process is thought to be hydroxyl radical (OH) attack on SO_2, which results in the formation of H_2SO_4 vapor. Then the acid vapor either condenses on existing particles or nucleation of new particles occurs in the presence of water vapor. Results from the outdoor chamber show the occurrence of both of these gas-to-particle conversion mechanisms under certain conditions. When SO_2 in background air is subjected to sunlight of variable intensity, fluctuations in the condensation nuclei count correspond to variations in sunlight intensity caused by clouds temporarily blocking the sun. Measurements of particle size distribution as a function of time, show the formation of fine particles as the intensity of sunlight increases rapidly. These observations are consistent with the hypothesized OH attack on SO_2. Hydroxyl radical concentrations will vary with changes in light intensity. When SO_2 concentrations are changing very slowly with time, the conversion rate is primarily dependent on fluctuations in OH concentration.

   The activity of H_2SO_4 in the gas phase controls the pathway for gas-to-particle conversion. At a certain level of activity H_2SO_4 will nucleate even in the presence of existing particle surface area. This phenomena has been observed with rapid changes in sunlight.

Aerosol samples have been collected on glass fiber and membrane filters, and elemental analysis of the collected particles have been performed using X-ray fluorescence. The X-ray fluorescence data and the data from an electrical aerosol analyzer allow estimation of the composition of the evolving aerosol as a function of time, relative humidity and other parameters of interest. Comparison of the mass of sulfur appearing in the aerosol particles with that lost from the gas phase also is an aid in the determination of the sulfur budget for the environmental system. Since X-ray fluorescence is non-destructive, further analysis of the same samples is possible, thus providing a reference against which results of other methods can be compared.

6. Publications, Presentation and Theses:

1. Fox, D.L., J.E. Sickles, M.R. Kuhlman, P.C. Reist and W.E. Wilson. 1975. Design and Operating Parameters for a Large Ambient Aerosol Chamber. J. Air Poll. Cont. Assoc. 25:1049-1053.

2. Fox, D.L., M.R. Kuhlman and P.C. Reist. 1976. Sulfate Aerosol Formation Under Conditions of Variable Light Density. Proceedings of International Conference on Colloids and Interfaces. Academic Press. In Press.

3. Reist, P.C., W. Marlow and G. Dwiggins. 1976. Aspects of the Performance of the Electrical Aerosol Analyzer Under Nonideal Conditions. J. Aerosol Sci. In Press.

4. Wright, R.S. 1976. M.S. Thesis. Feasibility Study for the Use of a Long-Path Infrared Spectrometer in an Outdoor Chamber.

5. Dwiggins, G.A. 1976. M.S. Thesis. The Effect of Trace Gaseous Constituents in the Air on Data from the Electrical Aerosol Size Analyzer.

7. Plans:

1. To continue studies in outdoor chamber on sulfate aerosol formation.

2. An exploring wire generator will be used for studies of the effect of pre-existing nuclei on aerosol growth.

1. Task Title: Formation of Atmospheric Aerosols - Smog Chamber Research.

2. Objective:

   To study the formation and growth of aerosols formed from the photo-oxidation of mixtures of SO_2, hydrocarbons, and NO_x.

3. Institution: University of Minnesota, Minneapolis, Minnesota
   Investigator: K.T. Whitby

4. EPA Project Officer: W.E. Wilson

5. Progress

   Studies by Kittelson and his students have been made of mixtures of NC + NO + SO_2 in the University of Minnesota's 18 m^3 smog chamber.

   Analysis of hydrocarbon + NO + SO_2 experiments has shown a very close coupling between aerosol and chemical behavior. Disappearance of NO and onset of O_3 formation are accompanied by a sudden increase in the rate of aerosol formation and a broadening of the aerosol size distribution.

   Measurements have been made by Kwok of wall losses in the 18m^3 smog chamber. Under typical sampling conditions the bag surface-to-volume ratio is 2.2 m^{-1}, and the first order wall loss constant is 0.19 hr.$^{-1}$.

   The chamber lights were upgraded to double the current light intensity of k_{dNO_2} = 0.2 min^{-1}.

6. Publications, Presentations, Theses:

   1. Kwok, Kui-Chiu. 1975. Coagulation and Wall Losses in a Smog Chamber. M.S. Thesis. Mechanical Engineering Department, University of Minnesota, MN.

   2. Kocmond, W.C., D.B. Kittelson, J.L. Yang and K.L. Demerjian. 1975. Study of Aerosol Formation in Photochemical Air Pollution. EPA-650/13-75-007.

   3. Kocmond, W.C., D.B. Kittelson, J.L. Yang, K.L. Demerjian and K.T. Whitby. 1975. Aerosol Formation in Simple Photochemical Systems. Environ. Sci. and Tech.

   4. Kocmond, W.C., D.B. Kittelson, J.L. Yang and K.L. Demerjian. Determination of Formation Mechanisms and Composition of Photochemical Aerosols. Calspan Corp., Buffalo, NY. August 31, 1973.

   5. Clark, W.E. and K.T. Whitby. 1975. Measurement of Aerosols by the Photochemical Oxidation of SO_2 in Air. J. Colloid Interface Sci. 51:477-490.

7. Plans: 1. To write papers and reports.

1. Task Title: Smog Chamber Study of Sulfur Dioxide Oxidation and Aerosol Formation Mechanisms.

2. Objective:

    To assess the SO_2 oxidation rates and mechanisms under varying ambient environments.

    To investigate chemical and aerosol behavior under homogeneous photo-oxidation conditions.

    To study surface and droplet catalytic effects on SO_2 oxidation as might be expected under in-cloud transformation and power plant plume conditons.

3. Institution: Calspan
    Investigator: W.C. Kocmond
                   J.Y. Yang

4. EPA Project Officer: B. Dimetriades

5. Progress:

    The Calspan smog chamber facility consists of a cylindrical chamber, 30 feet (9.14 meters) in diameter and 30 feet (9.14 meters) high, enclosing a volume of 20,800 ft^3 (590m^3). The inner chamber surface is coated with a fluoroepoxy-type urethane, which has surface energy and reactivity properties comparable to those of FEP Teflon. Illumination within the chamber is provided by 28.6kw of fluorescent blacklight and sunlamps installed inside 24 lighting modules and arranged in eight vertical channels attached to the wall of the chamber. Measured light intensity, using the k_d [NO_2] method reported by Stedman and Niki (1973), is $k_d \sim 0.35$ min^{-1}. Varying light intensities can be provided by selectively turning off some of the light modules and lamps. Air purification within the chamber is accomplished by recirculating the air through a series of absolute and activated carbon filters.

    To date over 60 experiments have been conducted using systems ranging from SO_2 in clean air, to irradiations of auto exhaust + NO_x + SO_2. A number of preliminary experiments have also been performed using the laboratory cloud + SO_2 system. Numerous tests were conducted to examine aerosol collection methods and sulfate analysis techniques. From an analysis of the smog chamber aerosol and chemistry data, the following points can be made:

    1. The SO_2 photooxidation rate in hydrocarbon + NO_x polluted air is accelerated over that for the SO_2 + clean air systems, and generally lies in the range of 1 to 3% hr^{-1}. Results of sulfate analysis show that the SO_2 photooxidation rate during the accelerated growth period is about 2.3% hr^{-1} for the propylene + NO_x + SO_2 system, and approximately 1.5% hr^{-1} for the cyclohexene + NO_x + SO_2 system.

    2. Total aerosol production is greatly accelerated in the propylene or cyclohexene + NO_x + SO_2 reaction systems over that observed for the HC + NO_x system alone. The measured maximum rate of aerosol formation was 20 times greater for the propylene + NO_x + SO_2 test mix compared to the propylene + NO_x system without SO_2. Comparison of the aerosol volume production data in these two systems suggests that organic aerosol formation may be

enhanced due to the presence of SO_2.

3. For the auto exhaust + SO_2 experiments, the average photooxidation rate of SO_2 as determined from chemical analysis was about the same for all experiments, with or without combustion nuclei. In these experiments, however, a HC/NO_x ratio of about 6:1 was used and NO disappearance did not occur in less than about six hours. During this lengthy period, any effects of the combustion nuclei on subsequent aerosol formation presumable would have been obscured. Additional tests of shorter duration are recommended to permit the determination of R_{SO_2} after NO oxidation is completed and appreciable ozone has been formed. Ratios of HC/NO_x of about 15:1 will be needed to significantly accelerate the NO oxidation process.

4. Initial particle concentrations were an order of magnitude higher for the auto exhaust tests using leaded fuel in comparison to tests with non-leaded fuel. Once irradiation was started, the maximum particle concentration and rate of aerosol production were also higher for the leaded fuel cases.

5. The chemical (barium perchlorate titrations) and aerosol (EAA data) methods for determining R_{SO_2} were only comparable during the initial stages of the auto exhaust experiments. Later, the EAA analysis was higher, suggesting that the aerosols thus formed were of a mixed nature (i.e. organics, nitrates and sulfates).

6. The largest amount of light-scattering aerosol was formed in the leaded fuel auto exhaust experiments.

7. Procedures have been established for producing realistic clouds within the Calspan smog chamber for studies of in-cloud SO_2 to sulfate transformation.

8. Efforts directed toward obtaining reliable aerosol samples and establishing usable analysis procedured for determining sulfate content are still in progress. Plans for the immediate future call for aerosol sampels to be analyzed for total sulfur at EPA using X-ray fluorescence and liquid ion chromatography. A portion of each sample will also be analyzed at Calspan using the barium perchlorate titration technique.

9. Auto exhaust + SO_2 and in-cloud SO_2 to sulfate transformation studies will be resumed when reliable sampling and analysis procedures are developed and verified.

6. Publications, Presentations and Theses: None.

7. Plans:

1. To study reaction rates of sulfur dioxide with auto exhaust and water droplets.

1. <u>Task Title</u>: Study of Vapor Pressures of Systems Forming Atmospheric Aerosols

2. <u>Objective</u>:

   To measure basic physical properties of certain multicomponent fluid mixtures along the equilibrium phase separation curves. The systems chosen are those involved in the formation of secondary atmospheric aerosols, with particular emphasis on the sulfuric acid-water mixture.

3. <u>Institution</u>: Clark College, Atlanta, Georgia
   <u>Investigator</u>: G. Brown

4. <u>EPA Project Officer</u>: W.E. Wilson

5. <u>Progress</u>: The laboratory for this project has been constructed and is essentially complete. The apparatus is designed to determine the total vapor pressure over bulk fluid mixtures by both capacitance manometer and ion gauge measurements.

   The composition of the vapor above the bulk mixtures is determined with the use of a time-of-flight mass spectrometer. If the initial chemical composition of the samples is not significantly affected by chemical reactions, this latter measurement can be converted to equilibrium partial pressures for the various constituents of the mixtures, thereby determining the boiling- and dew-point curves for the mixtures. The temperature of the mixture samples is controlled to within approximately 1° C in the range from -60° to $+10^{\circ}$C.

   Data are being taken on the sulfuric acid-water system.

6. <u>Publications, Presentations, Theses</u>: None

7. <u>Plans</u>:

   1. To continue data collection and study of the sulfuric acid-water system.

   2. When sufficient data on this mixture has been compiled, to perform similar measurements on mixtures containing HCl and HNO_3.

1. Task Title: Formation of Atmospheric Aerosols - Size Distribution
    Models for Atmospheric Aerosol.

2. Objective:

    To develop better multimodal models to describe the thousands of
    atmospheric size distributions measured in the atmosphere during the
    past few years.

    To develop useful categories for concentration, size distributions,
    etc.

3. Institution: University of Minnesota, Minneapolis, Minnesota
    Investigator: K.T. Whitby

4. EPA Project Officer: W.E. Wilson

5. Progress:

    Evidence from a variety of field studies suggests that atmospheric
    aerosols are in general multimodal, with two to three modes being
    observable. The mass or volume distribution is usually bimodal with
    a minimum observed in the 1-to-3-μm diameter range. The particles
    larger than a few microns originate from natural or man-made mechanical
    processes. The mechanically produced particles are hereafter called
    "coarse particles." The particles smaller than a few microns arise
    predominantly from condensation processes and are called "fine particles."
    The predominant man-made source of these fine particles is combustion
    or the condensation of chemical or photochemical reaction products on
    nuclei from combustion.

    The fine particle range may also show two distinct modes. For
    example, a trimodal size distribution was measured 30 m from the road-
    way during the GM Sulfate Study (Figure 1). A distinct first mode was
    indicated because the source (catalyst-equipped cars) emitted most of
    the aerosol in the 0.02 μm nuclei mode, and the accumulation mode (middle
    mode) was relatively small because the background on this day was
    very low.

    The first mode, in the vicinity of 0.02 μm diameter, results pri-
    marily from the direct emission of primary particles from combustion.
    The second submicron mode, in the 0.15 to 0.8 μm range by volume, is
    the result of either the coagulation of primary particles or the con-
    densation of reaction products or water on primary particles. The
    third mode, or coarse particle mode, consists of mechanically produced
    aerosols with the upper size limited by classification due to sedimenta-
    tion. There appears to be very little exchange of mass under most
    conditions between the fine and coarse particle ranges in the atmosphere.

    Most mass is inserted in the distribution either through the
    accumulation mode or through the coarse particle mode. Only under
    unusual circumstances near large sources of combustion aerosol (such as
    a freeway, or in a plume from a stack) is appreciable mass injected
    directly into the nuclei mode (Figure 2).

Size Distribution Models for Source Related and Urban Atmospheric Aerosols

Atmospheric volume, mass and chemical size distributions can be fitted by three independent log-normal distributions.

This procedure has been applied to a large number of size distributions measured with the Minnesota Aerosol Analyzing System (MAAS). After examining this data in some detail, the distributions were grouped into six categories (Table I):

Clean Background
Observed only in large clean air masses
Several hours away from combustion sources
No nuclei mode
VAC < $2\mu m^3/cm^3$

Average Background
Mixture of Clean Background, small amounts of aged urban plumes and local
  combustion aerosol
Small nuclei mode
VAC ≃ $5\mu m^3/cm^3$
VCP independent of VAC and dependent on local sources of dust

Background + Aged Urban Plumes
Average Background + a strong plume from a major urban area
Small nuclei mode determined by local combustion sources
VAC similar to that in an average urban area
VCP determined by local sources of dust

Background + Local Sources
Strong local combustion sources increase VAN to the urban concentrations
   of ≃ 0.6 without much increase in VAC over background
Distribution is very dependent on nature of sources

Urban Average
Nuclei mode determined by local sources, primarily automobiles
Accumulation mode determined primarily by aged aerosol from the general
  area; VAC = 30 on the average
Coarse particle mode determined by local sources

Urban + Sources
Strong local sources of combustion aerosol, (e.g. automobiles) increase both
  nuclei and accumulation modes
Coarse particle mode is influenced by the nature of the source; fine particle
  and coarse particle sources are usually unrelated
Concentration is widely variable in time

The size distributions for which the parameters are tabulated in Table I are plotted in Figure 3 and 4. A typical size distribution measured in the Labadie coal-fired power plant plume, located in St. Louis, is also shown in Figure 4. Although both background and plume aerosol distributions usually have small nuclei and coarse particle modes, most of the aerosol mass is in the accumulation mode.

Except for the clean background and Labadie plume distributions, the volume of aerosol in the coarse particle mode is relatively constant at about 30 $\mu m^3/cm^3$ (Table I, Figure 3,4). The accumulation mode volume is more closely related to anthropogenic contributions than is the coarse particle mode.

The nuclei mode is an indicator of close (less than 1/2 hour transport time) sources of combustion aerosol except in those cases where photo-chemically produced nuclei may be observed in relatively clean air (e.g., small accumulation mode). Number concentrations of about $10^5/cm^3$ of nuclei of size less than 0.01 μm have been observed in the Labadie plume during the summer of 1976, which are apparently due to homogeneous reactions in the plume.

The formation rate of new nuclei in a coal-fired power plant plume is only about 3.5 nuclei per $cm^3 \cdot sec$. These nuclei contained an insignificant amount of mass compared to the mass that condensed directly on the particles in the accumulation mode during the aerosol growth in the same plume.

General Mode Characteristics of the Physical Size Distribution

From modal characterization of the variety of aerosol size distributions, the following general conclusions have been reached:

1. Nuclei mode. For very fresh combustion aerosols from clean combustion (e.g., along a freeway), the geometric mean diameter by number (DGN) is about 0.01 μm. For more aged aerosols, DGN may approach 0.02 μm. The geometric standard deviation (SG) is usually between 1.5 and 1.7. Except for well-aged aerosols (e.g., away from sources on the earth's surface or well above the earth's surface), the nuclei mode accounts for most of the aerosol number and hence the Aitken nuclei count.

2. Accumulation mode. Average geometric standard deviation by volume (SGV) = 2.0 and average geometric mean diameter by volume (DGV) = 0.34 μm. Also, aged aerosols have a somewhat greater SGV than fresh aerosols; the range being from 1.8 for fresh aerosols to 2.2 for well-aged aerosols. In well-aged aerosols the nuclei mode disappears into the accumulation mode by coagulation and then the Aitken nuclei count becomes equal to the number of particles in the accumulation mode within the experimental error of the measurements (about ± 30%). This situation appears to be the normal condition at altitudes greater than about 200 m, and at the surface more than 30 km from sources of combustion aerosol.

3. Coarse particle (CP) mode. The average geometric standard deviation by volume of the coarse particle mode (SGV) = 2.3, and the average geometric mean diameter by volume (DGV) = 5 μm. The log-normal distribution parameters are more variable for the coarse particle mode than for the accumulation and nuclei modes; values of DGV having been observed between 3.5 and 25 μm. The mass concentration in the CP mode varies from a few to several hundred $\mu g/m^3$.

An examination of the relationship between the volume of coarse particles (VCP) and the geometric mean size of the coarse particle mode (DGVCP) shows that DGVCP is nearly constant up to VCP = 30 $\mu m^3/cm^3$ and equal to about 5 μm. Above 5 μm, DGVCP increases linearly with VCP.

6. <u>Publications, Presentation, Theses</u>:

1. Whitby, K.T. Modeling of Atmospheric Aerosol Size Distribution. Report on Grant #R800971, Sampling and Analysis of Atmospheric Aerosols. Submitted to: Atmos. Aerosol Res. Sec., Div. of Chem. and Phys., Air Pollution Control Office, Environmental Protection Agency, May 1975.

2. Whitby, K.T. and B.K. Cantrell. Size Distribution and Concentration of Atmospheric Aerosols. Presented at: 82nd Annual Meeting of the AIChE, August 30, 1976.

3. Whitby, K.T. Physical Characterization of Aerosols. Presented at: 8th Materials Research Symposium, National Bureau of Standards, September 21, 1976.

7. <u>Plans</u>:

1. To develop modal parameters using the latest data bases: the 1975 EPA trailer data from Glasgow, MO, the 1975 St. Louis urban plume data, and the 1976 Labadie power plant data.

2. Improved fitting procedures are being developed that can be used as part of a routine data reduction package.

Table I

Modal parameters and integral parameters
for six typical model atmospheric distributions.

	Nuclei Mode			Accumulation Mode			Coarse Particle Mode			Integral Parameters		
	DGV	σ_g	V	DGV	σ_g	V	DGV	σ_g	V	NT	ST	VT
Clean background	---	---	0	.35	2.1	1.5	6	2.2	5	796	40.7	6.50
Average background	.034	1.7	.037	.32	2.0	4.45	6.04	2.16	25.9	8.6E3	148	30.4
Background & aged urban plumes	.0283	1.6	.029	.36	1.84	44	4.51	2.12	27.4	1.6E4	938	71.4
Background & local sources	.021	1.66	.62	.25	2.11	3.02	5.60	2.09	39.1	4.1E5	352	42.7
Urban average	.038	1.81	.63	.32	2.16	38.4	5.7	2.21	30.8	1.4E5	1131	69.8
Urban & sources	.032	1.74	9.19	.25	1.98	37.5	6.02	2.13	42.7	2.2E6	3201	89.4

DGV = Geometric mean size by volume, μm

σ_g = Geometric standard deviation, unitless

V = Volume concentration in mode, $\mu m^3/cm^3$

NT = Total number concentration in distribution, $no./cm^3$

ST = Total surface area concentration, $\mu m^2/cm^3$

VT = Total volume concentration, $\mu m^3/cm^3$

21

GM MILFORD PROVING GROUNDS
SITE: GMPG 15   DATE: 18/29/75
RUN NO.: 15   TIME: 8:40 TO 9:00 HR EDT
WD: 354.9   CNC: 1.82E 85   U2:   1.35   NO/NOX: 0.30
WSP: 17.0   NTM: 1.83E 86   U3:   2.32   UAN: 1.30
RH: 73.8   ST: 4.53E 82   U3-: 3.67   UAC: 2.76
               UT: 7.16   U4+: 3.49   UCP: 4.89
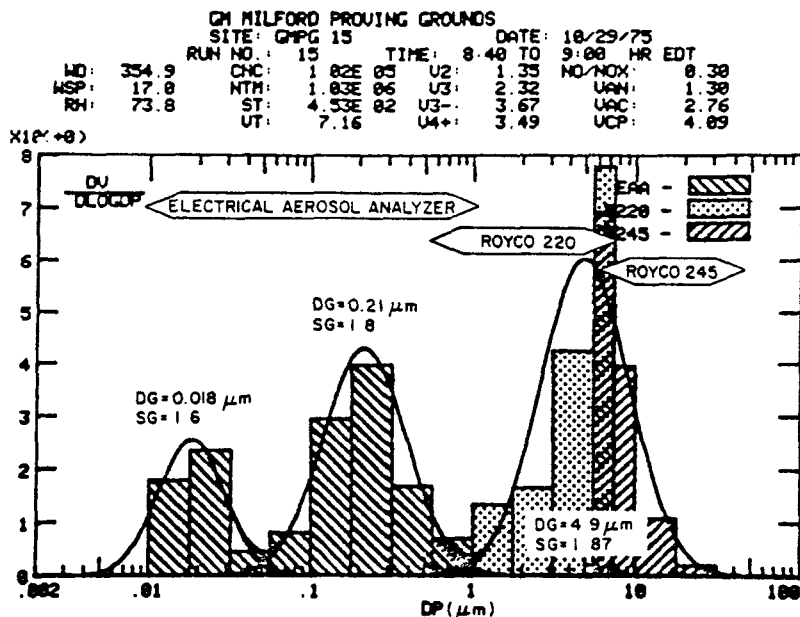
Figure 1. Trimodal volume distribution measured 30 m from the roadway
during the General Motors Sulfate Study, October, 1975. The
bars are actual data. Solid lines are the fitted log-normal
distributions.
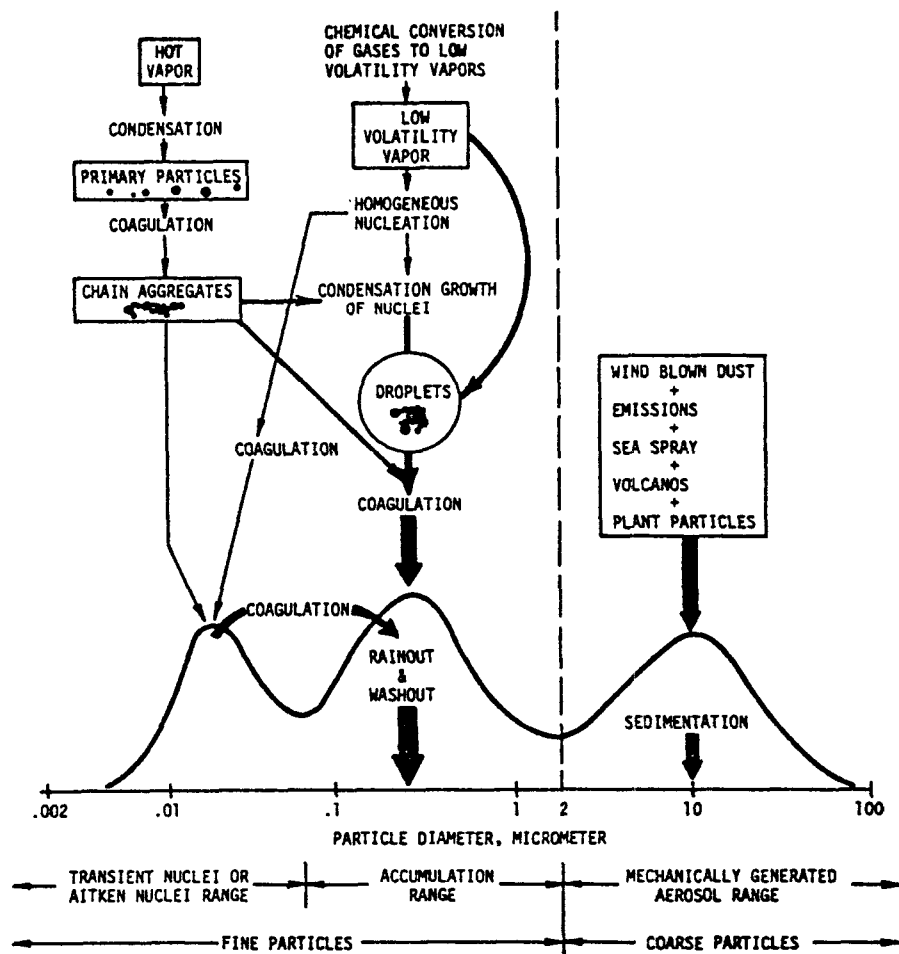
Figure 2. Schematic of the principal mechanisms of formation and
removal of a trimodal atmospheric aerosols size distribution.
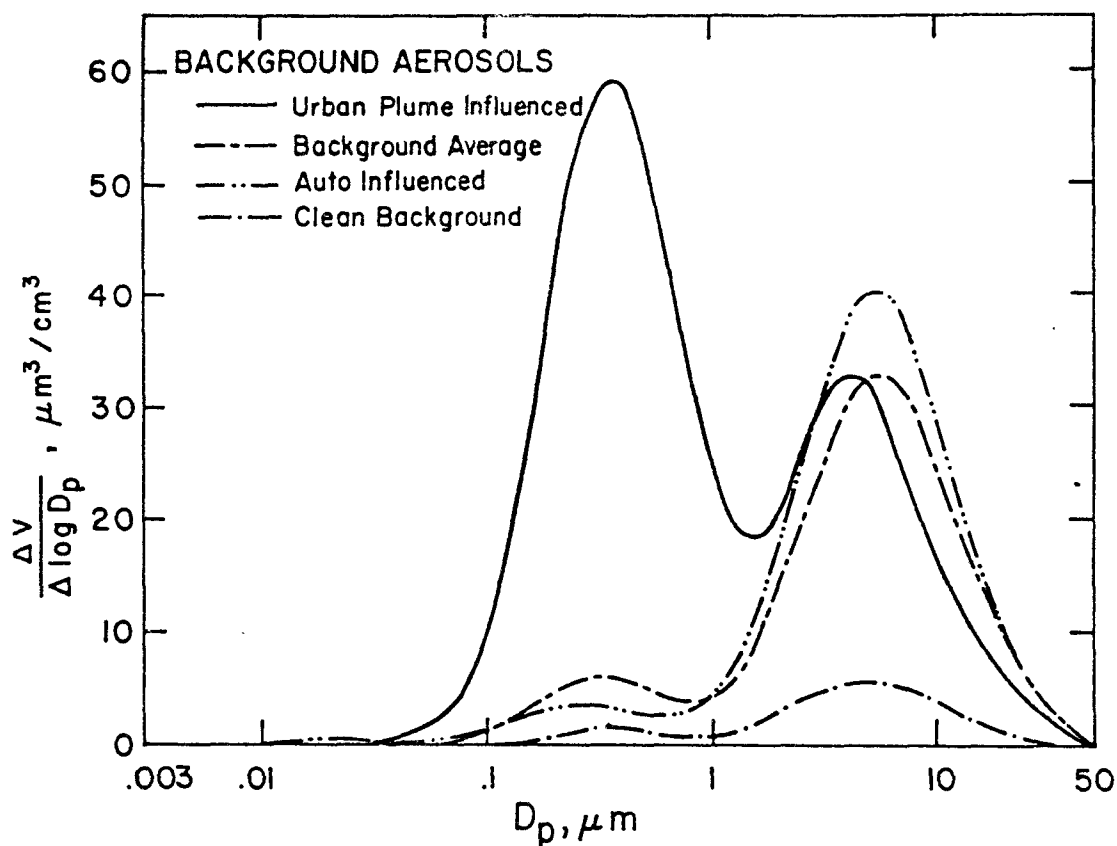
Figure 3. Volume size distributions of four background model aerosols. Note that except for the CLEAN BACKGROUND, the volume in the coarse particle mode is about the same.
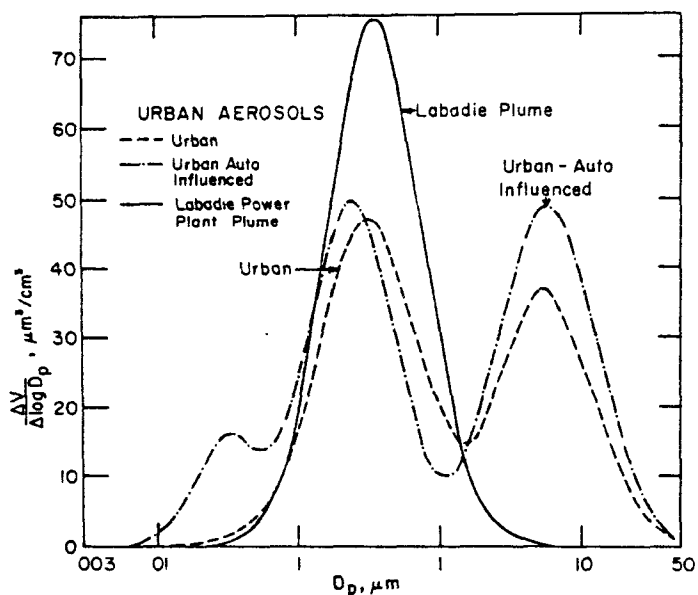
Figure 4. Volume size distributions of two model urban aerosol distributions and a typical size distribution measured in the plume of the Labadie coal fired power plant on 8-14-1974. The power plant plume has only the accumulation mode.

1. Task Title: Aerosol Dynamics.

2. Objectives:

   To study theoretical aspects of aerosol phenomena and develop a comprehensive model for the evolution of the size and composition distributions of the atmospheric aerosol.

3. Institution: University of Texas, Austin, Texas
   Investigator: J.R. Brock

4. EPA Project Officer: J.L. Durham

5. Progress:

   The various rate processes which alter the composition and concentration of urban particulate matter may be summarized by the following relationships:

$$
\begin{Bmatrix} \text{rate of change in} \\ \text{composition of some} \\ \text{size fraction of} \\ \text{urban aerosol} \end{Bmatrix} = - \begin{Bmatrix} \text{rate of change due} \\ \text{to advection} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change due} \\ \text{to convection and} \\ \text{dispersion} \end{Bmatrix}
$$

$$
+ \begin{Bmatrix} \text{rate of change due} \\ \text{to coagulation} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change due to} \\ \text{accretion and con-} \\ \text{densation} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change due} \\ \text{to nucleation} \end{Bmatrix}
$$

$$
+ \begin{Bmatrix} \text{rate of change due} \\ \text{to input of primary} \\ \text{sources} \end{Bmatrix} \tag{1}
$$

   with processes occurring at surfaces, such as deposition, appearing as boundary conditions. An exactly analogous relationship also describes the alteration of the concentration of the various size fractions making up the urban aerosol. Equations such as eq. (1) for the aerosol are coupled to rate relationships for the various chemical species participating in the aerosol growth processes.

   The detailed knowledge of the various rate processes which would permit accurate simulation by eg. (1) is not available for most urban regions; however, there is evidence that considerable simplification may be possible to permit fairly reliable simulation. As a case in point, we have carried out an initial simulation of the size distribution of the Denver aerosol during typical wintertime pollution episode conditons. These episode conditons show substantial evidence that the size distribution of the aerosol is determined by the relationships:

$$
\begin{Bmatrix} \text{rate of change of size} \\ \text{distribution of Denver} \\ \text{"pollution episode"} \\ \text{aerosol} \end{Bmatrix} = - \begin{Bmatrix} \text{rate of change due} \\ \text{to advection} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change} \\ \text{due convection} \\ \text{and dispersion} \end{Bmatrix}
$$

$$
+ \begin{Bmatrix} \text{rate of change due} \\ \text{to coagulation} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change due} \\ \text{to condensation} \end{Bmatrix} + \begin{Bmatrix} \text{rate of change due} \\ \text{to input of primary} \\ \text{sources} \end{Bmatrix} \tag{2}
$$

with deposition processes appearing as boundary conditions. Episode conditions are marked by well defined mixing heights and small, cyclical advective drainage flows. This permits a volume averaging procedure for eq. (2) in which dispersion and dry deposition appear explicitly in a lumped parameter for removal rate. The small, cyclical drainage flows suggested also the feasibility of a Lagrangian cell method in the simulation.

The input and transport of aerosol in a single cell was studied as it traversed the urban and surrounding areas of Denver at the rate of the drainage flow. Fig. 1 presents the moments (mass concentration, number concentration, and b_{scat}) of the calculated size distribution of the Denver aerosol for a two-day wintertime pollution episode as described by the volume average of eq. 2 in which the cell begins its traverse at Denver's southern edge. In the calculation of b_{scat}, the refractive index of the aerosol at 500 nm is taken as (1.55-0.22i).

A marked diurnal variation can be seen during the first day with a rapid decrease in the evening hours as the cell moves out of the city by following the drainage flows down the Platte River valley. Flow reversal the next day allows transport of the cell (now containing aged aerosol) once again over the city with resultant build-up of aerosol concentration.

The values of the various moments in Fig. 1 are all within the range of experimental observations. Thus, these quantities are all based through eq. (2) on independent estimates of the primary source emission rates. Figure 2 shows the mass density function at 12-hour intervals. Again the bimodal forms, the quantitative variation of the density function, and the locations of modes and saddlepoint are in apparent agreement with typical episode measurements for the various times (cell locations) shown. The presentation of the rate distributions of the various processes in Fig. 3 illustrates the power of a rigorous numerical model of the atmospheric aerosol. The importance of all the processes - coagulation, condensation (in this case sulfuric acid resulting from the ozone-olefin-SO_2 reaction), deposition, primary source input - may easily be studied in terms of their rates in the growth equation.

The fine particle mode grows mainly by coagulation and primary source input and is diminished by deposition (Fig. 3). The coarse particle mode grows mainly by primary source input with a minor contribution from coagulation (turbulent, gravitational, and Brownian coagulation are all considered), and is strongly diminished by deposition. Although this model represents a large simplification of typical episode conditions, it provides valuable insight into the aerosol dynamics. It has provided useful predictions about the mechanisms of particle growth and visibility effects discussed elsewhere.

The volume average of eq. (2) has been used to explain why the mass density functions of urban aerosols are multimodal. Apart from the explanation based on two major size classes associated with primary source inputs, we wished to determine if multi-modality could result from other processes as well (Figs. 4, 5 and 6). Fig. 4 indicates the test mass density function resulting from elimination of all aerosol processes except input of primary sources which were purposely chosen to give the uniform mass density functions displayed. Fig. 5, showing a sharply peaked unimodal function, results from addition of the processes of coagulation and dry deposition to the primary source input of Fig. 4. Finally, a marked bimodal from results if condensation with Kelvin cut off, coagulation, dry deposition and primary source input are all included in the evolution equation (Figure 6). Primary-source size distributions, modified

by coagulation and deposition, undoubtedly are the principal causal agents in the production of the currently reported multimodal densities (Figure 2). However, additional hither to unobserved modes may exist for the atmospheric aerosol owing to secondary aerosol production, particularly in those cases where condensable substances and aerosol form a "pollution cloud" (Figure 6).

6. Publications, Presentations, Theses:

1. P.B. Middleton and J.R. Brock. 1976. Simulation of Aerosol Kinetics. J. Colloid and Interface Sci. 59:249.

2. J.R. Brock. 1974. Repartition de la Charge d'Espace aer Voisinage d'un Faisceau de Particules. C.R. Acad Sc. Paris 287.

3. J.R. Brock and W.H. Marlow. Charged Aerosol Particles and Air Pollution. 1975. Environ. Letters. 10:53-67.

4. W.H. Marlow and J.R. Brock. 1975. Unipolar Charging of Small Aerosol Particles. J. Colloid and Interface Sci. 50:32-38.

5. P.B. Middleton and J.R. Brock. Studies in Aerosol Dynamics: The Denver Field Study Symposium. Environ. Monitoring Series. EPA.

6. Middleton, P.B. and J.R. Brock. 1976. On the Multimodality of Density Functions of Pollutant Aerosols. Atmos. Environ. 10.

7. P.B. Middleton and J.R. Brock. Dynamic Model for Urban Particulate Pollution. Submitted to: Atmos. Environ.

8. Brock, J.R. and R. Drake. Coagulation of Aerosols. Symposium on Aerosol A Science and Technology. Natl. A.I.Ch.E. Meeting, Atlantic City, NJ, August, 1976.

7. Plans:

1. Complete the computer program to permit atmospheric aerosol simulation for very general meteorological conditions directly according to eq. (2). The first application of this program will be the simulation of the aerosol growth processes for the city of Phoenix to permit testing of various control strategies.

2. To permit the solution of eq. (1) for the composition distribution of the atmospheric aerosol. This will permit us to simulate the chemical transformations which occur in the atmospheric aerosol.
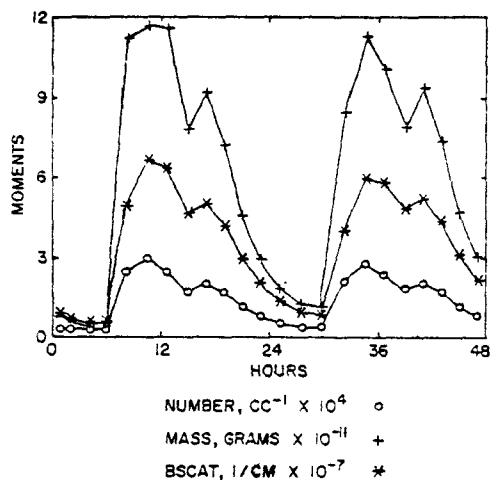
Figure 1. Moments of calculated
size distribution of
Denver aerosol for a two
day wintertime pollution
episode in Lagrangian cell
traversing city with
cyclical drainage flows.
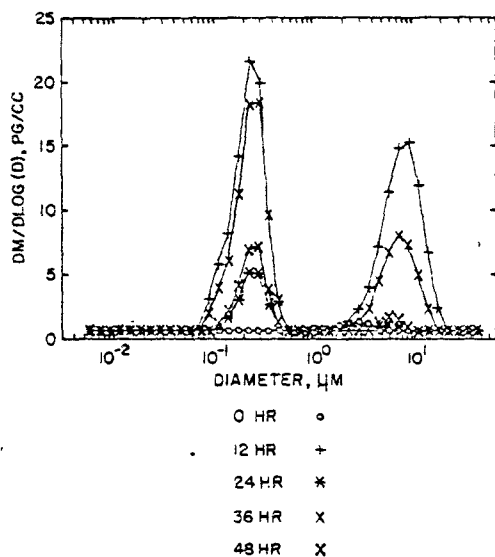
Figure 2. Mass density function of
Denver aerosol for two day
wintertime pollution episode
in Lagrangian cell travers-
ing city with cyclical
drainage flows.
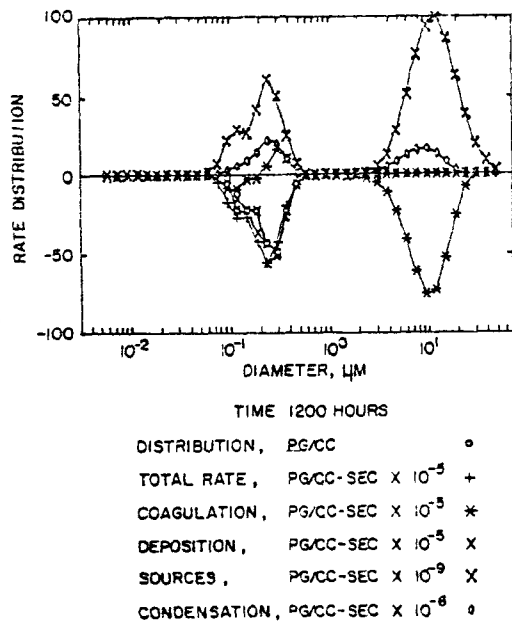
Figure 3. Rate distributions of
various processes shaping
size distribution during
two day wintertime pollution
episode for city of Denver.

1. Task Title: Biogenic Emission of Aerosol Precursors

2. Objective:

   To determine the contribution of naturally occuring bacterial sources to the total atmospheric sulfur load. Select monitoring sites showing good promise of biogenic sulfur production with a "clean" reference site nearby.

   To monitor atmospheric sulfur levels at selected sites along with meteorological data. (Wind speed, wind direction and temperature).

   To correlate sulfur levels with natural cycles (tides, day/night and seasonal).

3. Institution: EPA-ERC, ESRL-ARB
   Investigators: L.L. Spiller; N. Schmidt, Gilles Kay, G. DeJong, R. Reardon, G. Namie. (student aids)

4. EPA Project Officer: W.E. Wilson

5. Progress:

   (a) A method of collection of volatile sulfur compounds using selective filters treated with various silver salts and (OH-) anions was tested for temperature and humidity effects on collection efficiency. $AgNO_3$ treated filters were selected for H_2S absorbtion and LiOH treated filters for SO_2 absorbtion. X-ray fluorescence is used for analysis.
   (b) Further laboratory testing will be done on these filters to determine performance limits regarding air temperature,, humidity, flow rate, selectivity, and sulfur load extremes and to compare XRF non-destructive analysis with other destructive wet methods of higher accuracy but greater costs. (D.F. Natusch Method). (c) Design instruments and interface circuitry to support environmental studies anticipated in the near future. Future tests will be made at selected sites using a higher flow rate for shorter sampling time or, a much more accurate analytical method must be used. Currently we are using XRF with measurements at .06 $\mu m/cm^2$ or .46 ppb.

6. Publications, Presentations, Thesis:

   Presented before the Division of Environmental Chemistry, American Chemical Society. New Orleans, LA, March 20-25, 1977. Biogenic Sulfides in the Atmosphere Over a North Carolina Tidal Marsh.

7. Plans:

   To develop specially treated filters to selectively absorb different volatile sulfur compounds.

   To collect laboratory data on: collection efficiency, effects of temperature, humidity, various volatile sulfur selectivities, and ease and accuracy of analysis at low levels.

   To develop a field collection system with high portability.

1. Task Title: Metal Sulfite Complexes

2. Objective:

   To determine the existence and kinetices of metal sulfite complex formation.

   To devise methods for the determination of these complexes if they are found to exist.

3. Investigator: D. Lawing (Student Aide)

4. EPA Project Officer: J.L. Durham

5. Progress:

   Initially, the metal salt studied was $FeCl_3$ in solution with Na_2SO_3. The resulting solution was analyzed spectrophotometrically over a wavelength range of 600-400 nanometers. The complex, if formed, could not be isolated from the ionized species with this method.

   The next metal used was Copper in the form of $CuCl_2$, Cuprous Chloride. Literature research indicated that such a sulfite complex would break down due to hydrolysis in neutral solutions. To present this from happening, HCl was added to the solutions at a molar concentration equal to the $SO_3^=$ concentration.

   The absorption spectra still revealed no well-defined peaks from 800 to 200 nanometers. Oxidation of the Copper ion was one possible explanation of the transience of any complex formed.

6. Publications, Presentation, Theses: None

7. Plans:

   To undertake similar experiments with vanadium salts.

A. ATMOSPHERIC PROCESSES AND EFFECTS

2. <u>Aerosol Characterization and Sources</u>. The utilization of physical properties, elemental and chemical analyses, and microscopy for the characterization of atmospheric aerosols and the use of this information to determine the primary and secondary source contributions to urban pollution.

1. Task Title: Sources and Trace Metals in Urban Aerosols

2. Sub-Task Title: Urban, Non-urban, and Marine Aerosol Studies.

3. Objectives:

    Apply developed sample collection and PIXE analysis techniques to studies on urban, non-urban, and marine aerosols.

4. Institution: Department of Oceanography, Florida State University
                   Tallahassee, Florida 32306
    Investigator: John W. Winchester

5. EPA Project Officer: Ronald K. Patterson

6. Progress:

    Under this sub-task title eight major studies were performed. Each study used the Florida State University Tandem Van de Graaff Accelerator and Proton Induced X-Ray Emission to analyze for trace elements in collected aerosols.

    Study 1. Size fractionated aerosols, using the Battelle impactor, were collected in St. Louis during August, 1973. The results of this study show that:

    1.   Particle size distributions of S, Cl, K. Ca, Ti, V, Mn, Fe, Cu, Zn, Br, and Pb can be measured in samples from 0.7 m^3 of air collected over 12-hour intervals at 1 liter/min flow rate, with precision of single analyses generally 10-30%, except near the nanogram detection limit.
    2.   Some elements, e.g. Ca, Fe, Ti, K, show a tendency for highest concentrations in air measured in largest particle size fractions, and the pattern of distribution of concentration with size is relatively invariant. Predominantly dispersion source processes may account for their entry into the atmosphere.
    3.   Other elements, e.g. S, Pb, Zn, have substantial proportions of their atmospheric concentrations on smallest particles and show greater variability in particle size distribution patterns, suggesting aerosol formation processes of vapor condensation at high or low temperatures.
    4.   During 16-22 August 1973 an atmospheric change occurred from a period of low speed and mostly southerly air flow, with evident haze and air pollution, to higher speed and westerly shifting to easterly air flow, with improved visibility and air quality. The change was associated with drops in concentrations of Ti, Fe, Ca, K, and S but not Zn or Pb at the south site, and Ti but not the other elements at the central site. Transport of air pollution from industrial sources south of the city is indicated.
    5.   The central site showed diurnal variations during the first period where concentrations of Ti, Fe, Ca, K, and S were higher in samples taken from midnight to noon than in those from noon to midnight. Variations were greatest for intermediate sized particles.

Study 2. Time sequence samples, using the Jensen-Nelson "Streaker," were collected simultaneoulsy at 25 sites in St. Louis during August, 1975. From this study, correlations of elemental concentrations in the air with time (2 hr. resolution) and location, plus inter-element time correlations at a single site, inferences can be made about the transport of elemental constituents from pollution and natural sources, as well as gas-to-particle transformations of certain elements, such as sulfur.

Study 3. Fractionated aerosols were collected in north Florida by using a Battelle impactor. Size-specific aerosol removal processes can be evaluated by sampling urban, forest, and coastal locations, and by choosing approximately 48-hour sample-averaging intervals.

It was found that elements contained in the largest particles, especially those of >4µm, display the greatest degree of average concentration difference between sites, a result suggesting short atmospheric residence times and the importance of local dispersion sources and atmospheric cleansing processes in regulating the particle concentrations in air. Elements contained in particles of <2µm diameter showed little average concentration difference between sites unless they were regulated by large-scale sources and transport processes. Sulfur in the smallest particles showed a marked constancy of concentration, but it may be modified in the largest particle size ranges in relation to proximity to the seacoast. No evidence was found for dependence of particulate sulfur concentrations on local pollution sources.

Study 4. Size fractionated aerosols were collected in Miami, Florida. Miami provided an opportunity to observe elemental constituents of the aerosol as it may be modified from the predominately marine atmosphere background by urban nonindustrial activity.

Major sources of the elements are the tropospheric land-derived particles and added sea spray particles carried by prevailing southeasterly winds, soil dust constituents raised by human activity in the city, automotive emissions that contain lead and halogen elements, and emissions from stationary combustion sources that include oil- and gas-fired power plants and refuse incinerators.

This study was undertaken to evaluate the relative importance of these major sources for 14 elemental constituents.

Study 5. A data set from Bermuda, consisting of ten size fractioned distribution measurements of marine aerosol, was used in a 2-component model to resolve tropospheric from sea surface derived trace elements.

Study 6. Samples were collected in Bolivia, central Brazil, and Argentina, using Battelle cascade impactors, Jensen-Nelson "Streakers" and total particulate filters. These samples were collected for comparisons with data from the North American continent and for use in transport models.

Study 7. As an example of the application of the PIXE analysis technique to the study of sulfur and related trace elements from non-urban locations, comparisons were made between results from a remote continental station in the Southern Hemisphere, Chacaltaya Mountain, near LaPaz, Bolivia, and a mid-ocean station in the Atlantic of the Northern Hemisphere, at Bermuda. Size fractionated samples were collected at both sites.

Study 8. Biased data set averaging has been used to examine aerosol elemental composition data for air mass directional effects. Samples collected in north Florida during spring and summer 1973 were influenced by local and remote continental sources and additionally by maritime sources when air flow was southerly. Judgements of air movements during the collection of 32 5-stage cascade impactor samples were made by examination of daily surface weather maps, 3-hourly surface winds in Tallahassee, and semi-diurnal balloon soundings to 1524 meters. Averages of elemental abundances as a function of particle size, determined by proton-induced X-ray emission, PIXE, were computed for a 14-sample set biased toward marine air flow conditions and for a 6-sample set biased toward continental air flow, excluding 12 additional samples where air flow characteristics were variable or periods of very low wind speed were experienced. By regarding Fe to be of continental origin in all samples, qualitative indications of provenance were observed.

7. Publications:

1. J.W. Winchester, D.L. Meinert, J.W. Nelson, T.B. Johansson, R.E. Van Grieken, C.Q. Orsini, H.C. Kaufmann and K.R. Akselsson. In: Proc. 2nd Intl. Conf. Nucl. Methods in Environmental Res., Columbia, MO, July, 1974, USERDA Conf-740701, pp. 385-394.

2. J.O. Pilotte, J.W. Nelson and J.W. Winchester. Application of multi-station Time Sequence Aerosol Sampling and Proton Induced X-Ray Emission Analysis Techniques to the St. Louis Regional Air Pollution Study for Investigating Sulfur-Trace Metal Relationships. In: Proc. ERDA X and Gamma Ray Symposium, Ann Arbor, MI, May 19-21, 1976 (Conf. 760539).

3. T.B. Johansson, R.E. Van Grieken and J.W. Winchester. Elemental Abundance Variation with Particle Size in North Florida Aerosols. Journal of Geophysical Research. 1976. 81:1039-1046.

4. K.A. Hardy, K.R. Akselsson, J.W. Nelson and J.W. Winchester. Elemental Constituents of Miami Aerosol as a Function of Particle Size. Environmental Science and Technology. 1976. 10:176.

5. D.L. Meinert and J.W. Winchester. Chemical Relationships in the North Atlantic Marine Aerosol. Journal of Geophysical Research. (In Press)

6. L.C.S. Boueres, F. Adams, J.W. Winchester, C.Q. Orsini, J.W. Nelson, T.A. Cahill and D.R. Lawson. Sulfur and Heavy Metals in South American Urban and Non-urban Atmospheres. In: Proc. of the World Meteorological Organization Technical Conference on Atmospheric Pollution Measurement Techniques, Gothenburg, Sweden, October 11-15, 1976. Conf. Proc. (In Press)

7. J.W. Winchester. Sulfur and Trace Metal Relationships in Non-urban and Marine Aerosols Studies Using Proton Induced X-Ray Emission. Nuclear Instruments and Methods. (In Press)

8. T.B. Johansson, R.E. Van Grieken and J.W. Winchester. Marine Influence on Aerosol Composition in the Coastal Zone. Journal de Recherches Atmosphériques. 1974, pp. 762-776.

8. <u>Plans</u>:

This grant is completed. A final report is forthcoming.
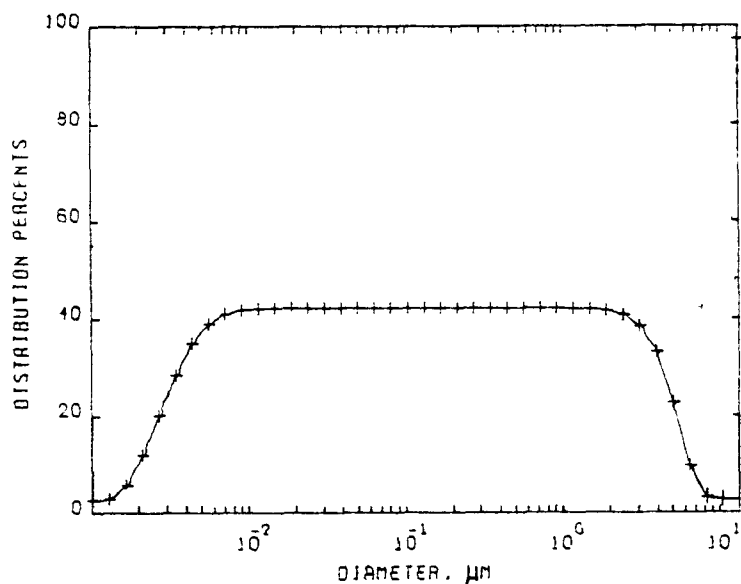
Figure 4. Mass density resulting from only input of primary sources. Primary sources input rates chosen to yield a rectangular density. 100% units = 100pg/cc
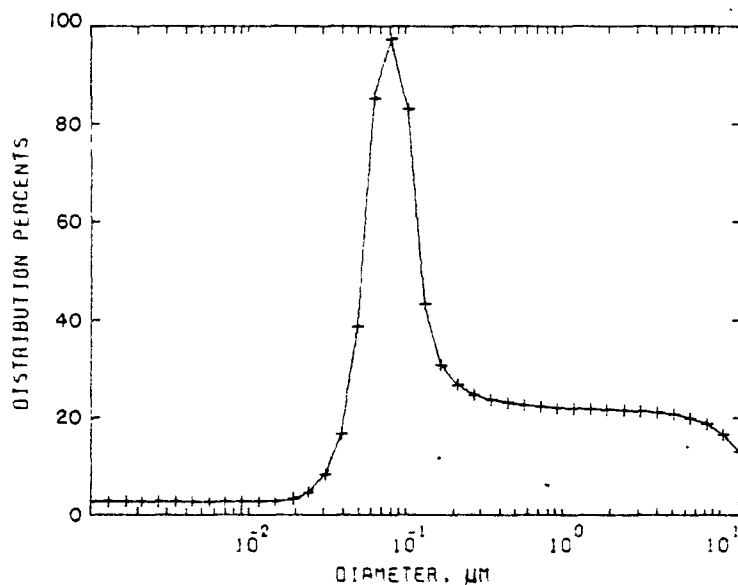
Figure 5. Unimodal mass density resulting from input of primary sources of Fig. 4 coagulation, and deposition.
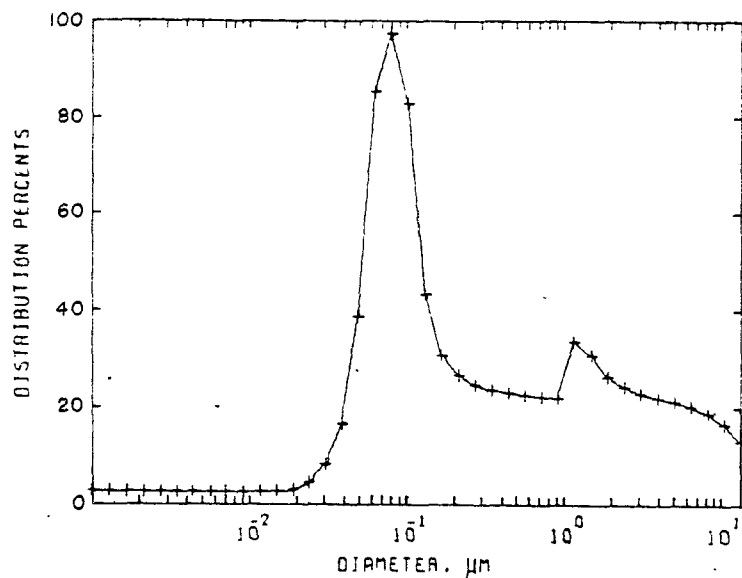
Figure 6. A bimodal mass density resulting from input of primary source of Fig. 4 plus coagulation, deposition, and condensation, including the Kelvin term for variation of vapor pressure with curvature.

1. <u>Task Title</u>: Relationship of the Smog Aerosol to Pollution Sources

2. <u>Objective</u>:

    To develop experimental and theoretical methods for relating the properties of the pollution aerosol to the characteristics of emission sources.

3. <u>Institution</u>: California Institute of Technology, Pasadena
    <u>Investigator</u>: S.K. Friedlander

4. <u>EPA Project Officer</u>: W.E. Wilson

5. <u>Progress</u>:

    Homogeneous nucleation in ambient urban air was documented by watching time profiles of condensation nuclei and carbon monoxide before and after changes from daylight savings time to standard time. An increase in condensation nuclei occurred soon after sunrise both before and after the time change, while the CO increase tended to be shifted an hour along with anthropogenic activity; therefore, some homogeneous nucleation occurs soon after sunrise.

    Quantitative experiments were conducted using a 60 m^3 Teflon reactor. The bag was filled with ambient air of varied aerosol loadings. The air in the bag was doped with SO_2, NO_x, and propylene to facilitate formation of sulfate aerosol by homogeneous gas phase reactions. Reaction rates varied from 0.288 ppb SO_2/hour to 144.0 ppb SO_2/hour by varying the concentrations of reactants from near ambient levels to levels higher than ambient. Experimental results indicate that homogeneous nucleation becomes more important as rates of aerosol production increase and initial aerosol loadings decrease.

    A theoretical model has been developed which predicts the relative amounts of aerosol accumulating on new and original particles as functions of time, aerosol formation rate and amount of pre-existing aerosol. The evolution of the size distribution of the initial aerosol as a result of condensational growth can also be calculated: agreement with experimentation is very good.

    The distribution of aerosol nitrate compounds with respect to particle size is also under study. A new technique has been developed for the measurement of aerosol nitrate deposited on the stages of an impactor. The method has been applied to the aerosol collected with the low pressure impactor at various locations in and around Los Angeles. Preliminary results indicate a bimodal distribution of nitrate with respect to particle size.

6. <u>Publications, Presentations, Theses</u>:

    1. Heisler, S.L. and S.K. Friedlander, Growth Mechanisms for Urban Aerosol Particles. In: Proceedings of the International Colloquium on Drops and Bubbles, California Institute of Technology-JPL. August 1974, Vol. II, p.553.

    2. Grosjean, D. and S.K. Friedlander. Gas-to-Particle Distribution Factors for Organic and Other Pollutants in Los Angeles. J. Air Poll. Control Assoc.

3. Grosjean, D. 1975. Solvent Extraction and Organic Carbon Determination in Atmospheric Particulate Matter: The Organic Extraction-Organic Carbon Analyzer (OE-OCA) Technique. Anal. Chem. 47(6):797-805.

4. Roberts, P.T. and S.L. Friedlander. 1976. Analysis of Sulfur in Deposited Aerosol Particles by Vaporization and Flame Photometric Detection. Atmos. Environ. 10:403.

5. Roberts, P.T. and S.K. Friedlander. 1976. Photochemical Aerosol Formation SO_2, 1-Heptene, and NO_x in Ambient Air Environ. Sci. and Technol. 10:573.

6. Heisler, S.L. and S.K. Friedlander 1976. Gas-to-Particle Conversion in Photochemical Smog: Growth Laws and Mechanisms for Organics Atmos. Environ. 10:215.

7. Friedlander, S.K. Gas-to-Particle Conversion: A Key Problem in Air Pollution. Presented at: The Research Directors' Conference, California Institute of Technology-Industrial Associates, Pasadena, CA April 19, 1976.

8. Friedlander, S.K. Gas-to-Particle Conversion. Presented at: The Department of Meteorology Seminar Series, University of California, Los Angeles, CA April 21, 1976.

9. Flagan, R.C. and S.K. Friedlander Particulate Formation in Pulverized Coal Combustion - A Review Presented at: The AIChE National Meeting, Atlantic City, NJ August 31, 1976.

10. Friedlander, S.K. Fundamentals of Gas-to-Particle Conversion - A Review. Presented at: The AIChE National Meeting, Atlantic City, NJ August 31, 1976.

11. Roberts, P.T., Gas-to-Particle Conversion: Sulfur Dioxide in a Photo-chemically Reactive System Ph.D. Thesis California Institute of Technology, Pasadena, CA May 1975.

12. Heisler, S.L. Gas-to-Particle Conversion in Photochemical Smog: Growth Laws and Mechanisms for Organics Ph.D. Thesis California Institute of Technology, Pasadena, CA July 1975.

7. Plans:

1. To analyze data and conduct additional experiments involving simultaneous formation of organic and sulfate aerosols. Previous work on this grant indicates that condensable organic products tend to accumulate in larger size ranges than sulfates because of the Kelvin effect. By using a low pressure impactor it will be determined whether simultaneous condensation of organics and sulfates results in a larger average size for sulfate con-taining aerosols than condensation of sulfates alone.

2. Experiments to determine the effect of different types of sources including the marine aerosol, NO_x pollution and agricultural fertilizers on particle size distribution will be continued.

3. Low pressure impactor data collected during the Santa Monica Freeway Sulfuric Acid Aerosol Project will be analyzed. The freeway and background data will be compared to permit estimation of the sulfur distribution with respect to particle size in primary automobile emissions.

1. Task Title: A Study of the Identity and Sources of Atmospheric Aerosols.

2. Objective:

    To develop and apply optical and electron microscopy procedures
    for the identification and characterization of atmospheric aerosols.

3. Institution: IIT Research Institute, Chicago, Illinois
    Investigator: R.G. Draftz

4. EPA Project Officer: J.L. Durham

5. Progress:

    1.   In November 1975, IIT Research Institute and the EPA conducted an
    airborne dust sampling study in Maricopa County, AZ, to characterize the
    types and sources of suspended dust impacting on the city of Phoenix.
    The purpose of this study was to discover whether high suspended dust
    concentrations in the city are due to particles transported from
    surrounding deserts or from local sources.

    Suspended dust samples were collected with a network of hi-volume
    filters and impactors located in and outside of Phoenix. These fixed
    monitoring sites were supplemented with dust samples collected with an
    EPA helicopter at heights from 30 to 500 meters.

    Dust concentrations measured with hi-volume filters averaged
    200 $\mu g/m^3$ for samples located 3 to 20 meters above ground level and
    130 $\mu g/m^3$ for samples measured 30 to 500 meters above ground. Therefore,
    dust concentrations decreased with height.

    The dust particles were identified by optical and electron micro-
    scopy. The majority of particles contributing to high dust concentrations
    were minerals -- feldspars, quartz, calcite, mica, and clays. Carbon-
    aceous particles from auto exhaust and rubber tire particles were also
    present as minor components in every sample, even those collected in
    sparsely populated rural areas.

    The size, composition, and concentrations of these particles, com-
    bined with meteorological data, indicate that the particle sources were
    predominately local to the sampling sites. Vehicular traffic and
    farming are judged to be the primary contributors to the high dust
    concentrations in Phoenix. Particles from industrial sources were
    insignificant.

    2.   Aerosols were collected in powerplant and urban plumes emanating
    from St. Louis, MO, during July and August, 1975. The samples were
    collected at various distances and altitudes with an instrumented
    aircraft. Polarized light and electron microscopy were used to identify
    the types of aerosols formed and transported in the plume.

    Sulfuric acid or ammonium sulfate was the major, respirable com-
    ponent found in every sample. Minerals, flyash and a very unusual
    carbonaceous aerosol were minor components of each sample. These samples

provided the first direct evidence of sulfuric acid in urban and power-plants and also provided proof that they are transported at distances of up to 200 miles.

6. Publications, Presentations, Theses:

1. Microscopical Analysis of Aerosols Transported from St. Louis. Presented at: American Chemical Society Meeting, New York City, NY, April, 1976.

2. Aircraft Collection and Microscopical Analysis of Ambient Aerosols from Urban Atmospheres. Air Pollution Control Association Meeting, Portland, OR, June, 1976.

3. Comparison of Elemental and Microscopical Analyses of Atmospheric Aerosols. American Chemical Society Meeting, New York City, NY, April, 1976.

4. Similarities of Atmospheric Aerosols from Four Major U.S. Cities. Eighth Aerosol Technology Meeting, Research Triangle Park, NC, October, 1975.

5. Morphology of Airborne Dust in Maricopa County, Arizona. In preparation for presentation at: the 1977 AAAS Symposium on Denver Dust, Denver, CO, February, 1977.

7. Plans:

1. A new filter/impactor substrate has been discovered which may permit non-destructive analysis of atmospheric aerosols by microscopy, X-ray spectroscopy and chemical analysis. The present substrates are not compatible for all analyses, therefore increasing the number of samples that must be collected to obtain a reliable and complete characterization of aerosols. Laboratory tests and limited field trials will be performed to evaluate the suitability of this substrate for multiple non-destructive analyses.

2. Microscopical image analysis will be developed to permit quantitative measurement of aerosol size and concentration for total samples, as well as for individual particle types within a sample. Polarized light, UV fluorescence, dispersion and chemical staining by optical microscopy will be explored as methods to enhance aerosol discrimination and detection. Backscattered electron and micro X-ray emission imaging will be applied to submicron aerosols as a means of performing particle size by aerosol type.

1. Task Title: Analysis of Air Pollutants by Mass Spectroscopy.

2. Objective:

To examine the usefulness of high-resolution mass spectroscopy without prior chemical separations in determining the composition of the organic portion of the atmospheric aerosol.

To investigate the composition of real aerosol samples at various urban sites.

3. Institution: University of Washington, Seattle, Washington
   Investigator: A.L. Crittenden

4. EPA Project Officer: R. Patterson

5. Progress:

High-resolution mass spectroscopy was shown to be a useful means of characterizing the organic fraction of the urban aerosol. Quantitative accuracy was limited, particularly for compounds of low abundance. Some ambiguities were found in the assignment of origins of ions formed in the mass spectrometer.

Major constituents of fine particles in urban atmospheres are sulfuric acid or sulfates, and hydrocarbons. Other compounds that can be detected include phenols, aromatic carboxylic acids (and possibly esters) and aliphatic dibasic acids. Evidence was found of several other difunctional compounds, including nitrate or nitrite species.

Strong evidence was found for the presence in some urban aerosols of compounds reported by others as products of the oxidation of toluene in smog chamber reactions. Less evidence was found for products of the oxidation of terpenes.

A few samples of automobile exhaust particulates have been analyzed. The occurrence of benzoic acid and the benzol ion in mass spectra appear to be possible indicators of automotive contribution to the organic components.

Results for a large number of compounds are provided for 88 aerosol samples collected at sites located in the greater Los Angeles, Seattle, St. Louis and Denver Areas.

6. Publications, Presentations, Theses:

1. Crittenden, A.L. Analyses of Air Pollutants by Mass Spectroscopy. EPA-600/3-76-093, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976. 287pp.

2. Schuetzle, D., A.L. Crittenden and R.J. Charlson. 1973. Application of Computer Controlled High Resolution Mass Spectrometry to the Analysis of Air Pollutants. J. Air Poll. Control Assoc. 23:704.

3. Schuetzle, D., D.R. Cronn, A.L. Crittenden and R.J. Charlson. 1975. Molecular Composition of Secondary Aerosol and Its Possible Origin. Environ. Sci. Technol. 9:838.

4. Knights, R.L., D.R. Cronn and A.L. Crittenden; Diurnal Patterns of Several Components of Urban Particulate Air Pollution. Presented at: The Pittsburgh Conf. on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March 1975.

5. Cronn, D.R. 1975. Analysis of Atmospheric Aerosols by High-Resolution Mass Spectrometry. Thesis to be submitted to: University of Washington, WA.

7. Plans:

Project terminated and reported in:

Crittenden, A.L. Analysis of Air Pollutants by Mass Spectroscopy. EPA-600/3-76-093, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976. 287pp.

1. Task Title: Chemical Characterization of Model Aerosols

2. Objective:

    To identify the molecular structure of components of aerosols formed
    from individual hydrocarbons under simulated atmospheric conditions.

    To relate aerosol constituents to the type of aerosol precursor and
    chemical reaction.

3. Institution: Battelle-Columbus Laboratories, Columbus, Ohio
    Investigators: David Mendenhall, P.W. Jones, C.J. Riggle, A.D. Graffeo,
                    D.F. Miller, W.E. Schwartz

4. EPA Project Officer: R.K. Patterson

5. Progress:

    Model aerosols were generated by irradiating individual hydrocarbons,
    toluene and 1-heptene in air in the presence of NO_x or NO_x/SO_2. The collected
    aerosols were subjected to analysis by mass spectrometry and chromatographic
    techniques, both with and without chemical derivatization. The organics
    associated with the vapor phase were collected with a chromatographic adsorbant
    trap and analyzed by gas chromatography with mass spectrometric detection.

    The organic species associated with 1-heptene aerosol reaction products
    were tentatively identified as n-hexaldehyde, cyclohexanol (or an n-hexenol),
    and 1-heptene epoxide. The aerosol from 1-heptene revealed over 130 peaks
    on direct mass spectral analysis in a heated probe (Figure 1). The high
    molecular weight products are evidently formed by condensation of fragments
    from individual 1-heptene molecules.

    The gas-phase species from toluene include compounds tentatively iden-
    tified as simple transformation products of the hydrocarbon (Figure 2).
    Analysis of the aerosol from toluene, after derivatization with a trimethyl-
    silylating reagent, revealed a number of more highly oxidized products whose
    structures were inferred from m/e values of their parent ions (Figure 3).

    The products observed had undergone little or no oxidative degradation,
    and a considerable degree of ring substitution had taken place. Minor
    differences were observed between toluene/NO_x and toluene/NO_x/SO_2. No
    organic sulfur-containing compounds were detected. All major products were
    common to both experiments. Of the nine major products - Benzaldehyde,
    Nitrophenol, Nitrotoluene (3 isomers), and Nitrocresols (4 isomers); eight
    contain a nitro group.

    In the toluene/NO_x/SO_2 system, an additional major product formed which
    appears to be a polar compound of molecular weight 122. This compound doesn't
    contain sulfur, and its mass spectrum is consistent with that of methyl-p-
    benzoquinone, but has not been verified with a standard.

    The Ames test for mutagencity was carried out with unfractionated
    aerosols from both 1-heptene and toluene. No carcinogenic properties were
    revealed in any of the aerosol samples tested.

6. Publications, Presentations, Theses:

1. G.D. Mendenhall, P.W. Jones, A.P. Graffeo, W.E. Schwartz and W.E. Wilson. The Composition of Certain Atmospheric Aerosols. In: 171st American Chemical Society Meeting, New York, NY, April 1976.

2. W.E. Schwartz, P.W. Jones, D.F. Miller and G.D. Mendenhall. Organic Composition of Model Aerosols. California Air Environment. In Press.

7. Plans:

The project has been terminated and reported in:

Schwartz, W.E. Chemical Characterization of Model Aerosols. EPA-650/3-74-011, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1974. 130pp.

Schwartz, W.E., G.D. Mendenhall, P.W. Jones, C.J. Riggle, A.P. Graffeo and D.F. Miller. Chemical Characterization of Model Aerosols. EPA-600/3-76-085, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1976. 80pp.

43

FIGURE 1. CHEMICAL IONIZATION MASS SPECTRUM OF 1-HEPTENE AEROSOL
(SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE
TEMPERATURE RAISED FROM 25 TO 200 C

FIGURE 2. METHANE IONIZATION GC-MS ANALYSIS OF VAPOR PHASE
ORGANIC COMPOUNDS ASSOCIATED WITH TOLUENE/NO_x
AEROSOL
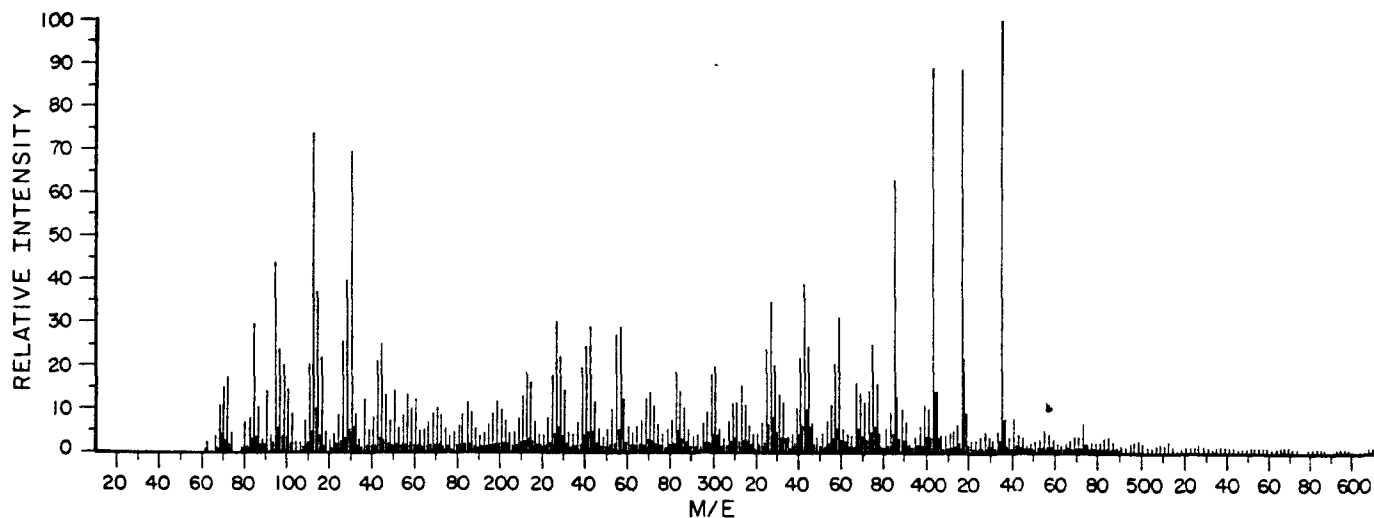
FIGURE 3. RECONSTRUCTED GAS CHROMATOGRAMS OF TOLUENE AEROSOLS DERIVATIZED WITH BSTFA

45

1. Task Title: Sources and Trace Metals in Urban Aerosols.

2. Sub-Task Title: Aerosol Properties Relavent to Health Effects.

3. Objectives:

   Design experiments which apply sensitive X-Ray analysis techniques to the measurement of aerosols related to human respiratory uptake and deposition.

4. Institution: Department of Oceanography, Florida State University
   Investigator: John W. Winchester

5. EPA Project Officer: Ronald K. Patterson

6. Progress:

   The particle size distribution of lead, bromine, chlorine and calcium in exhaled aerosols from a human subject breathing normally polluted air was measured using proton induced X-Ray emission (PIXE) analysis. This experiment in the respiratory deposition of aerosols utilized two similar air sampling devices, one for sampling the ambient air directly and one into which the subject supplied all the air from his exhaled breath. Both devices were operated by a vacuum pump which drew air at a constant rate by means of critical flow orifices. The sampling devices used 5 and 6 stage Battelle-type cascade impactors, which operated at flow rates of 12 liters per minute and 1 liter per minute, and gave resolution down to 0.5 and 0.25 -μm diameter, respectively, on the impaction stages. Two aerosol sources were employed: cha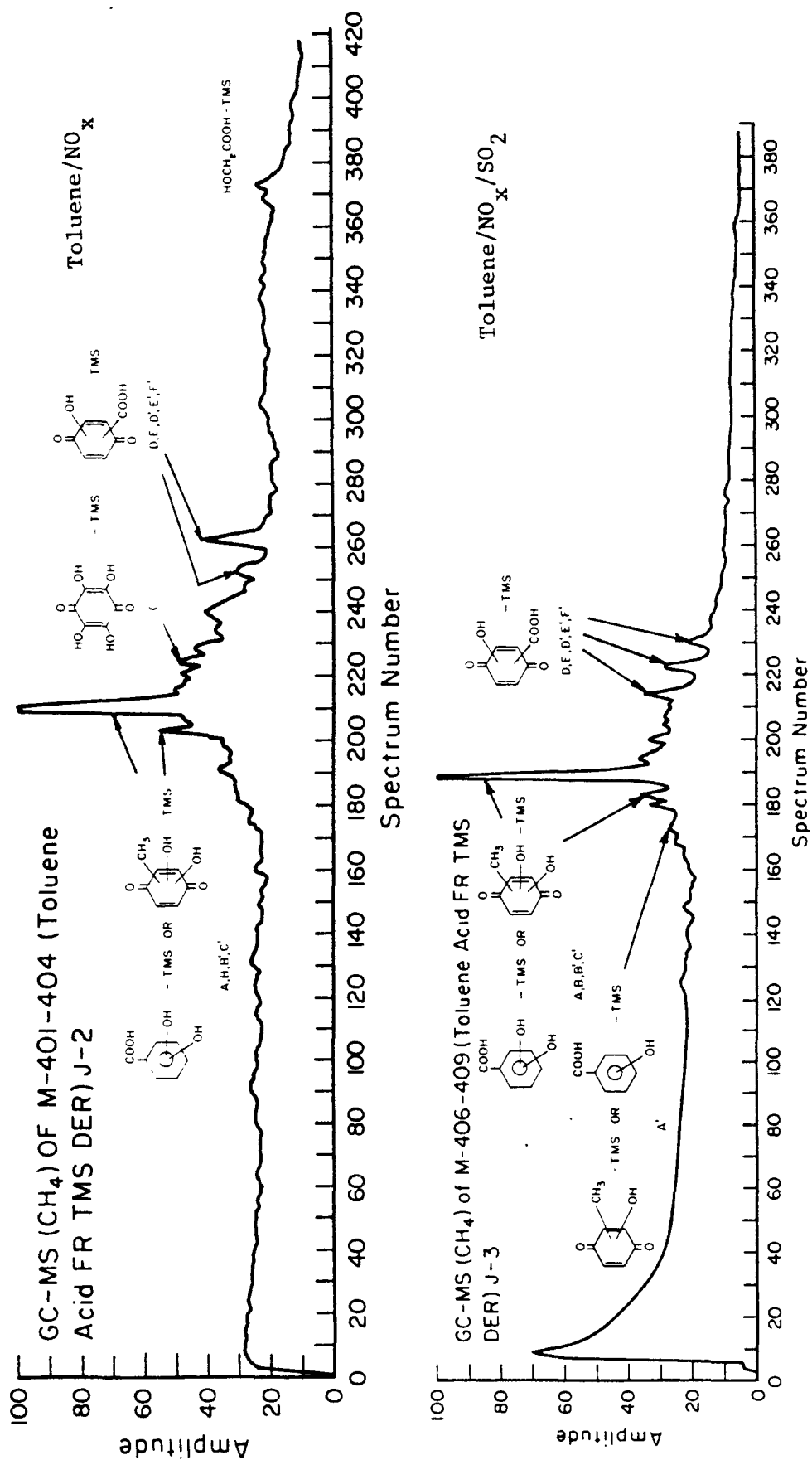lk dust generated by blackboard erasers and lead halide aerosols generated by an automobile operating at idling speed in a semienclosed space near the subject. Three experiments were conducted using the two sources separately and combined. Using PIXE analysis Ca, Pb, Br, and Cl were easily measured in samples collected over a ten-minute interval.

   Figure 1 is a plot of the apparent respiratory deposition fraction for calcium, lead, bromine and chlorine. A similar pattern is shown for all elements, with a minimum deposition well under 50% in the region of 0.5μm diameter (aerodynamic equivalent for unit density spheres) and deposition well over 50% for both smaller and larger particles. In this study feasibility was demonstrated for direct determinations of trace element respiratory depositions in human subjects breathing aerosols at ambient air concentrations.

   Another study under this sub-task title utilized the data from the above study and a Los Angeles freeway study to calculate the fraction of atmospheric lead expected to be deposited in the respiratory tract as a function of particle size for the upwind and downwind freeway sites. The calculation indicates the qualitative finding that differences in a particle size distribution combined with differences in the efficiency of respiratory deposition may determine the overall magnitude of lead deposition by aerosol inhalation. Emperical deposition curves for pulmonary, tracheobronchial, and nasopharyngial regions published by the Task Group on Lung Dynamics, were used to estimate the extent and location of lead aerosol deposition, based on the measured Los Angeles size distributions (Figure 2). For individual upwind and downwind sites, respectively, total lead deposition summed over all particle sizes are

33% and 35% for pulmonary, 5.4% and 5.7% for tracheobronchial, and 9.3% and 7.5% for nasopharyngeal regions; these values do not indicate significant differences in total deposition of lead with aerosol age. However, within particle size classes the differences were significant, and these were expected to be linked with the points of deposition within the lung.

7. Publications:

1. G.G. Desaedeleer, J.W. Winchester, and K.R. Akselsson. Monitoring Aerosol Elemental Composition in Particle Size Fractions for Predicting Human Respiratory Uptake. Nuclear Instruments and Methods (In Press).

2. G.G. Desaedeleer and J.W. Winchester. Trace Metal Analysis of Atmospheric Aerosol Particle Size Fractions in Exhaled Human Breath. Environmental Science and Technology, Vol. 9, October, 1975, pp.971-972.

8. Plans:

This grant is complete. A final report is forthcoming.
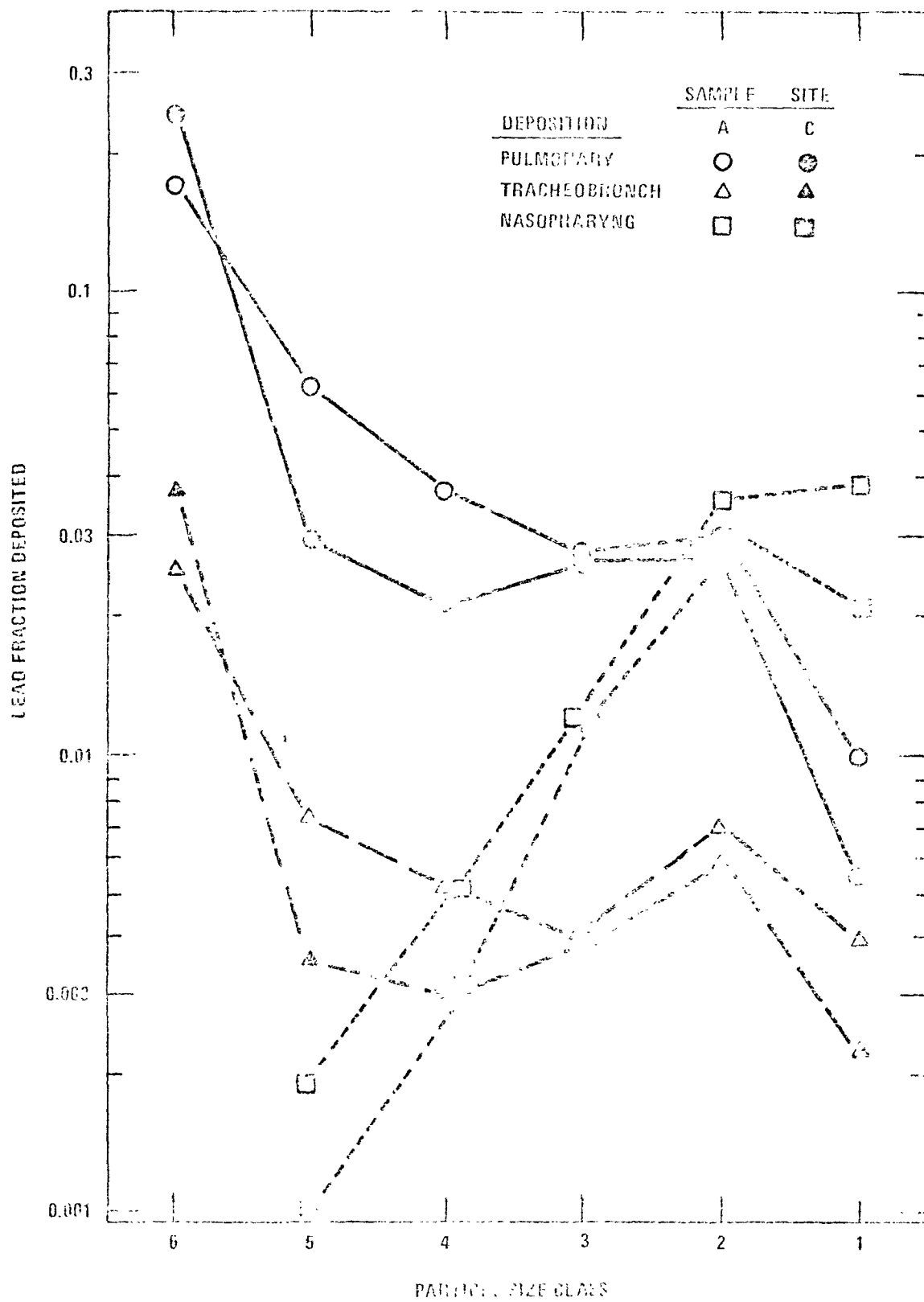
Figure 2.
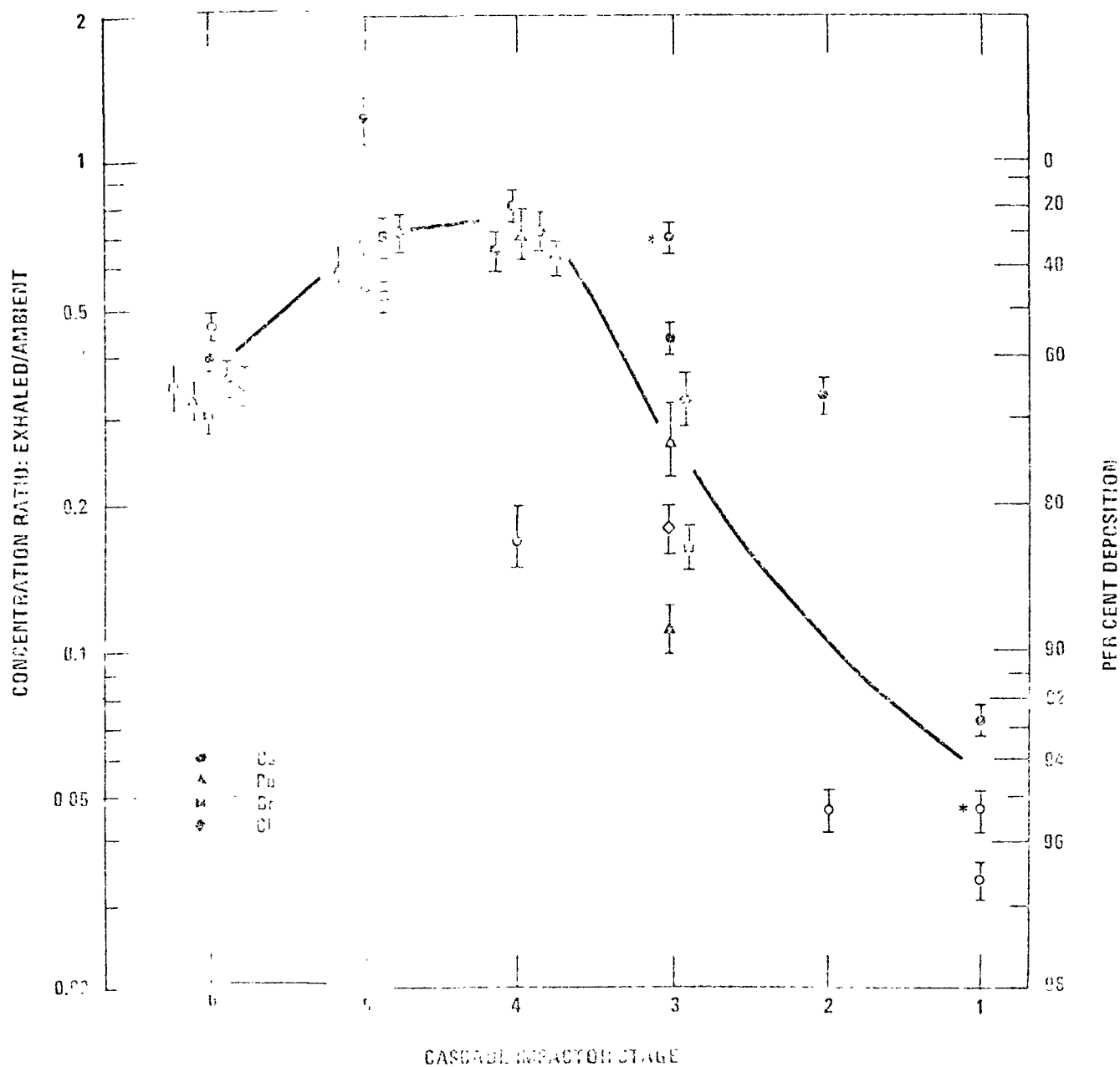
Figure [...] as a function of particle size for simultaneous exhaled and ambient [...]
Solid po[...] [...] nators are exhaust and exhaust experiments: open points are for [...] Pb, Cl, Br data for stages 6 [...] 5 by small impactor, stages 4 and [...] by [...] [...] data by small impactor except where marked by *. Error bars represent [...] [...] [...] [...] deviations in the ratios.

49

1. Task Title: Aerosol Sources Program

2. Objective: To collect ambient aerosols with the goal of identifying
   aerosol sources through wind-directional sampling and
   sensitive analysis techniques.

3. Institution: EPA, Aerosol Research Branch

4. EPA Project Officer: Ronald K. Patterson

5. Progress: Samples were collected in Miami, St. Louis, and Pittsburgh
   between May and July, 1975. Modified Battelle type samplers were
   operated by an Aerosol Research Branch designed wind-directional
   programmer which operates up to four (4) selectable wind sectors
   with two degree resolution. Florida State University Streaker
   samplers were also used and both types of samples were analyzed
   by Proton-induced X-Ray Emission at Florida State.

   A report on the Miami and St. Louis analysis results was
   prepared for OAQPS (Tom Pace) in October, 1975. The final draft
   report on the data analysis and interpretation of the Miami results
   is being prepared under EPA Contract #68-02-2406 by Dr. Kenneth A.
   Hardy, Florida International University. St. Louis and Pittsburgh
   data reduction and interpretation will begin next month under the
   same contract.

6. Publications, Presentations, and Theses: None

7. Plans: Prepare reports on St. Louis and Pittsburgh results by July, 1977.

1. <u>Task Title</u>: Aerosol Microscopy

2. <u>Objective</u>:

   To carry out research studies of the structure, composition and sources of pollutant aerosol particles and other environmental studies that may be assigned through the use of electron-optical and optical X-ray analytical methods.

3. <u>Institution</u>: Environmental Protection Agency, ESRL, ARB, Research Triangle Park, North Carolina.
   <u>Investigator</u>: J. Gerhard

4. <u>EPA Project Officer</u>: J. Gerhard

5. <u>Progress</u>:

   The following more recent tasks are completed: Tampa Aerosol Study; Texas Dust Storm Study; Iron Foundry, Utah Study; Cal-Nevada Study; Asbestos in Building Materials and Respiraton Filter Deposit examinations.

6. <u>Publications, Presentations, Thesis</u>: None

7. <u>Plans</u>:

   Written reports of the analytical results of all future studies will be distributed to all interested personnel as expediently as possible.

1. Task Title: Field Expedition to Phoenix, Arizona

2. Objective:

   To determine the importance of dust transported from the surrounding deserts on the mass loadings measured in the Phoenix area.

3. Institutions: ARB - ESRL   Jack L. Durham
                  AMAD - ESRL   Ken Scherer
                  EPA - LV   Jeff Van Ee
   Investigators: IIT Research Institute - Richard Snow, Jean Graf, and Ronald Draftz.
                  P. Durham, J. Frazier, and L. Quinn (EPA student aids)

4. EPA Project Officer: Jack L. Durham

5. Progress:

   During November, 1975, airborne and ground-level dust samples were collected for the purpose of characterizing the types and sources of suspended dust impacting Phoenix. Wind profile measurements were also made.

   Dust concentrations measured with hi-volume filters averaged 203 $\mu g/m^3$ for samplers located 30 to 20 meters above ground level. Dust concentrations ranged from 130 $\mu g/m^3$ to 30 $\mu g/m^3$ measured 30 to 500 meters above ground level. The dust concentrations decreased with height.

   The dust particles were identified by optical and electron microscopy. The majority of particles contributing to the high dust concentrations were minerals -- feldspars, quartz, calcite, mica, and clays. Carbonaceous particles from auto exhuast and rubber tire particles were also present as minor components in every samples, even those collected in sparsely populated rural areas.

   The size, composition, and concentrations of these dust particles, combined with meteorological data, indicate that the particle souces were predominantly local to the sampling sites. Vehicular traffic, and to some extent farming, are judged to be the primary contributors to the high dust concentrations in Phoenix. Particles from industrial sources were insignificant.

6. Publications and Presentations:

   1. Graf, J., R.H. Snow, J.L. Durham, and K.L. Scherer. Morphology of Airborne Dust in Marcopia County, Arizona. Presented at: AAAS Meeting, Denver, February 1977. To be published in Proceedings.

   2. Suck, S., E. Upchurch, and J. Brock. Dust Transport in Maricopa County, Arizona. Presented at AAAS Meeting, Denver, February 1977. To be published in Proceedings.

   3. Graf, J., R.H. Snow, and R.G. Draftz. Aerosol Sampling and Analysis - Phoenix, Arizona. (EPA-600/3-77-015 February, 1977). IIT Research Institute, Chicago). 136 pages.

7. Plans: Project is complete.

1. Task Title: Analytical Support for Aerosol Studies

2. Objective:

    Provide or arrange for the analysis of ambient aerosol samples collected in the field and adapted existing analytical analysis techniques to aerosol samples.

3. Institution: Environmental Protection Agency, Aerosol Research Branch
    Investigator: R.K. Patterson; Joe Frazier and Kevin Peterson(Student Aids)

4. EPA Project Officer: Ronald K. Patterson

5. Progress:

    An ion chromatograph was installed and modified with an automatic sampling system. This system is being used to determine the $SO_4^=$, $SO_3^=$, NO_2^-, $NO_3^=$, Br^-, Cl^-, NH_4^+, Na^+, and K^+ content in ambient aerosols.

    Progress is being made on determining the organic carbon content of fractionated ambient aerosols using a temperature programmable furnace and a flame ionization detector system. The major setback in this effort has been finding a collection medium which does not interfer with the analysis.

    Other analytical techniques such as Proton-induced X-Ray Emission and Computerized High Resolution Mass Spectrometry have been evaluated through grants.

6. Publications, Presentations, Theses: See Winchester and Crittenden grants.

7. Plans:

    1. Release RFP for an "Analytical Support for Aerosol Studies" contract, in order to relieve our equipment of approved routine techniques.

    2. Continue to research our ion chromatography capabilities as they relate to ambient aerosols.

    3. Continue to pursue a suitable technique for determining organic carbon in fractionated ambient aerosol samples.

A. ATMOSPHERIC PROCESSES AND EFFECTS

3. Visibility and Radiation Effects. Measurement of pertinent aerosol properties and determination of relationships between concentration, composition, size and effects.

54

1.   Task Title: Opticle Effects of Atmospheric Aerosol

2.   Objective:

   To develop experimental and analytic techniques for understanding sources of aerosol particles and their integral optical effects.

3.   Institution: University of Washington, Seattle, Washington
   Investigator: A.P. Waggoner

4.   EPA Project Officer: T.G. Ellestad

5.   Progress:

   Condensed water interacts with aerosol particles in ways that depend on the molecular nature of the particles. Using this interaction, instruments were designed that measure the scattering behavior as a function of relative humidity to determine the molecular form of $SO_4^=$ when it is present as a major constituent of the fine particle mass. $SO_4^=$ (as H_2SO_4 or $(NH_4)_2SO_4$) was found to dominate midcontinent rural US haze, and was found present as acid sulfate approximately one half the time.

   These results were obtained at a single site near St. Louis in 1973, and at three sites in rural Michigan, Missouri and Arkansas in 1975. An instrument was constructed to facilitate making these measurements. The form of the sulfate aerosol (salt or acid) was shown to be related to long range transport in that marine tropical air from South and East was predominately acid, and air from the North and West was predominately salt.

   The almost continuous $SO_4^=$ domination at all three sites indicates that the rural haze is the product of a multitude of sources covering an area larger than one $SO_4^=$ removal/SO_2 oxidation distance. These results have direct bearing on such subjects as SO_2 control via tall stacks or via scrubbers, and the sources of rural and urban $SO_4^=$.

   Experimental measurements have been made of SO_2 oxidation rate in solution with O_2 and O_3 under a range of temperatures and pH. The study showed that the rates of conversion of SO_2 to SO_4 measured in plumes are consistent with O_3 solution oxidation rates which should exist in warm clouds.

6.   Publications:

   1.   Larson, T.V., R.J. Charlson, E.J. Knudson, G.D. Christian and H.H. Harrison. 1975. The Influence of a SO_2 Point Source on the Rain Chemistry of a Single Storm in the Puget Sound Region. Water Air and Soil Poll. 4.

   2.   Vanderpol, A.H., F.D. Carsey, D.S. Covert, R.J. Charlson and A.P. Waggoner. 1975. Aerosol Chemical Parameters and Air Mass Character in the St. Louis Region. Science. 190:(7 Nov).

3. Waggoner, A.P., A.H. Vanderpol, R.J. Charlson, T.V. Larsen, L. Granat and C. Tragardh. 1976. Sulfate as a Cause of Tropospheric Haze. Nature. 261(13 May).

4. Porch, W.M., D.S. Ensor, R.J. Charlson. 1975. Visibility of Distant Mountains as a Measure of Background Aerosol Pollution. Applied Optics. 14.

5. Weiss, R.V., A.P. Waggoner, R.J. Charlson, N.C. Ahlquist. Sulfate Aerosol: Its Geographical Extent. Science. In Press.

6. Bolin, B., R.J. Charlson. 1976. On the Role of the Tropospheric Sulfur Cycle in the Short-Wave Radiative Climate of the Earth. AMBIO. 5(2).

7. Covert, D.S., R.J. Charlson, R. Rasmussen, H. Harrison. 1975. Atmospheric Chemsitry and Air Quality. Reviews of Geophysics and Space Physics. 13(3).

8. Scheutzle, D., D. Cronn, A.L. Crittenden and R.J. Charlson. 1975. Molecular Composition of Secondary Aerosol and Its Possible Origin. Env. Sci. and Tech. 9(9).

7. Plans:

1. To conduct field experiments in the Oregon-Washington area this fall to define the magnitude of impact and help identify sources of urban and rural aerosol in this region.

2. Laboratory and field experiments are being designed to investigate the role of urban emissions in altering the nature and persistence of high humidity hazes and fogs. Data to be examined include the: relationships between the aerosol concentration of Pb, $SO_4^=$, Fe and optical absorption to determine the source and nature of materials that may cause heating of air aloft and altering stability; role of long range transport, RH, temperature, incidence of rainfall along trajectory as these affect $SO_4^=$ acid/salt character of the aerosol; character of visibility distributions from airports and other sources as a function of site location to determine the causes of reduced visibility.

A. ATMOSPHERIC PROCESSES AND EFFECTS

4. <u>Heterogeneous Reactions</u>. Measurement of the rates and mechanisms of reactions involving gases with surfaces or condensed phases.

1. <u>Task Title</u>: The Role of Gas-Solid Interactions in Air Pollution.

2. <u>Objective</u>:

   To assess the importance of heterogeneous surface reactions of gaseous pollutants such as SO_2 with constituents of urban aerosols and ground level surfaces in the urban environment.

3. <u>Institution</u>: The Aerospace Corporation, Los Angeles, California
   <u>Investigator</u>: H. Judeikis

4. <u>EPA Project Officer</u>: J.L. Durham

5. <u>Progress</u>:

   Measurements have been made on the capacities for SO_2 removal over various solids (Table 1). The dependency of reactivities and capacities on various experimental conditions have been examined and surface reaction products have been analyzed. Measured capacities ranged from several tenths of a gram of SO_2 removal per gram of solid for materials such as MgO and MnO (particularly for humidified reaction mixtures)-to several milligrams of SO_2 per gram of solid for materials such as charcoal. Both reactivities and capacities were found to be generally independent of SO_2, O_2, and total pressures. Reactivities were found to be generally independent of relative humidity; capacities were not. Capacities measured with humidified reaction mixtures were frequently an order of magnitude greater than those found for dry mixtures. X-ray photoelectron (ESCA) and wet chemical techniques identified sulfate as the only sulfur-containing surface reaction product.

   Laboratory measurements have been made of deposition velocities for SO_2 at ground level surfaces (Table II). The apparatus used accounts for gas-phase mass transport of SO_2 so that obtained values are due solely to the physical and/or chemical processes responsible for SO_2 removal at the surface. Here also, removal was found to accur via capacity limited reactions. Results show the dependencies of reactivities and capacities on SO_2, O_2, total pressure, and relative humidity were qualitatively similar to those discribed above.

   Also examined was the potential role of additional environmental factors on SO_2 removal. Pre-treatment of selected solids with dilute ammonia (or NaOH) was found to enhance initial reactivities by a factor of approximately 5, while pre-treatment with dilute H_2SO_4 (HCl) reduced initial reactivities by one order of magnitude.

   In order to remove soluble sulfates, several solids were washed with distilled water after their reactivity toward SO_2 was completely expended (footnote 3 of Table 1). This treatment restored initial reactivities within experimental error, thus suggesting that precipitation could restore the reactivity of ground-level surfaces in the actual environment.

6. <u>Publications, Presentations, Theses</u>:

   1. Judeikis, H.S. Heterogeneous Removal of SO_2 from the Atmosphere. Presented at: 8th Aerosol Technology Meeting, Chapel Hill, NC, October 6-8, 1975.

2. Judeikis, H.S. and T.B. Stewart. 1976. Laboratory Measurement of SO_2 Deposition Velocities on Selected Building Materials and Soils. Atmos. Environ. 10:769.

3. Judeikis, H.S. Heterogeneous Interactions of Atmospheric SO_2. Presented at: Workshop on the Chemistry of Atmospheric Sulfur, Philadelphia, PA, October 12-14, 1976.

7. <u>Plans</u>:

1. To complete and publish work on SO_2 in SO_2-O_2-N_2-H_2O mixtures.

2. Begin studies on the addition of ammonia and/or hydrocarbon + NO_x to the reaction mixtures.

Table I. Reactivities and Projected Atmospheric Rates for
Heterogeneous Removal of SO_2

Solid	ϕ^1	SO_2 Removal[2] %/hour
MgO	1.0×10^{-3}	32
Fe_2O_3	5.5×10^{-4}	18
Mojave Fly Ash	5.0×10^{-4}	16
Al_2O_3	4.0×10^{-4}	13
MnO_2	3.0×10^{-4}	10
PbO_2	7.0×10^{-5}	3
Charcoal	3.0×10^{-5}	1
NaCl	3.0×10^{-6}	0.1
$MnCl_2$	$<1.0 \times 10^{-6}$	<0.03
River Bend Fly Ash[3]	$<1.0 \times 10^{-6}$	<0.03

[1] ϕ is the fraction of SO_2-solid collisions that lead to SO_2 removal.

[2] Projected atmospheric removal rates assuming an urban aerosol loading of 100 $\mu g/m^3$ having the same reactivity as the indicated solid.

[3] Measurements on this material as received indicated a high sulfate content and low reactivity. Experiments on the same material after washing with distilled water to remove soluble sulfates gave a reactivity comparable to that measured for Mojave Fly Ash.

[4] 20-30% uncertainty

[5] The data is for metal exposure to SO_2. With prolonged exposures, the reactivities gradually diminish and ultimately approach zero, indicating SO_2 removal occurs by capacity limited reactions.

Table II. Deposition Velocities for SO_2 Removal

Material[1]	ϕ[2]	Deposition Velocity cm/sec
Cement - I[3]	3.2×10^{-4}	2.5
Ready Mix Cement[3]	2.6×10^{-4}	2.0
Exterior Stucco - I[3]	2.3×10^{-4}	1.8
Cement - II[3]	2.0×10^{-4}	1.6
Exterior Stucco - II[3]	1.1×10^{-4}	0.86
Adobe Clay Soil	8.4×10^{-5}	0.66
Sandy Loam Soil	8.3×10^{-5}	0.65
Asphalt	5.1×10^{-6}	0.04

[1] Roman numerals indicate different sources for the materials used.

[2] ϕ is the fraction of SO_2-solid collisions that lead to SO_2 removal.

[3] Cured.

1. <u>Task Title</u>: Structure and Reactivity of Adsorbed Oxides of Sulfur and Other Small Sulfur-Containing Molecules.

2. <u>Objectives</u>:

   To determine the structure and reactivity of adsorbed oxides of sulfur and other small sulfur-containing molecules which may exist on atmospheric aerosols.

3. <u>Institution</u>: Texas A&M University, College Station, Texas
   <u>Investigator</u>: J.H. Lunsford

4. <u>EPA Project Officer</u>: J.L. Durham

5. <u>Progress</u>:

   It has been observed that under rather mild conditions, sulfur dioxide undergoes a variety of surface reactions. One such reaction occurs between SO_2 and magnesium oxide. On the basis of spectroscopic data, it is evident that sulfite ions are readily formed on the surface, and that except at elevated temperatures of more than $200^{\circ}C$, it is not possible to oxidize these to the sulfate form with molecular oxygen. A limited number of these sulfite ions may, however, be photochemically oxidized to SO_3^- ions on the surface of magnesium oxide in the presence of adsorbed water vapor and oxygen or nitrous oxide.

   The reaction between H_2S and molecular oxygen or air was carried out at $25^{\circ}C$ over magnesium oxide, MnNaY and NaY zeolites, and amorphous silica-alumina. The surface products, as determined by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy, were different on each of the surfaces. On magnesium oxide sulfide ions, elemental sulfur, and sulfite ions were observed, as well as S_3^- and S_2O^- ions. Only elemental sulfur was formed on the zeolite samples, and no reaction products were detected on the amorphous silica-alumina. Clearly, it is difficult to form $SO_4^=$ from H_2S at moderate temperatures using molecular oxygen as an oxidizing agent.

   Although these experiments indicate the difficulty in oxidizing a reduced form of sulfur to sulfate ions, it is possible to do so provided the correct catalyst is used. The oxidation of SO_2 has been catalyzed, for example, by manganese ions in aqueous solution. SO_2 may be oxidized to sulfate ions by hydrated Mn^{2+} ions in MnNaY zeolites and on amorphous silica alumina.

   Nitrogen dioxide has been found to be a more effective oxidizing agent than molecular oxygen. At pressures of several torr, NO_2 is capable of oxidizing SO_2 to $SO_4^=$ at $25^{\circ}C$ on the surface of silica gel and amorphous silica alumina. Nearly monolayer coverages are obtained after several hours of reaction. The XPS spectrum of the S(2p) and N(2p) lines for sulfur and nitrogen on the surface of silica gel and in ammonium sulfate are depicted in Figure 1.

5. Progress (cont'd):

Results show that the radical anions S_3^- and S_2O^- were also formed as by-products of the reaction on magnesium oxide. It appears that elemental sulfur from the Claus reaction, probably in the form of S_2, reacts with lattice oxide ions of MgO yielding S_2O^-. The same ion could also be formed by ultraviolet irradiation of adsorbed COS or CS_2.

The formation of H_2S^- was detected using EPR spectroscopy. This ion may be produced by the low temperature reactions of H_2S with trapped electrons on the surface of MgO. The EPR spectrum was previously attributed to the H_2S^- ion; however, using sulfur-33 labelled H_2S, we demonstrated that the paramagnetic molecule contained two non-equivalent sulfur atoms.

6. Publications, Presentations, and Thesis:

1. M.J. Lin and J.H. Lunsford. 1975. Photooxidation of Sulfur Dioxide on the Surface of Magnesium Oxide. J. Phys. Chem. 79:892-897.

2. M.J. Lin and J.H. Lunsford. 1976. Electron Paramagnetic Resonance Evidence for the Formation of S_2O^- on Magnesium Oxide. J. Phys. Chem. 80:635-639.

3. M.J. Lin and J.H. Lunsford. 1976. An EPR Study of $H_2S_2^-$ on Magnesium Oxide. J. Phys. Chem. 80:2015-2018.

4. M.J. Lin. Structure and Reactivity of Sulfur-Containing Molecules Adsorbed on Magnesium Oxide. Ph.D. Dissertation, Texas A&M University, TX.

7. Plans:

1. To investigate the formation of sulfate ions on surfaces, starting with reduced forms of sulfur and oxidizing agents such as molecular oxygen, ozone and nitrogen dioxide.

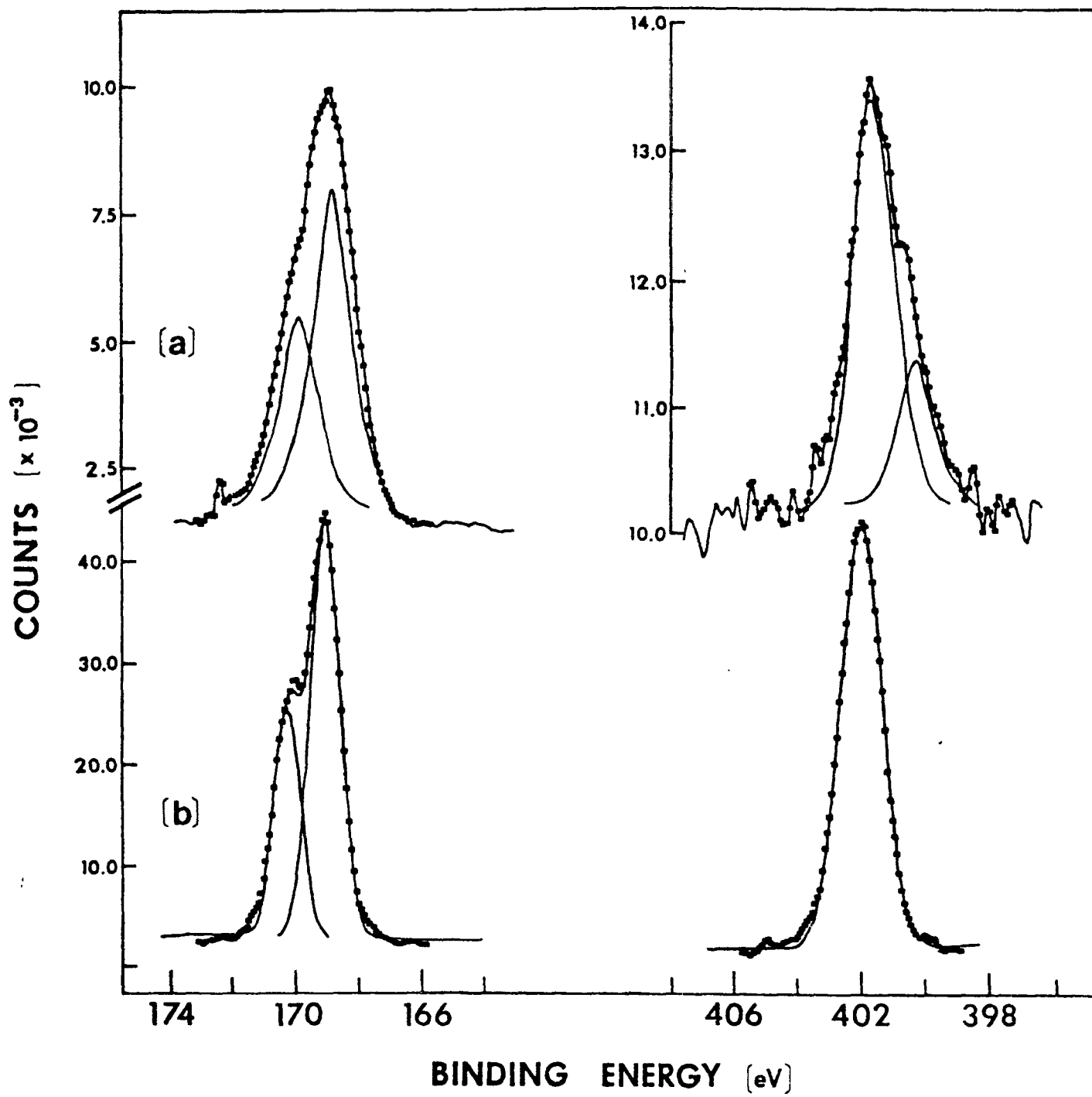2. To emphasize the quantitative aspects of these surface reactions.

Figure 1. S(2p) and N(1s) photoelectron lines from (a) silica gel exposed to SO_2 and NO_2 and (b) $(NH_4)_2SO_4$.

1. <u>Task Title</u>: Structure and Reactivity of Adsorbed Oxides of Sulfur.

2. <u>Objective</u>:

    To develop photoelectron and infrared spectroscopy as a technique for studying oxides of sulfur on aerosols.

    To determine the mechanism for the oxidation of SO_2 to $SO_4^=$ on surfaces.

    To identify ions such as S_2O^- which may be produced during the photochemical reaction of H_2S with SO_2 on magnesium oxide.

3. <u>Institution</u>: Texas A & M University, College Station, Texas
    <u>Investigator</u>: J.H. Lunsford

4. <u>EPA Project Officer</u>: J.L. Durham

5. <u>Progress</u>:

    The past year has been devoted to photoelectron studies of sulfur species on pure oxides, collecting flyash samples from the River Bend Power Plant, and collecting atmospheric aerosols which were near the Labadie Power Plant in St. Louis. In order to identify surface species by photoelectron spectroscopy, the energy of the emitted photoelectron must be converted into a binding energy for sulfur. This is not a simple problem since most of the samples of interest are insulators and charring effects become serious. By employing a standard of gold evaporated onto the samples, along with an electron flood gun, binding energies with an error less than ±0.5 eV have been obtained. It has also been necessary to develop computer programs for smoothing and deconvolution of the data.

    A study of SO_2 and H_2O adsorbed on $MgO/Mg(OH)_2$ confirms our earlier conclusions, based on infrared spectra, that surface sulfite ions are formed at 23°C. The deconvoluted photoelectron spectrum of this species is compared with the spectrum of elemental sulfur, S_8, in Fig. 1a and 1b. Heating the sample in O_2 at elevated temperatures (200°C) was required for the oxidation of surface sulfite ions to sulfate ions.

    The Riverbend flyash sample revealed that most of the sulfur exists on the surface as sulfate ions (Fig. 2a). A number of other elements were detected in a broader scan of the flyash.

    An unsmoothed spectrum from an aerosol sample collected in St. Louis shows that two types of sulfur are present; one is a sulfate ion and the other resembles an inorganic sulfide ion or an aromatic sulfide (Fig. 2b). The samples also contained nitrogen in the form of ammonium ions, which is consistent with the results of other laboratories.

    Limited progress has been made in determining the mechanism for the oxidation of SO_2 to $SO_4^=$ on surfaces. In stack gases, NO_x may be

the oxidant rather than O_2. In an effort to investigate this possibility SO_2 and NO_2 were sequentially adsorbed or coadsorbed on MgO, and the surface spears were identified by infrared and photoelectron spectroscopy. Preliminary results indicate that the adsorption of SO_2 first (yielding surface sulfite ions), followed by exposure to NO_2 resulted in the partial oxidation to $SO_4^=$ ions at $25°C$; however, coadsorption did not yield a more oxidized form of sulfur. This may be explained by the fact that NO_2 adsorbs as ions which are not capable of oxidizing SO_2, whereas, molecular NO_2 oxidizes the surface sulfite to sulfate ions. As indicated previously, molecular oxygen is not capable of oxidizing sulfite ions at room temperature.

SO_2 and H_2 were found to react at $25°C$ on magnesium oxide, forming a paramagnetic species which has been identified at S_2O^-. Hyperfine splitting due to sulfur-33 was used to confirm the identification. The previously studied S_3^- ion is also formed. Thus the Claus reaction yields elemental sulfur in the form of S_2, $S_3...S_8$, $...S_n$ molecules. The S_2 molecules react with surface oxide ions, forming S_2O^-. This ion requires a degassed MgO surface for its formation, but it is stable in the presence of air.

6. Publications, Presentations, Theses:

    1. A paper is scheduled to appear in the Journal of Physical Chemistry.

    2. A review of the literature on adsorbed oxides of sulfur has been completed and will be published.

7. Plans:

    1. To develop photoelectron spectroscopy as a technique for studying atmospheric aerosols and for following in the laboratory the oxidation of SO_2 on surfaces.

    2. To focus on the mode of oxidation of SO_2 to SO_3 or $SO_4^=$ on surfaces by investigating the reactions which occur in thin aqueous films on metal oxide surfaces. Silica and alumino silicates will be investigated using both O_2 and N_2O as oxidants. On pure surfaces it is anticipated that the oxidation reactions will be slow; however, introducing transition metal ions should catalyze the reactions. Work will continue on the surface analysis of atmospheric aerosols.
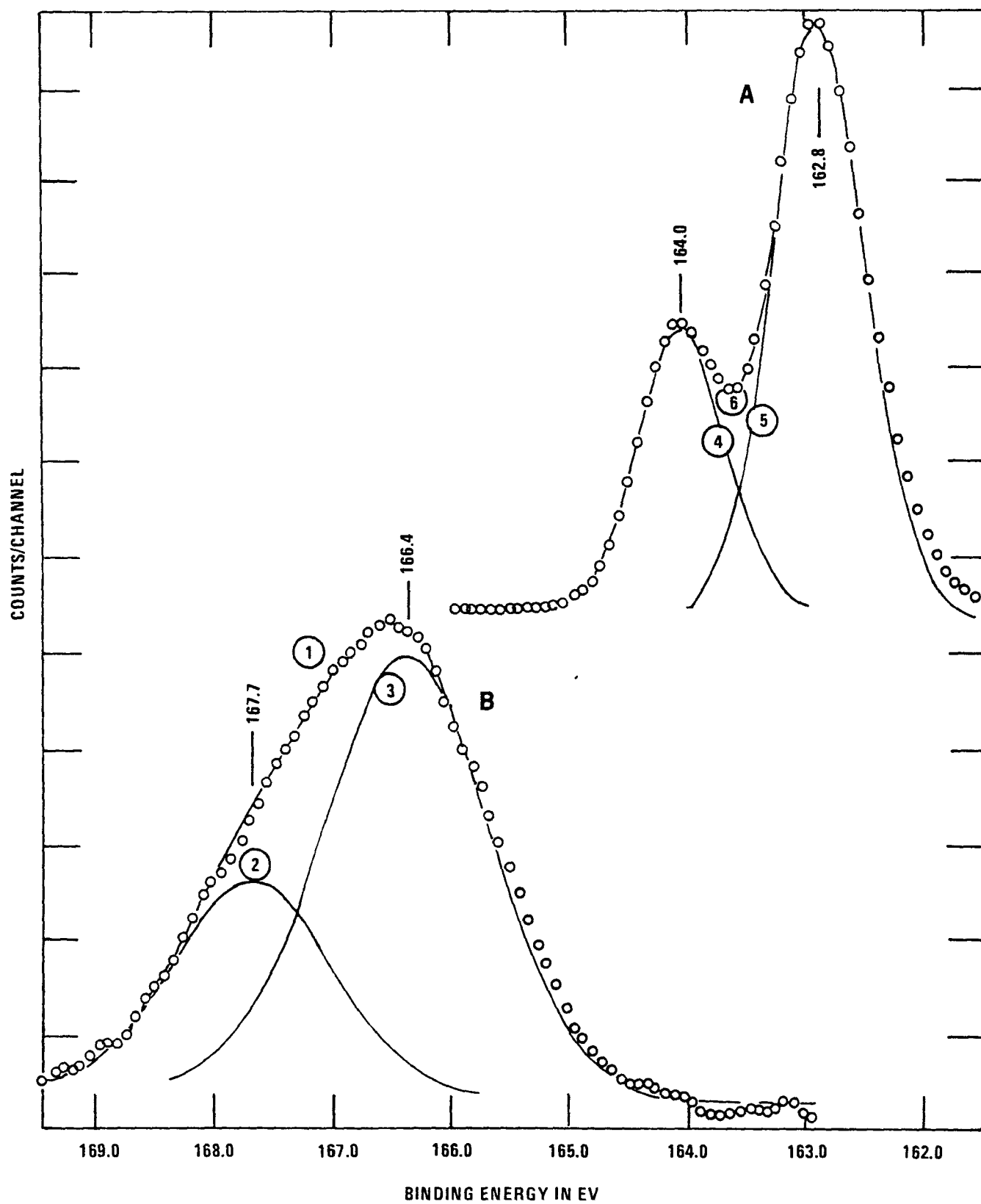
Figure 1. Photoelectron spectra of sulfur 2p: (A) elemental sulfur, S_8, (B) SO_3^{2-} ions on MgO.
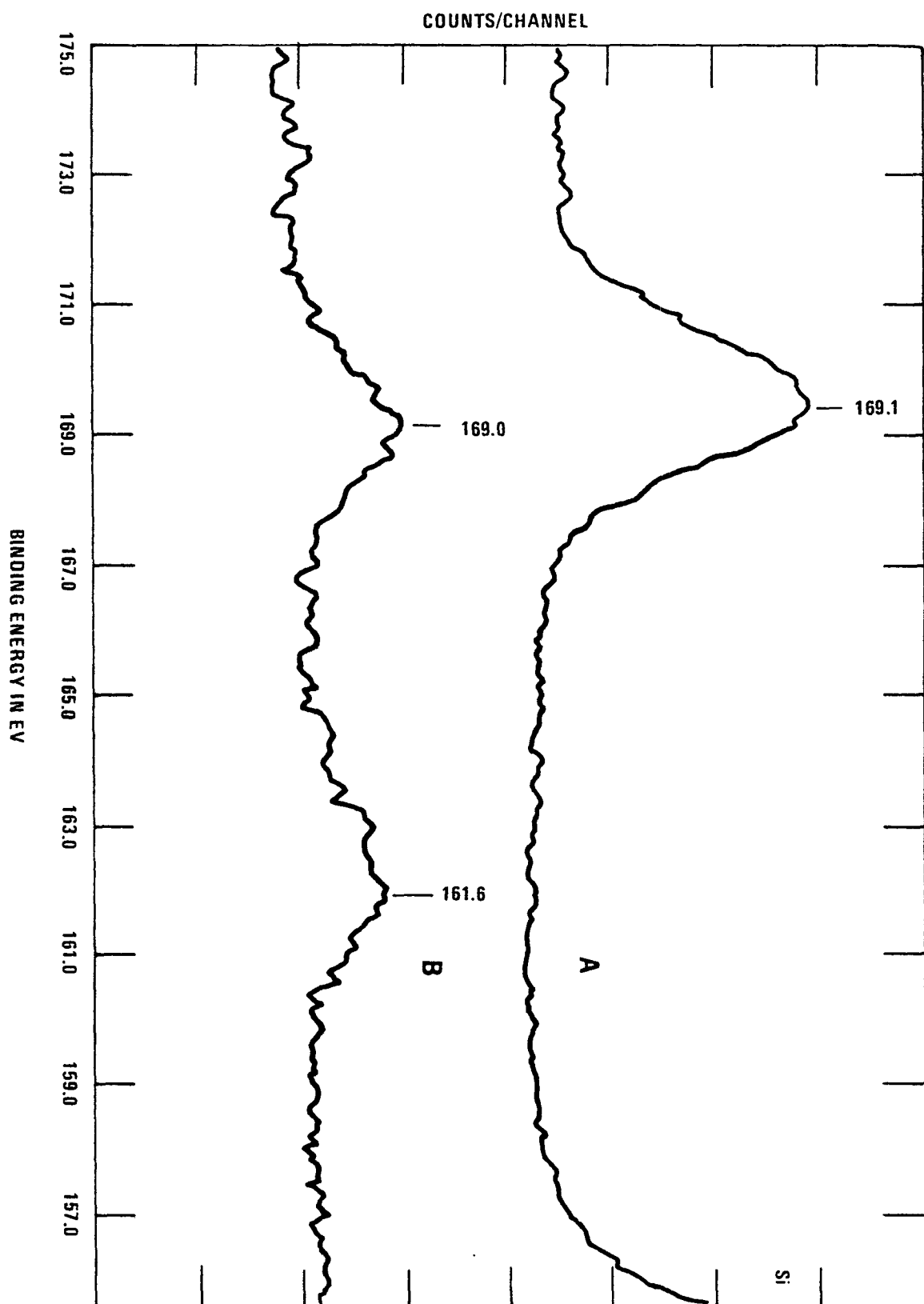
COUNTS/CHANNEL

169.1

169.0

161.6

A

B

Si

BINDING ENERGY IN EV

Figure 2. Photoelectron spectra of sulfur 2p: (A) SO_4^{2-} on flyash, (B) SO_4^{2-} and reduced form of sulfur on an atmospheric aerosol.

1. Task Title: Reactions of Sulfur Dioxide in Aerosols.

2. Objective:

    To measure the extent of reaction of sulfur dioxide in aerosols, particularly as influenced by PH and various catalysts.

3. Institution: The University of Texas at Austin, Austin, Texas
   Investigator: D.M. Himmelblau

4. EPA Project Officer: J.L. Durham

5. Progress:

    Various models have been set up to represent the mass transfer and reactions of sulfur dioxide with aerosol particles. Reaction rate coefficients have been calculated based on the available literature. However, due to the varying set-ups of previous investigators, it is difficult to predict reaction rate coefficients for the experiments to be carried out in this investigation. About four orders of magnitude difference have been determined from one experiment to another from the articles in the literature.

    A reaction tube has been set up with adjustable residence times so that the reactions of sulfur dioxide with the aerosols can be measured under controlled conditions. Particle size distributions have been measured for two aerosol generators and various supplementary parts of the equipment have been assembled.

    Since the amount of sulfur that is accumulated in the aerosol particles is so small, radioactive sulfur-35 will be used to determine the overall transfer to the aerosol particles.

6. Publications and Presentations, Theses: None

7. Plans:

    1. To complete the assembly of all the experimental apparatus.

    2. To test the individual components.

    3. To calibrate the various pieces of equipment.

    4. To establish that aerosols of known size can be transmitted through the reaction section and caught in the sampling filter without substantial losses.

    5. To estimate the reaction rate coefficients by using radioactive sulfur dioxide.

1. Task Title: Mass Transport Models

2. Objective:

   Develop a mathematical model of the absorption of SO_2 by water and compare with experimental results.

3. Institution: Northrop Services, Inc., RTP, NC.
   Investigator: John Overton

4. EPA Project Officer: J.L. Durham

5. Progress: In order to model the absorption of a gas by a liquid, several factors must be taken into consideration: (1) diffusion or transport processes within the aerosol, (2) transport of gas through the gas-liquid interface, (3) the chemistry of the species within the liquid.

   The absorption of SO_2 (at ppm concentrations) by pure water is a very simple system with respect to the above factors. This is because only a few products are formed in the water by the SO_2 and only one (reversable) kinetic equation is necessary to describe the significant chemical reactions. Further, this reaction is sufficiently fast in both directions to be considered instantaneous; i.e. equilibrum maintained point wise within the liquid. The reaction is:

$$SO_{2\ell} \quad \overset{H_2O}{\underset{\leftarrow}{\rightarrow}} \quad H_3O^+ + HSO_3^-$$
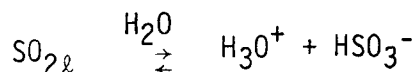
where $SO_{2\ell}$ is the liquid phase SO_2 (H_2SO_3).

   Because of the chemical equilibrium, and the fact that $[SO_{2\ell}]$ $<<[HSO_3^-]$ (for the particular experimental conditions considered) the concentration, $[HSO_3^-]$, which makes up over 99% of the dissolved SO_2, approximately satisfies the molecular diffusion equation without chemical reaction terms. i.e.,

$$\frac{\partial[HSO_3^-]}{\partial t} \quad \sim \quad D \frac{\partial^2[HSO_3^-]}{\partial x^2}$$

D = diffusion coefficient.

   The effect of the chemistry is taken into account by the gas-liquid interface boundary condition. This condition is that the current, J, at the interface is,

$$J = - D \frac{\partial[HSO_3^-]}{\partial x} = k \left\{[SO_{2g}] - H[SO_{2\ell}]_i\right\}$$

where

   k = a mass transfer coefficient,
   H = Henry's law constant
$[SO_{2\ell}]_i$ = interface value of $[SO_{2\ell}]$

$[SO_{2g}]$ = gas phase value of SO_2.

70

assuming charge neutrality one finds that $[SO_2\ell] = K^{-1} [HSO_3^-]^2$; K = chemical equilibrium constant. Thus, at the interface,

$$D \frac{\partial [HSO_3^-]}{\partial x} = -k \left\{ [SO_{2g}] - \frac{H}{K} [HSO_3^-]_i^2 \right\} .$$

The experimental data simulated is for a bulk water system and was taken from F.P. Terraglio and R.M. Manganelli, The Absorption of Atmospheric Sulfur Dioxide by Water Solution's, JAPCA, 17(6), June 1967.

In the experiment, 20 Petri dishes, each with water to the same level, were placed in a chamber. SO_2 was introduced into the chamber and kept at a constant level. Approximately every six minutes a dish was removed and analysed for the quantity of dissolved SO_2. Thus a set of data, dissolved SO_2 versus time, was obtained. For purposes of the model, the essence of the experimental setup is illustrated in Figure 1.

Numerical simulations of the model are compared to the experimental data in Figure 2. The diffusion coefficient (D) and transfer coefficient (k) were varied to produce the best fit. The values used for the plots in Figure 2 are $D = 1.5 \times 10^{-4} cm^2/sec$ and $k = .75$ cm/sec. (D is too high by a factor of 10, which indicates mixing in the liquid by means other than molecular diffusion).

Assuming the water thickness = 1 μm, $D = 10^{-5}$ cm^2/sec, and R = 1, an insight into the relative importance of the factors that would be important in aerosols was obtained. Figure 3 is a plot of the fractional saturation concentration of HSO_3^- in the interface and in the liquid as a function of time. As can be seen, for times greater than 10^{-2} second, the surface and average values are essentially the same. This behavior indicates a nearly spatially uniform distribution of HSO_3^-. This condition is equivalent to an infinite diffusion coefficient. Thus the major factors to be considered are the chemistry and the resistance to transport through the air-liquid interface.

6. Publications, Presentations and Theses: None

7. Plans:

The physics and chemistry of liquid aerosols are, in general, much more complex than indicated by the model presented here. Thus, models and programs that can handle more complicated cases are being developed.

$$J = -K([SO_{2g}] - H \cdot [SO_{2\ell}])$$

AIR

WATER

← SURFACE OF WATER

$\dfrac{\partial C}{\partial X} = 0$ (current = 0)

← BOTTOM OF CONTAINER
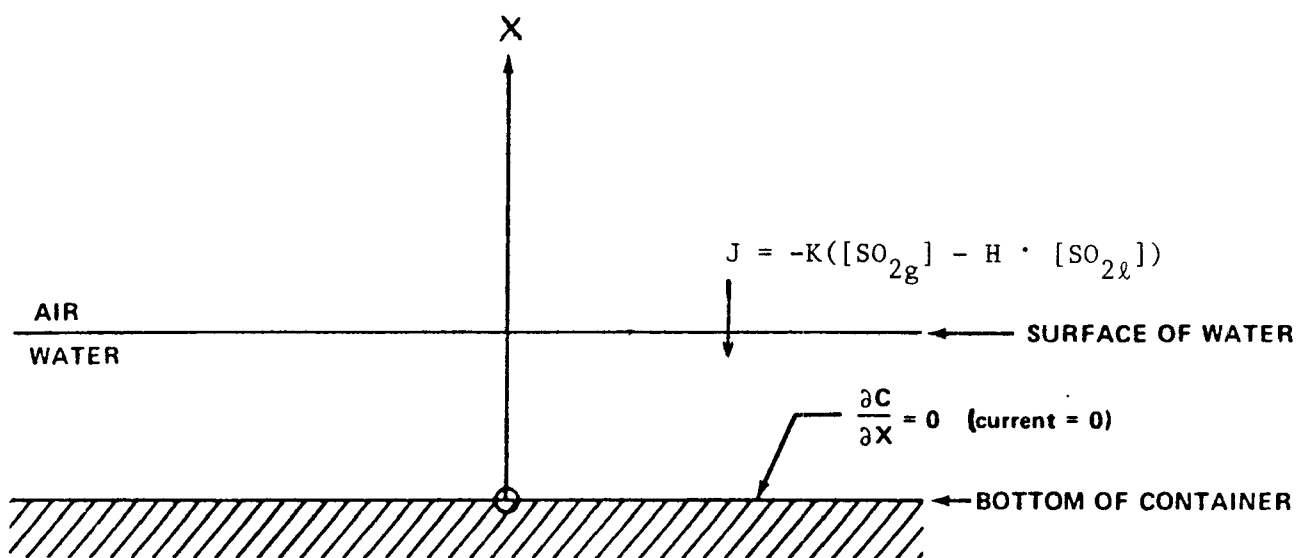
Figure 1 .
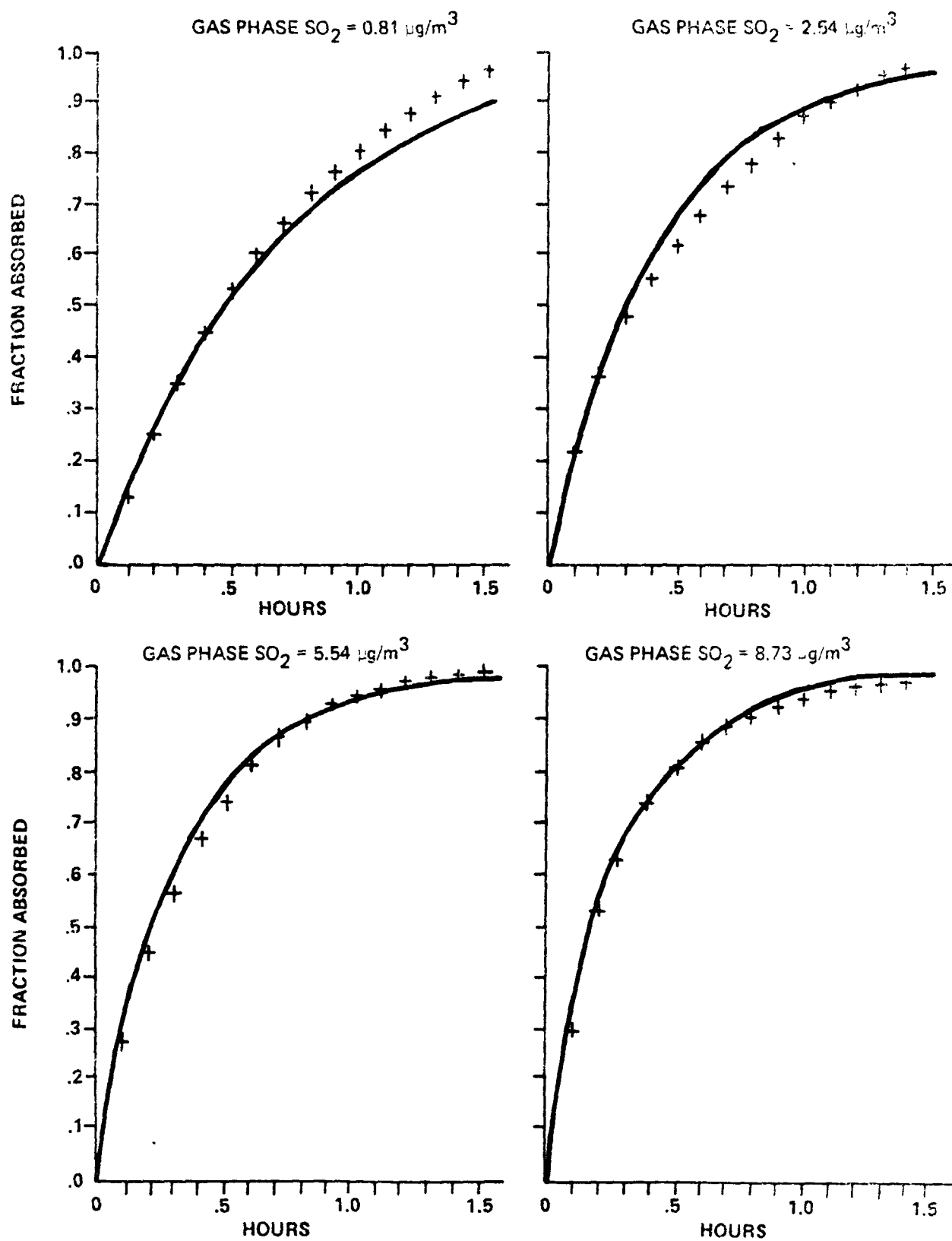
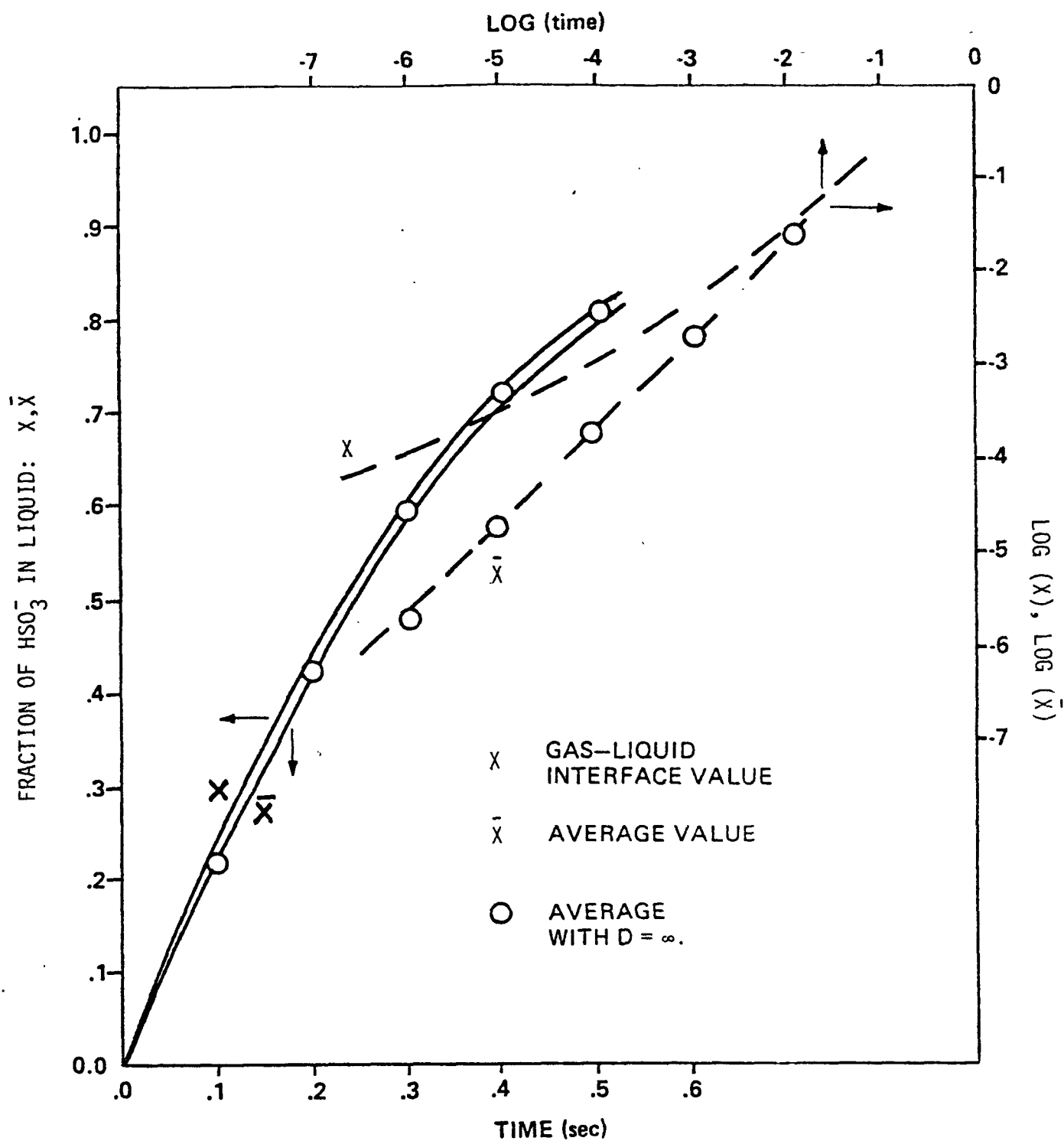Figure 2. SIMULATION OF THE ABSORPTION OF SO_2 BY WATER (EXPERIMENT: +; SIMULATION: -)

Figure 3.   FRACTION OF SURFACE AND AVERAGE CONCENTRATIONS OF
DISSOLVED SO_2 ($\approx HSO_3^-$) IN H_2O OF DEPTH = 1 μ

A. ATMOSPHERIC PROCESSES AND EFFECTS

5. Technique Development. Development of new instruments or techniques required for the aerosol research program.

1. Task Title: Formation of Atmospheric Aerosols - Nonideal Characteristics of Impactors.

2. Objective:

   To study the nonideal characteristics of single-stage and cascade impactors that are important for their correct application in aerosol sampling. Both laboratory and commercial impactors have been studied.

3. Institution: University of Minnesota, Minneapolis, Minnesota
   Investigator: K.T. Whitby

4. EPA Project Officer: W.E. Wilson

5. Progress:

   In a thesis study by A.K. Rao, the performance of the impactor stages was found to be significantly affected by the nature of the aerosol and the collection surface. With dry, solid surfaces or dry, solid aerosols, bounce and blowoff was severe. Liquid aerosols or liquid-coated collector surfaces were close to the Marple theory in behavior. Glass fiber filter media surfaces reduced bounce, but significantly changed the impactor characteristics. Whatman filter paper collection surfaces did not reduce particle bounce appreciably.

   Experimental studies of slotted impactors by Willeke show that they perform with a sharpness of cut close to the theoretically predicted value, if used under the conditions of the numerical mode. Sideways flow entrance and impaction onto a fibrous surface may change the collection efficiency considerably (Figure 1).

6. Publications, Presentations, Theses:

   1. Rao, A.K. An Experimental Study of Inertial Impactors. Ph.D. Thesis. Mechanical Engineering Department, University of Minnesota, MN, June 1975.

   2. Rao, A.K. and K.T. Whitby. Nonideal Collection Characteristics of Single-Stage and Cascade Impactors. Accepted by Am. Ind. Hyg. Assoc. J. 1976.

   3. Willeke, K. and J.J. McFeters. 1975. The Influence of Flow Entry and Collecting Surfaces on the Impaction Efficiency of Inertial Impactors. J. Colloid Interface Sci. 53:121-127.

   4. Marple, V.A. and K. Willeke. Inertial Impactors: Theory, Design and Use. In: Fine Particles: Aerosol Generation, Measurement, Sampling, and Analysis (B.Y.H. Liu, ed.), pp. 411-446, Academic Press, New York, 1976.

   5. Willeke, K. 1975. Performance of the Slotted Impactor. Am. Ind. Hyg. Assoc. J. 36:683-691.

7. Plans:

Work on the nonideal behavior of impactors and cyclone samplers will continue in the Particle Technology Laboratory under the direction of Dr. B.Y.H. Liu.

- - ARB POLYETHYLENE STICKY FILM
—— DOWCORNING OIL-COATED
      GLASS PLATE
—·— GLASS FIBER FILTER
      (GELMAN TYPE A)
---- GLASS PLATE
○ 110 μm PSL
○ 0.794 μm PSL
△ 0.790 μm PSL

COLLECTION EFFICIENCY - %

$$(\text{STOKES NUMBER})^{1/2} = \left(\frac{C\rho_p V_0 D_p^2}{9\mu_g D_j}\right)^{1/2}$$
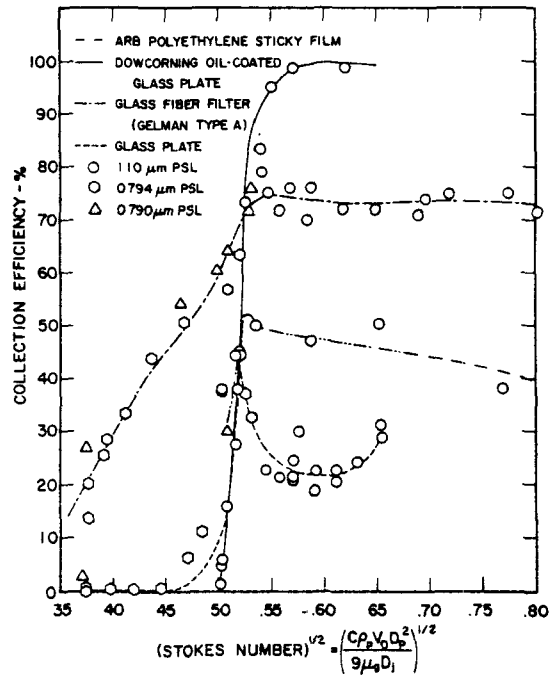
Figure 1. Experimental impaction efficiency curves obtained with a
          single-stage impactor using different collection surfaces,
          PSL aerosol, and a jet-to-plate ratio of 1 (Rao, 1975).

          Note the low efficiencies for the collection of dry particles
          on a dry surface. Also note that when a glass fiber filter is
          used as a collection surface, the efficiency of collection is
          below the ideal curve for Stokes numbers larger than the ideal
          curve and is greater for Stokes numbers less than the ideal.

1. Task Title: Sources and Trace Metals in Urban Aerosols

2. Sub-Task Title: Development and Application of Analytical and Sampling
   Techniques

3. Objectives:

   To develop a sensitive elemental analysis and sampling technique
   capable of handling very small samples.

4. Institution: Department of Oceanography, Florida State University
   Tallahassee, Florida 32306
   Investigator: John W. Winchester

5. EPA Project Officer: Ronald K. Patterson

6. Progress:

   The Jensen-Nelson sampler (Streaker") was developed and has
   been applied successfully to various aerosol studies. The samples
   consist of strips of 0.4μm pore size Nuclepore filter firmly
   attached to frames. The sampler is simply a sliding-sucking ori-
   fice moved by a clock motor at the rate of 1 mm/hr along the length
   of the filter so as to draw about 1 liter/min of air through a
   continuously-moving 2 mm x 5 mm rectangular area of the filter.
   The device is positioned in the field so that the air is drawn
   upward from the under-side of the filter thereby excluding particles
   30 μm and larger.

   In the analysis laboratory, the sample is moved automatically
   for successive bombardments by a stepping motor drive with electric
   control. The analysis techniques used on these samples are Proton-
   Induced X-Ray Emission (PIXE) and Proton Elastic Scattering Analysis
   (PESA) which yield elemental composition using the proton beam of a
   Van de Graaff accelerator. Under routine PIXE analysis conditions,
   85 bombardments, corresponding to a week of sampling time are currently
   performed in four hours of accelerator time. Other combinations of
   filter pore size, orifice area, and orifice speed can be introduced.
   For urban atmospheres, however, the loading obtained with the above-
   mentioned design is optimum: giving routine detecting limits in the
   order of 10 - 100 ng/m^3 for sulfur and heavier elements by PIXE; and
   sensitivity sufficient to measure lighter elements by PESA.

   For both PIXE and PESA analyses, the proton beam is collimated
   to a rectangular area of 2 mm x 5 mm and inside the streak. The X-
   rays or the scattered protons are detected at backward angle and
   give rise to a pulse-height spectrum resolvable into the individual
   elements in the sample. With this arrangement, the time resolution
   is 2 hours.

   New collection surfaces for the Battelle-type cascade impactor
   were designed so that size fractionated aerosol samples could be
   analyzed by PIXE and PESA techniques. For special sampling needs
   two larger stages were designed for the Battelle sampler which allows
   the collection of 16.0, 8.0, 4.0, 2.0, 1.0, 0.5, 0.25, and <0.25μm
   particles.

Proton-induced X-ray emission analysis has been shown to be a fast, inexpensive, reliable, and convenient method for routine multi-elemental trace analysis. The major component procedures of such an analysis are sample preparation, bombardment, and analysis of pulse-height spectra. To meet the dual goals of a rapid and an unambiguous analytical technique, each of the component procedures must be optimized. As part of this grant sub-task title, a status report was written on the optimization of PIXE pulse-height spectra analysis. This analysis was based on a model of the radiation environment in which an energy dispersive detector is placed in PIXE analysis; and on the intrinsic characteristics of the detector. The present model has been coded in the Fortran program, REX. The parameters of the model are sought using a least squares minimization.

7. Publications:

1. J.W. Nelson, B. Jensen, G.G. Desaedeleer, K.R. Akselsson, and J.W. Winchester. 1976. Automatic Time Sequence Filter Sampling of Aerosols for Rapid Multi-element Analysis by Proton Induced X-Ray Emission. Advances in X-Ray Analysis. 19:415-425.

2. H.C. Kaufmann, K.R. Akselsson, and W.J. Courtney. 1976. REX: A Computer Program for PIXE Spectrum Resolution of Aerosols. Advances in X-Ray Analysis. 19:355-366.

3. B. Jensen and J.W. Nelson. Novel Air Sampling Apparatus for Elemental Analysis. In: Proc. 2nd Intl. Conf. Nucl. Methods in Environ. Res., Columbia, MO, July 1974. Report Issued October, 1975.

4. T.B. Johansson, R.E. Van Grieken, J.W. Nelson, and J.W. Winchester. 1975. Elemental Trace Analysis of Small Samples of Proton-Induced X-Ray Emission. Anal. Chem. 47:855-860.

5. J.W. Nelson and D.L. Meinert. 1975. Proton Elastic Scattering Analysis-A Complement to Proton-Induced X-Ray Emission Analysis of Aerosols. Advances in X-Ray Analysis. 18:598-605.

6. J.W. Nelson, J.W. Winchester and R. Akselsson. Aerosol Composition Studies Using Accelerator Proton Bombardmen. In: Proc. 3rd Conf. on Appl. Small Accelerators, Vol. 1, CONF-741040-P1, USERDA, Denton, Texas, October 1974.

7. R. Akselsson, J.W. Nelson, and J.W. Winchester. 1975. Proton Scattering for Analysis of Atmospheric Particulate Matter. Bull. Am. Phys. Soc., 20:155 and Conf. Proc. (In Press).

8. H.C. Kaufmann and R. Akselsson. 1975. Non-Linear Least Squares Analysis of Proton-Induced X-Ray Emission Data. Advances in X-Ray Analysis. 18:353-361.

9. R.E. Van Grieken, T.B. Johansson, K.R. Akelsson, J.W. Winchester, J.W. Nelson, and K.R. Chapman, 1976. Geophysical applicability of Aerosol Size Distribution Measurements Using Cascade Impactors and Proton Induced X-Ray Emission. Atmospheric Environment. 10:571-576.

10. T.B. Johansson, R.E. Van Grieken, J.W. Nelson, and J.W. Winchester. 1975. Element Trace Analysis of Small Samples by Proton-Induced X-Ray Emission. Analytical Chemistry, 97:855.

11. T.B. Johansson, R.E. Van Grieken and J.W. Winchester. Interpretation of Aerosol Trace Metal Particle Size Distribution. In: Proc. 2nd InH. Conf. Nucl. Methods in Environ. Res., Columbia, MO, July, 1974. Report Issued October, 1975.

8. <u>Plans</u>:

This grant is complete. A final report is forthcoming.

1. Task Title: Formation of Atmospheric Aerosols - Development of a Sulfur Aerosol Analyzer.

2. Objective:

    To develop an instrument to continuously measure aerosol sulfur at ambient atmospheric concentrations using a commerical flame photometric dector and a newly developed pulsed electrostatic precipitator.

3. Institution: University of Minnesota, Minneapolis, Minnesota
   Investigator: K.T. Whitby

4. EPA Project Officer: W.E. Wilson

5. Progress:

    An instrument which combines a pulsed electrostatic precipitator and a flame photometric detector to measure ambient sulfur aerosols has been developed. A laboratory version of the instrument is currently operating and will be used to measure sulfur aerosol concentrations in the Los Angeles freeway study. The present instrument configuration will detect sulfur aerosols down to 1-2 $\mu g/m^3$ as sulfur. A heater located upstream of the instrument will be used to discriminate between sulfuric acid and other sulfur aerosols.

6. Publications, Presentations, Theses:

1. Kittelson, D.B., R.L. McKenzie, B.Y.H. Liu, D.Y.H. Pui and F.D. Dorman. National Bureau of Standards/University of Minnesota Sulfur Particle Analyzer Project. EPA-IAG-P5-0684, NBS/EPA Energy/Environment Project, semi-annual report from NBS to EPA Office of Energy, Minerals, and Industry. Washington, D.C., 20460

1. Task Title: Simultaneous Comparison of the Electrical Aerosol Analyzer and the Diffusion Battery for Atmospheric Aerosol.

2. Objectives: To make simultaneous performance evaluations of the Electrical Aerosol Analyzer (EAA) and the diffusion battery (DB) while sampling atmospheric aerosol.

3. Institution: University of Paris
   Investigator: J. Bricard

4. EPA Project Officer: T. Ellestad

5. Progress:

   In preparation for making size distribution measurements with diffusion battery and condensation nuclei counter (CNC), the CNC's response as a function of particle size was studied with sodium chloride nuclei produced by a Liu generator. Contrary to the existing literature, the CNC response showed a marked dependence on particle size below 0.06 μm diameter. The phenomenon was observed both for expansion-release counters using water as the condensing fluid and for continuous-flow counters employing butyl alcohol. This finding has important implications beyond size distribution reduction from diffusion batteries: previous estimates of coagulation coefficients, nucleation rates, and other ultra-fine aerosol behavior may need revision.

6. Publications, Presentations, and Thesis: None

7. Plans:

   1. Compare performances of the EAA and the diffusion battery on laboratory-generated aerosol.

   2. Compare size distributions of atmospheric aerosol as measured by the EAA and the diffusion battery.

1. <u>Task Title</u>:   Determination of Sulfate Ion Concentrations in Human and
    Animal Serum using High Pressure Liquid Chromatography

2. <u>Objective</u>:

    To develop a simple means of measuring human and animal serum
    sulfate concentrations in subjects which have been exposed to aerosol
    sulfate and sulfite pollution.

    To determine if increased exposure to aerosol sulfates necessarily
    results in an increased sulfate concentration in blood serum or if
    other reactions occur.

    These projects are being done in cooperation with Dr. E. Sawicki.

3. <u>Institution</u>:   Environmental Protection Agency, ESRL, ARB
    <u>Investigator</u>:   L.L. Spiller and R.F. Reardon (student aid)

4. <u>EPA Project Officer</u>:   W.E. Wilson

5. <u>Progress</u>:

    The serum sample is dialyzed using Fisher dialysis tubing (cat.
    no. 8-667D). This is done to prevent the large proteins in the serum
    from damaging the column of the chromatograph. Other methods for
    removing these proteins have changed the results of the analysis.

    The sample is analyzed for sulfate on the high pressure liquid
    chromatograph (HPLC).

    A blank made from the deionized water used in dialysis is run on
    the HPLC.

    A first attempt at analyzing human and rabbit serums have yielded
    results which were well within the range of expected values and were
    very promising.

6. <u>Publication, Presentation, Theses</u>:   None

7. <u>Plans</u>:

    Current plans include analysis of samples which have been "spiked"
    with very high levels of Na_2SO_4, Na_2SO_3 and $NaNO_2$ in order to determine
    the efficiency of the procedure and to see if the serum proteins react
    in any way with the added ions.

1. Task Title: Comparison study of data collected with the dichotomous and high-volume samplers.

2. Objective: To meet the requirements for a masters thesis and to establish a data base from which the Aerosol Research Branch can make recommendations to other agencies and interested individuals regarding the use of these samplers.

3. Institution: University of North Carolina, School of Public Health, Chapel Hill
   Investigator: Tim McCarthy (student aid).

4. EPA Project Officer: W.E. Wilson

5. Progress: Samples were collected from January through March, 1977, on the roof of the EPA Monitoring station (Cameo Bldg.) in downtown Durham. The dichotomous samples have been analyzed and the analysis of the hivol samples are in progress.

6. Publications, Presentations, and Theses: None

7. Plans: To complete comparison study by July, 1977.

1. Task Title: A Cyrogenic Procedure for Concentrating Rating Trace
Gases in the Atmosphere

2. Objective:

To determine the distribution, atmospheric loading, sources and
sinks of halogenated compounds; the effect of fluorocarbons on the
depletion of ozone.

3. Institution: EPA-ERC, ESRL-ARB
Investigator: L.L. Spiller, M. Miller

4. EPA Project Officer: W.E. Wilson

5. Progress:

Detection of small concentrations of gaseous air pollutants has
been achieved by the use of the fourier transformer spectrometer,
nitrogen-colled photo-detectors and infrared paths of 400 meters or
more. For measurement of many of the trace gases on the ambient air,
a detection sensitivity of 10^{-10} atmos. or better required. To
achieve such low detection, the pollutants have to be concentrated by
separating them from the nitrogen, oxygen and water vapor. Cyrogenic
condensation followed by distillation thus appeared to be the most
feasible technique for concentrating pollutants. Results were obtained
on 14 days between January and July 1975.

Fluorocarbon -11 values ranged from about 1.3 x 10^{-10} atmos. at
RTP, NC to 8 x 10^{-10} atmos. at New York City.

6. Publications, Presentations, Theses:

Infrared Measurement of Fluorocarbons, Carbon Tetrachloride,
Carbonyl Sulfide, and Other Atmospheric Trace Gases, APCA Journal, 25,
No. 12, December 1975, pages 1220-1226.

7. Plans:

To develop defining techniques for fluorocarbon F-11, F-12, and
F-114 determination.

1. Task Title: Collection of Atmospheric NO_2 by Treated Filters

2. Objective:

    Develop a simple and inexpensive method of measuring ambient NO_2 levels in the atmosphere.

3. Institution: EPA-ERC, ESRL-ARB
    Investigator: L.L. Spiller and G.L. Kay (student aid)

4. EPA Project Officer: W.E. Wilson

5. Progress:

    The lab setup has made use of an NO_2 permeation tube, a temperature bath, and a bendix NO_2 analyzer to similate ambient NO_2 concentrations and measure filter efficiency.

    Treat a specific type filter with a NO_2-absorbing solution. Allow the solution to dry onto the filter.

    Place the treated filter in a filter holder and use a critical orifice followed by a vacuum pump to draw a specific flow rate of air through the treated filter.

    After exposing the filter, analyze the concentration of NO_2 on the filter using a quick and accurate method such as ion chromatography.

    To date, using only the Bendix analyzer, an efficiency of 94-98% in NO_2 pickup has been observed using a Fisher 9-802 cellulose filter, a triethanolamine-Sodium methoxide-5% Guaiacol solution, a humidity range of 20-60%, and a flow rate of 350-380 cc/minute. These results have not been confirmed using the ion chromatograph analysis.

6. Publications, Presentations, Theses: None

7. Plans:

    Current plans involve confirming the efficiency by use of ion chromatography, increasing the efficiency of the filter system to 100%.

    To increase the flow rate.

    To maintain high efficiency, and reduce the amount of guaiacol in the treatment solution (the guaiacol interferes with ion chromatography analysis).

1. Task Title: Instrumentation for Monitoring Meteorological Data

2. Objective:

    To develop a portable electronic systems to monitor wind speed, wind direction, and temperature.

    To develop systems to control pollutant samplers as a function of meteorological parameters.

3. Institution: EPA-ERC, ESRL-ARB
   Investigators: L.L. Spiller and G. DeJong (student aid)

4. EPA Project Officer: W.E. Wilson

5. Program:

    A digitally programmed instrument to monitor wind speed/direction and to selectively control up to 4 different environmental samplers was built and is being used in field projects. Circuitry to interface a digital tape recorder (used by the power industry to monitor power demand) to existing meteorological instruments is being developed. The recorder can store over 30 days of continuous time related data on 3 channels, which can be easily transferred to a computer. This will save much time and error involved in manually transferring data from strip charts to computer punch cards.

6. Publications, Presentations, Theses: None

7. Plans:

    Portable AC power generators, along with an AC line regulator will be installed in the EPA mobile laboratory. These generators will enable tne van to be used for monitoring atmospheric sulfur at locations of high biogenic activity which are remote from human disturbances. Low sulfur fuels will be used in the generators. A Meloy Model SA-285 Sulfur Gas Analyzer, which is capable of monitoring at 1 to 2 ppb levels, will be used.

1. **Task Title**: Improvement of "Streaker" Technique for Automated Collection and Analysis of Aerosols.

2. **Objective**:

   To develop a new, more effective "streaker" technique including separation of aerosols into coarse and fine fractions.

   To intercompare streaker collections - PIXE analysis with other analytical techniques.

3. **Institution**: Florida State University, Tallahasse, Florida
   Investigators: W. Nelson, J. Winchester, J. Jenson

4. **EPA Project Officer**: W.E. Wilson

5. **Progress**:

   A circular, 2-stage streaker which uses an impaction stage followed by a filter to give separate collection of fine and coarse particles has been constructed and is being tested. The series Nucleopore technique to obtain 2-stage particle size resolution is also being tested. Streaker results from the G.M. Sulfate Study have been compared with those of the EPA dichotomous sampler. Satisfactory agreement (5% or better) was found for measurement of automobile-generated sulfate.

6. **Plans**:

   Tests will be made to determine the adequacy of using the Nucleopore filter as a critical orifice to provide flow control.

   FSU will participate in an EPA sponsored intercomparison of aerosol measurement methods in West Virginia during Spring-1977.

7. **Publications, Presentations, and Thesis**: None

B. AUTO-EXHAUST CATALYST PROGRAM

Determination of chemical and physical properties of sulfuric acid aerosol produced by automobile catalysts.

1. Task Title: Roadway Aerosol Studies During General Motors Sulfate
   Dispersion Study

2. Objective:

   To determine the mass flow rate of particulate sulfur during
the GM Sulfate study and derive the percent of fuel sulfur converted to
aerosol sulfur.

3. Institution: Washington University, St. Louis, Missouri
   Investigators: E.S. Macias, R.A. Fletcher, J.D. Husar and R.B. Husar

4. EPA Project Officer: L.L. Spiller

5. Progress:

   The fine particulate sulfur concentration was determined 15 m
from the road, at five different heights. The win velocity profile was
measured at three heights. Samples were collected at 30 min. intervals
using TWO MASS samplers. Particulate sulfur was determined by the flash
vaporization-flame photometric detection method. Samples taken before
and after the test track runs were used to correct for background sulfate
and determine the automobile contribution.

   The flow rate per unit length of the roadway (Q/L) was calculated
from the fine particulate sulfur concentration as a function of: height
$C_s(z)$; and the component of the velocity profile perpendicular to the
roadway $U(z)$, according to the following integral:

$$Q/L = \int_0^h C_s(z)U(z)\ dz \ .$$

   The average emission rate per car/unit length of roadway can be
calculated by dividing flow rate by traffic density. The particulate
sulfur flow rate from the roadway averaged over the entire experiment
was 6.0 ± 1.2 µg/m/sec. For the traffic density of this experiment,
1.52 cars/sec, the particulate sulfur-emission rate per car was 4.0 ±
0.8 g/m (6.4 ± 1.6 mg/mile). This emission rate corresponds to a
13 ± 3% conversion of the fuel sulfur emitted as particulate sulfur
using the known fuel-sulfur content and estimated fuel consumption rate.

6. Publications and Presentations:

   1. Macias, E.S., R.A. Fletcher, J.D. Husar and R.B. Husar. 1976.
   Dispersion and Mass Flow Rate of Particulate Sulfur from Catalyst-Equipped
   Cars. In: The GM/EPA Sulfate Dispersion Experiment: Selected EPA
   Research Papers. EPA-600/3-76-035, p.81.

   2. Wilson, W.E., L.L. Spiller, T.G. Ellestad, P.J. LaMother, T.G. Dzubay,
   R.K. Stevens, E.S. Macias, R.A. Fletcher, J.D. Husar, R.B. Husar,
   K.T. Whitby, D.B. Kittelson, and B.K. Cantrell. GM Sulfate Dispersion
   Experiment: Summary of EPA Measurements. J. of Air Poll. Control Assoc.
   In Press.

3. Macias, E.S., R.A. Fletcher, J.D. Husar and R.B. Husar. Dispersion and Mass Flow Rate of Particulate Sulfur from Catalyst-Equipped Cars. Presented at: Symposium on the GM/EPA Sulfate Dispersion Experiment, Research Triangle Park, NC April 12, 1976.

4. Macias, E.S., R.A. Fletcher, J.D. Husar and R.B. Husar. Particulate Sulfur Emission Rate from a Simulated Freeway. Presented at: American Chemical Society Meeting, San Francisco, CA, August 31, 1976.
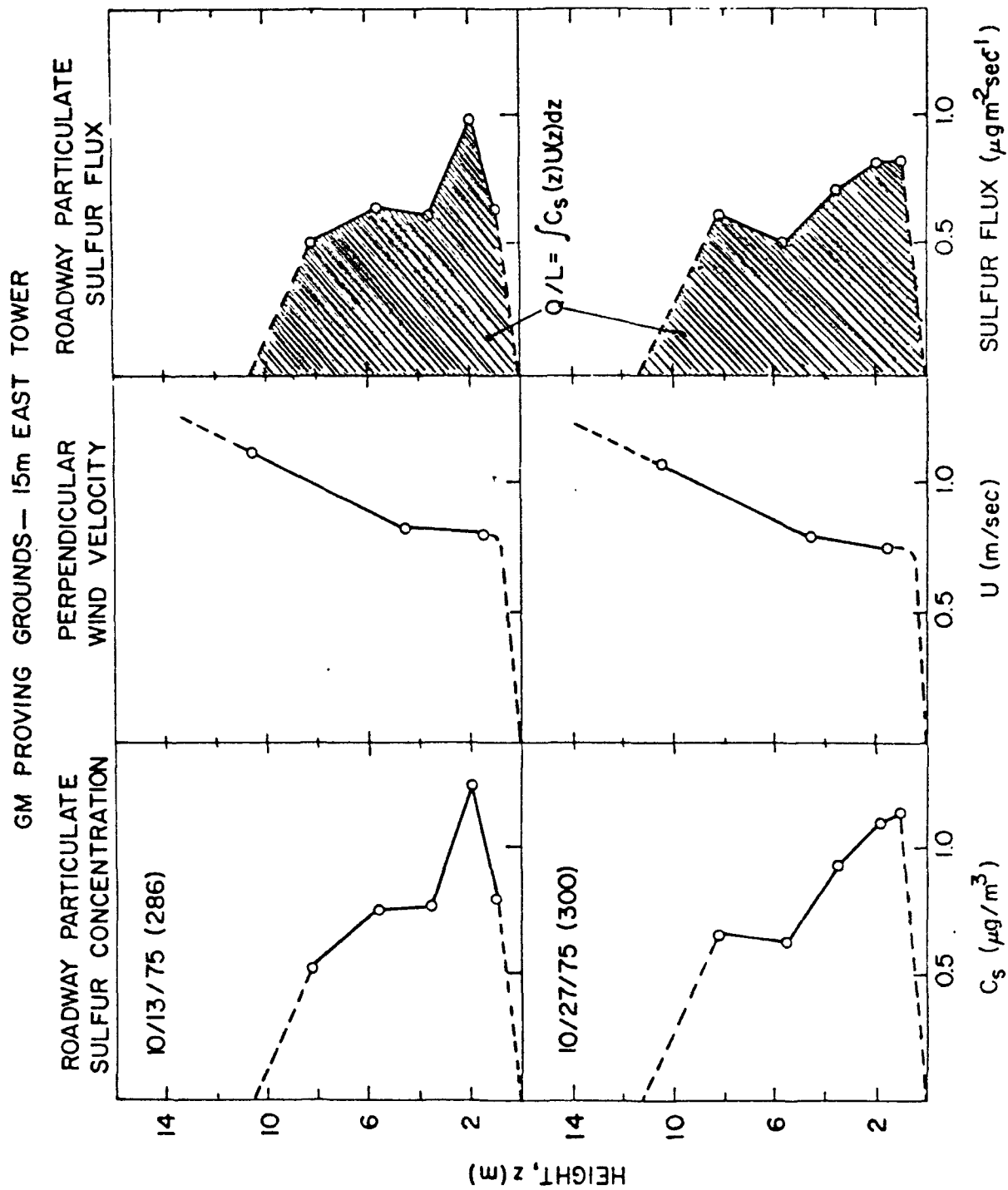
7. <u>Plans</u>:

This task is complete.

Figure 1. The vertical profile of roadway particulate sulfur concentration, wind velocity perpendicular to the roadway, and roadway particulate sulfur flux determined from runs 286 and 300.

1. Task Title: Formation of Atmospheric Aerosols - Aerosol Size Distributions and Concentrations Measured During the General Motors Sulfate Study.

2. Objective:

    To collect data on catalyst-equipped cars during October, 1975.

3. Institution: University of Minnesota, Minneapolis, Minnesota
    Investigator: K.T. Whitby

4. EPA Project Officer: L.L. Spiller

5. Progress:

    GM and the EPA conducted a freeway simulation study at the GM Milford Proving Ground using only catalytic converter-equipped cars. During the study nearly 900 aerosol size distribution measurements were made, both on and off the test track. At the same time, sulfate and other measurements were also being taken.

    For measurements on the track, a 1975 four-door sedan was equipped with an optical particle counter, electrical analyzer, condensation nuclei counter, and filter sulfate samplers. Samples were collected over an 18-sec. period into an automated grab bag, where the sample was held for the two minutes required for the measurement cycle of the in situ analyzers. Measurements were also collected with a similar in situ measuring system, as well as with a dichotomous sampler from an EPA mobile laboratory located about 30 m from the roadway.

    The log-normal fitting procedure was used to characterize all of the size distributions. The amount contributed by the cars during the test period was obtained by subtracting the averages of the background aerosol size distributions before and after the test period from the average during the test period (Table I).

    The average volumes added to the nuclei and accumulation modes for the car and EPA van were determined, and in both cases, about 70% of the aerosol volume is added to the nuclei mode (Table II).

    Background aerosol volume size distributions measured during the test show three distinct modes with mean sizes of approximately 0.03, 0.24, and 6.0 μm (Figure 1). Aerosol distributions measured during the run, both on and off the track, also exhibit three modes. Those at 0.24 and 6.0 remain essentially unchanged while the smaller mode contains more volume than the background aerosol, and now has a mean size of about 0.02 μm (Figure 2). The exact amount of the increase in volume of the smallest mode was greatly dependent on meteorological parameters. The volume increase varied from about 20 μm^3/cm^3, when the wind direction was parallel to the track; to 2 μm^3/cm^3, when the wind blew across the track (Figure 3). On days when the wind was parallel to the track, approximately 1/3 to 1/2 of the increase in volume during the test runs over background appeared in the 0.24 μm mode. No significant increase for the 0.24 μm mode was noted when the wind blew across the track.

Conclusions:

1. Difference distributions calculated by taking the difference between the average size distributions during the test and the average of the background distributions before and after the test suggest that most of the aerosol volume (and hence mass) is emitted in the size range smaller than 0.1 μm.

The geometric mean diameter by volume of this nuclei mode aerosol is about 0.02 μm. Figure 1 compares the size distribution of aerosol measured during the test period of GM Run 15 with the background. It is clear that the size distribution of the accumulation mode (center mode) and coarse particle mode (right-hand mode) have not changed significantly. It is also clear that the nuclei mode (left-hand mode) is contributed almost entirely by the cars on the roadway.

When the wind blows across the roadway (short aging time), most of the aerosol contributed by the cars is smaller than 0.1 μm. When the wind blows along the roadway (long aging time), coagulation transfers 1/3 to 1/2 of the aerosol to the mode in the 0.1 to 1 μm size range (Figure 3). Therefore, most of the aerosol growth from the 0.01 to 0.1 μm size range to the 0.1 to 1 μm range occurs in the atmosphere after emission and dilution at the tail pipe.

2. The highest contributions observed on the track were during GM Run 12 on October 23 when the average wind direction during the run was 181°, or the wind was blowing almost directly down the track (Table 1). The total fine particle volume (VFP) contribution for GM Run 12 is 3.35 $\mu m^3/cm^3$ at the trailer and 37.1 $\mu m^3/cm^3$ as measured by the car on the inside lane. Run 7 is shown for comparison. During Run 7 the wind was from the southwest, at 197°.

3. The arithmetic average over the 12 GM runs for which data can be averaged for the trailer gives means of 1.49 and 0.63 $\mu m^3/cm^3$ for ΔVAN and ΔVAC respectively, or a total fine particle contribution of 2.12. A somewhat comparable average for ΔVAN for the car is 7.00 $\mu m^3/cm^3$.

4. When the wind was blowing almost directly across the track, values of VAN measured in the car were significantly higher on the downwind side. For example, for GM Run 4, wind W-SW, the average values on the downwind leg near the track were VAN = 10.1, compared to an upwind value of 4.32 $\mu m^3/cm^3$.

5. The geometric mean diameter by volume for the aerosol as emitted by the cars is about 0.02 μm. When the wind was directly parallel to the roadway, as it was for GM Run 12, coagulation increased the mean size to about 0.04, and significant mass was transferred to the accumulation mode.

6. Correlation of particle sulfur measurements with fine particle volume show that, within the accuracy of the measurements, the particle sulfur can be accounted for by assuming that the aerosol is sulfuric acid in equilibrium with water vapor.

6. Publications, Presentations, Theses:

1. Whitby, K.T., D.B. Kittelson, B.K. Cantrell, N.J. Barsic and D.F. Dolan. Aerosol Size Distributions and Concentrations Measured During the General Motors Proving Grounds Sulfate Study. EPA-600/3-76-035. April 1976.

2. Ibid., Submitted to: Environ. Sci. Tech. November 1976.

7. Plans:

1. To conduct a roadway study in Los Angeles during October 1976 in order to measure aerosols, gases and particle chemistry.

Table I

Typical and High Average Aerosol Volumes
Measured by the Car and EPA Trailer

Measurement	Background		Test		Difference		
	VAN^a	VAC^b	VAN	VAC	ΔVAN	ΔVAC	ΔVFP^c
Trailer GM 7	.07	10.2	1.96	10.4	1.88	0.2	2.08
Car GM 7	.05	8.43	4.56	9.79	4.51	1.36	5.87
Trailer GM 12	.10	17.2	2.35	18.3	2.25	1.10	3.35
Car GM 12	.15	12.2	22.9	26.6	22.7	14.4	37.1

a) Volume in the Aitken nuclei mode, $\mu m^3/cm^3$

b) Volume in accumulation mode, $\mu m^3/cm^3$

c) Fine particle volume = $\Delta VFP = \Delta VAN + \Delta VAC$, $\mu m^3/cm^3$

Table II

Average Volumes Added to the Nuclei Mode
(ΔVAN) and the Accumulation Mode (ΔVAC) for
the Car Outside Compared to the EPA Van

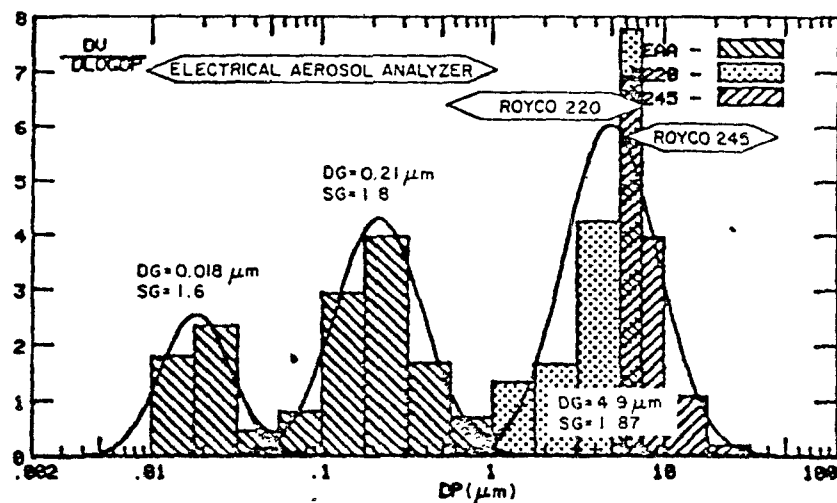|	ΔVAN	ΔVAC	$\Delta VTOT$	$\Delta VAN/\Delta VATOT$
Car	8.57	3.62	12.19	.70
EPA Van	1.49	0.63	2.12	.70

(All volumes in $\mu m^3/cm^3$)

Figure 1. Example of a distinctly trimodal volume size distribution
measured by the EPA trailer in situ aerosol instruments
during GMPG Run 15 on 10/29/75. The size ranges measured
by each instrument are shown. Note the excellent matching
between the instruments where they overlap. The geometric
mean sizes and geometric standard deviations are typical
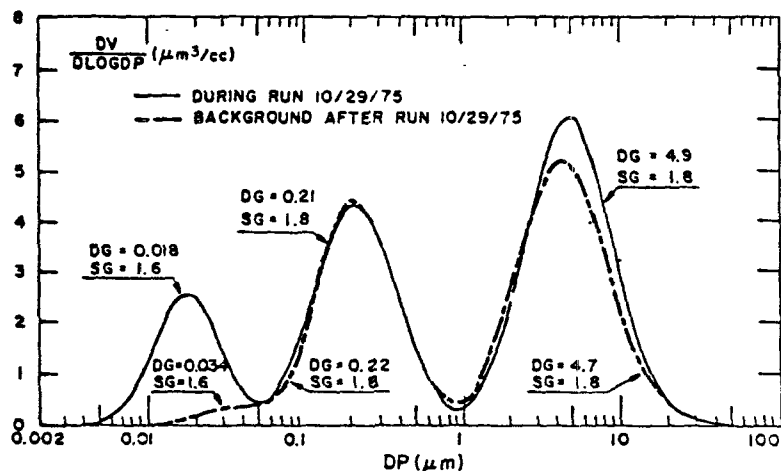of those measured during the test periods.

Figure 2. Trimodal model distributions measured by the EPA trailer
during GMPG Run 15 on 10/29/75. The model distributions
were obtained by fitting the data shown in Figure 1. Note
that during the test the accumulation and coarse particle
modes (center and right-hand modes) have not changed
significantly from the background conditions. On the other
hand, practically all of the volume of the nuclei mode (left-
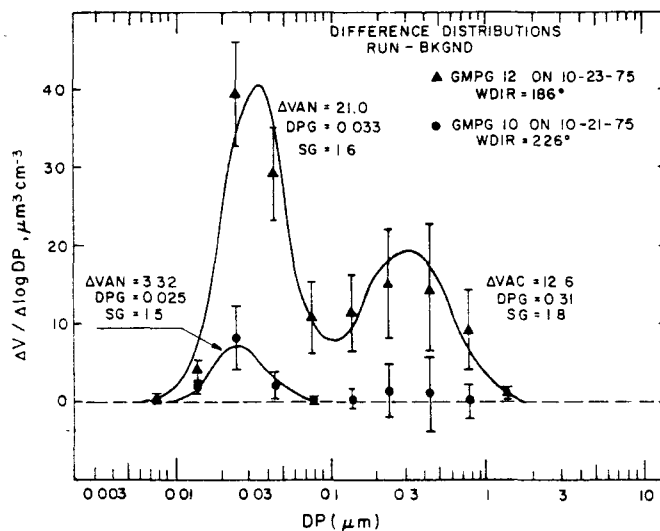hand mode) is contributed by the cars on the roadway.

Figure 3. Shown are different distributions calculated from averages
of the size distributions measured by the car on the
roadway during the indicated runs and measurements of
background aerosol made before and after the test period.
Included in the figure are the volume (V), (V), mean
geometric size (DPG), and geometric standard deviation for
the resulting modes. These are based on a fit of the
difference data using the log-normal fitting procedures.

1. Task Title: Sources and Trace Metals in Urban Aerosols.

2. Sub-Task Title: Freeway Aerosol Studies

3. Objectives:

   Design a measurement program capable of determining trace aerosol pollutants along roadways which can be used to evaluate: time nariation patterns of elements analyzed; area and height dependence; extent of mixing with local and regional components of aerosol pollutants; and baseline assessment along an urban freeway.

4. Institution: Department of Oceanography, Florida State University
                Tallahassee, Florida 32306
   Investigator: John W. Winchester

5. EPA Project Officer: Ronald K. Patterson

6. Progress:

   Jensen-Nelson samplers ("Streakers") were placed at five locations along a roadway running through a residential neighborhood in Tallahassee, Florida. Four samplers were located around a nearby house, and one was located inside the house. Samplers 1 and 2 were located 7 meters from the roadway, and 2 to 5 meters above the ground, respectively. Sampler 3 was 7 meters from the roadway, behind a hedge. Sampler 4 was 24 meters from the roadway and 15 meters away from an adjacent sampler (#5), which was located inside a closed, air conditioned house. All samplers were collected continuously over a one-week period on $0.4\mu m$ pore size Nuclepore filter strips. The Streaker samples were analyzed by Proton induced X-Ray Emission (PIXE) techniques. Each 2-hour sample collected by each Streaker underwent 85 separate analyses. The X-Ray spectra were fitted by computer and reduced for S, Cl, K, Ca, Fe, Br, and Pb, with sensitivities between 10-100nq.

   Time variations over 2-hour sampling periods showed daily variations in Pb, Br, Fe, and Ca. Pb and Br gave constant ratios (0.235 ± 0.069) and were correlated with traffic patterns. Fe and Ca variations followed the Pb and Br patterns and were thought to be generated from roaddust mechanically disturbed by automotive traffic. Sulfur and chloride did not show diurnal variation. Chlorine concentrations were generally quite low except in sea breezes.

   Table I presents the mean concentrations and standard deviations for the elements determined at the five sampling locations. Locations 1 and 2 correlate well and show little height differentiation. Location 3 shows the effects of filtration by the hedge. Location 4 shows lower aerosol concentrations because of diffusion. Location 5 shows low concentrations for all elements except potassium,which is being generated inside the house.

   Aerosol analysis of short sampling periods allows one to make conclusions on the behavior of trace elements in the atmosphere and their potential effects on human receptors. Elemental concentrations as a function of time and diurnal variation patterns give evidence of local emissions (in this case for automotive emissions), and their relationships to human activity. Because of the short sampling times, some of this study's data show large variations which indicate aerosol input from other sources and/or meteorological effects. Therefore, the prediction of pollutant uptake by inhalation has to be assessed in conjunction with the following considerations: a.) the occurrence of the elements over short

time periods, representative of human exposure; b) the exposure of humans relative to the cycles of their daily activity. The results of this study have been applied to a predictive model to show the consequences of a proposed widening of the roadway.

In another study under this sub-task title, PIXE analysis was used to assess the aerosol sulfur baseline along an urban freeway. In September 1974, before the 1975 vehicles equipped with catalytic emission control devices were in use, a sampling plan was developed which used six Battelle-type cascade impactors to fractionate aerosols collected during five selected 2-hour intervals, near the San Diego Freeway in Los Angeles. These impactors were operated simultaneously on three towers at 2 and 7 meters above road level, 35 meters upwind, and 35 meters downwind of the traffic lanes. Particles as a function of time were sampled continuously for 100 hours from three 7-meter heights using time-series "Streaker" filter samplers with two-hour time resolution. All samplers were analyzed for S, Cl, K, Ca, Fe, Br, and Pb using PIXE analysis.

Table 2 shows results from the first sampling period, 1530-1730, Thursday, 12 September 1974. Clearly the freeway is a major source of lead, not sulfur. Streaker data show parallel fluctuation in sulfur at all three sites, downwind and upwind of the freeway. This supports the hypothesis that particulate sulfur is non-automotive in origin.

The abundance of lead permits a prediction of the expected increase in elevation of particulate sulfur concentrations along roadways when non-catalytic automobiles burning leaded gasoline are replaced by catalytic automobiles burning non-leaded fuel. If the following information is available . prediction of sulfate increases will be more effective.

(1) The relative contents of lead in gasoline now and of sulfur in gasoline to be used with catalytic converters. As a national average, both values are about 0.05% by weight.

(2) The relative emission factors for lead and sulfate aerosol from automotive sources.

(3) The relative particle size distributions of present automotive lead aerosol and catalytic sulfate aerosol; their response to relative humidity, particle coagulation during aging, and other atmospheric effects.

7. Publications and Presentations:

1. G.G. Desaedeleer, J.W. Winchester, J.O. Pillotte, J.W. Nelson, and H.A. Moffitt. Proton Induced X-Ray Emission Analysis of Roadway Aerosol Time Sequence Filter Samples For Pollution Control Strategy. JAEA Conference Proceedings, Vienna, Austria, March, 1976. (In Press).

2. K.R. Akselsson, K.A. Hardy, G.G. Desaedeleer, J.W. Winchester, W.W. Berg, T.B. VanderWood, J.W. Nelson. 1976. X-Ray Techniques For Aerosol Sulfur Baseline Assessment Along An Urban Freeway. Advances in X-Ray Analysis,19:415-425.

8. Plans: This grant is complete and final report will be forthcoming.

Sampling Sites

TABLE I

Weekly mean values and standard deviation of the distribution –
expressed in ng/m^3 and in % (standard deviation/mean value) respectively –
of S, Cl, K, Ca, Fe, Br and Pb concentrations measured over one week
in two hours sampling periods.

Element
(ng/m^3)

	1	2	3
S	725.±360.(49.7)	689.±383.(55.6)	743.±441.(59.4)
Cl	482.±591.(123.)	414.±587.(142.)	380.±534.(154.)
K	<58.± 22.(37.9)	<50.± 16.(32.0)	<54.± 25.(46.3)
Ca	288.±253.(87.8)	247.±143.(57.9)	172.±115.(66.9)
Fe	156±143.(91.0)	147.± 88.(59.9)	126.± 75.(59.5)
Br	104.±64.(61.5)	87.± 46.(52.9)	61.± 30.(49.2)
Pb	450.±240.(52.6)	387.±179.(46.3)	285.±134.(47.0)

	4	5
S	432.±280.(64.8)	236.±144.(61.0)
Cl	233.±339.(146.)	111.±109.(98.2)
K	<52.± 60.(115.)	<203.±287.(141.)
Ca	92.± 63.(68.5)	<36.± 43.(119.)
Fe	81.± 47.(58.0)	26.± 40.(154.)
Br	38.± 16.(42.1)	15.± 7.(46.4)
Pb	174.± 80.(46.0)	63.± 28.(44.4)

TABLE II

Sulfur and lead concentrations found at Freeway Sites, A, C, D.

Stage	Size Range	S ng/m^3			Pb ng/m^3		
		A	C	D	A	C	D
6*	<0.25	1640	1680	1790	95	1410	1200
5	0.25-0.50	207	205	308	46	145	277
4	0.5-0.50	117	211	288	29	189	176
3	1.0-2.0	105	124	147	26	237	246
2	2.0-4.0	90	102	99	26	216	198
1	4.0-	75	67	76	21	40	61

*Figures for stage 6 are not corrected for filter efficiency.

1. Task Title: Dynamics of Automotive Sulfate Emissions.

2. Objective:

   To apply an aerosol dynamic model to estimate the size and composition of ultrafine sulfuric acid aerosols generated by catalyst-equipped automobiles.

3. Institution: University of Texas, Austin, Texas
   Investigators: J.R. Brock, K. de Bower, and S.H. Suck.

4. EPA Project Officer: J.L. Durham

5. Progress:

   A numerical model (see Task) has been applied to represent dispersion and advection of sulfate aerosol from automobiles on a ten lane expressway for winds perpendicular and parallel to the expressway. The automotive sulfate aerosol interacts through coagulation with the ambient aerosol. In addition, the size distribution changes with humidity. Through use of a reactive dispersion model termed EPOSOD, we have also studied the reaction of the sulfate highway plume with ambient levels of ammonia for very stable meteorological conditions (Figure 1).

6. Publications, Presentations, Thesis:

   1. Suck, S.H., K. de Bower and J.R. Brock. Dynamics of Automotive Sulfate Emissions. A.C.S. Symposium on Automotive Sulfate Emissions, August 1976.
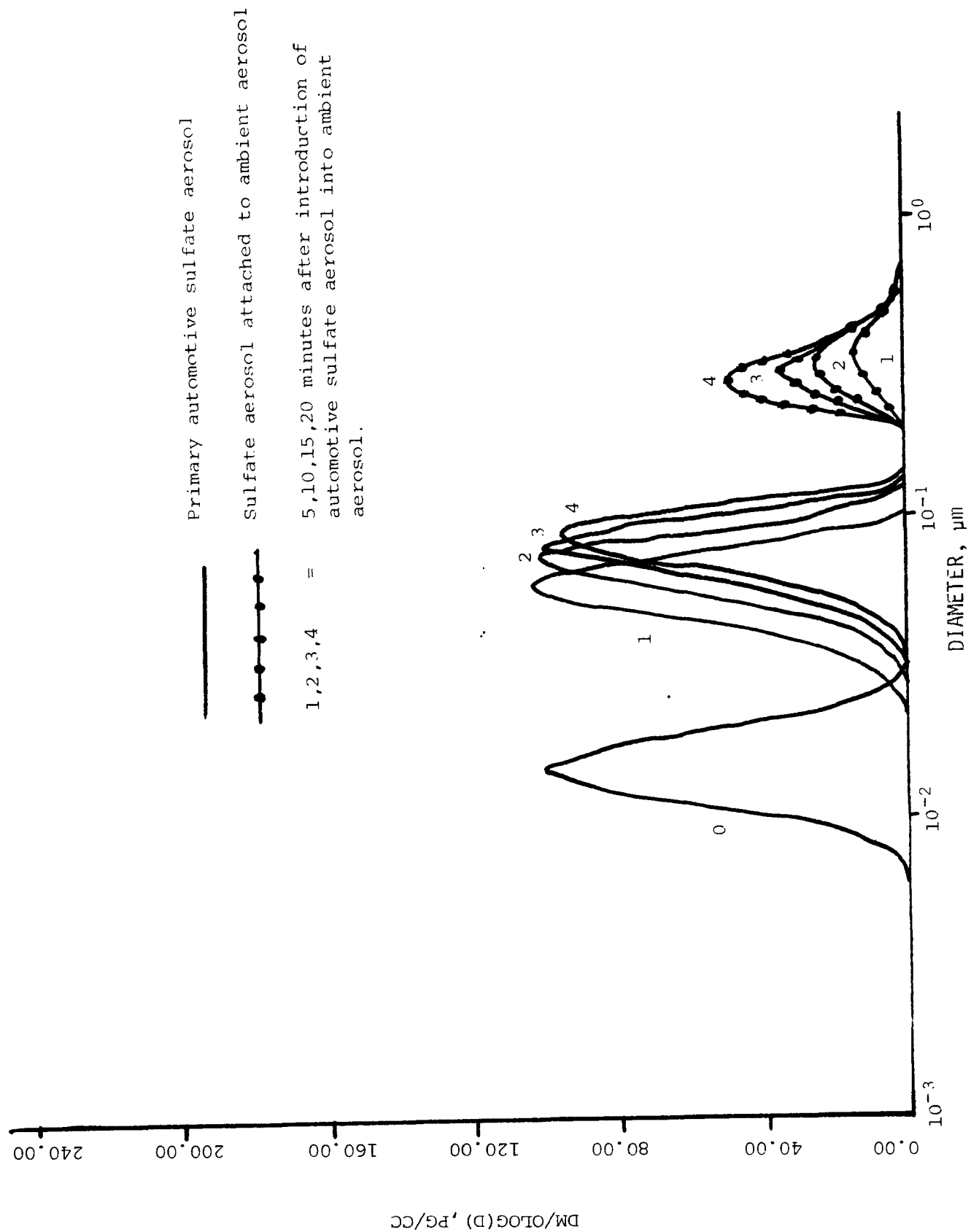
7. Plans:

   This task is complete.

Primary automotive sulfate aerosol

Sulfate aerosol attached to ambient aerosol

1,2,3,4 = 5,10,15,20 minutes after introduction of automotive sulfate aerosol into ambient aerosol.

FIGURE 1. Attachment of Automotive Sulfate Aerosol to Ambient Aerosol

105

1. Task Title: The General Motor-Environmental Protection Agency Sulfate Dispersion Experiment in October 1975 at the General Motor, Milford Test Track

2. Objective:

    To measure roadside sulfate exposures from a fleet of 100 percent-catalyst-equipped vehicles.

3. Institution: EPA-ERC, ESRL-ARB
   Investigator: L.L. Spiller, M. Miller

4. EPA Project Officer: W.E. Wilson

5. Progress:

    EPA investigators measured for sulfates, sulfuric acid, sulfur dioxide and particle size at towers and in mobile laboratories at several distances just off the test track. It has been established that most of the aerosol mass emitted from the air injection catalyst equipped vehicles was in the form of ultrafine sulfur aerosol in the size range between 0.01 and 0.1 μm. The background measurements before and after operation of the vehicle fleet and the ultrafine sulfur-containing aerosol was almost completely absent.

    Sulfuric acid was measured inside the equipped vehicle while it was running in the test track. More than two-thirds of the sulfate emitted by the vehicle was measured as sulfuric acid 20 meters off the test track.

6. Publications, Presentations, Theses:

    General Motors Sulfate Dispersion Experiment: Summary of EPA
      Measurements

7. Plans:

    Test is completed and results evaluated.

1. Task Title: Atmospheric Behavior of Catalyst-Generated Aerosols from Source to Receptor.

2. Objective:

    To predict the deposition efficiencies of sulfuric acid aerosols (0.01 to 10 μm) in the lungs.

3. Institution: ARB-ESRL
   Investigator: J.L. Durham and R. Orr (Student Aide)

4. EPA Project Officer: W.E. Wilson

5. Progress:

    Catalyst-equipped automobiles emitted sulfuric acid, which nucleates and forms sulfuric acid solution droplets in the atmosphere. Whitby made measurements of the roadway size distribution during the GM-EPA experiment (November 1975). He found a mode in the volume distribution with a mean geometric diameter of 0.033 μm and geometric standard deviation of 1.6. Such small sizes of sulfuric acid solution droplets could exhibit growth and lung deposition behavior that is different from that of larger droplets. Calculations of growth were performed for which it was assumed that the final size of an inhaled droplet is determined by the dry mass of sulfuric acid and the Kelvin equation (which relates vapor pressure to surface curvature). The relative humidity of the lungs was taken to be 99%. The deposition was calculated for the nasopharnyx (NP), tracheobronchial (TB), and pulmonary (P) compartments using the ICRP values for a tidal volume of 1450 cm^3.

    Typical values are given in Table 1 for the final size and acid normality of ambient sulfuric acid solution droplets (rh = 50%) that are inhaled (rh = 99%).

    For the value of 0.035 μm (n the roadway gmd), the concentration is lowered from 11N in atmosphere (rh = 50%) to 1N in the lungs (rh = 99%). The final concentration of smaller diameters will be greater. Ambient droplets with diameters greater than about 0.5 μm will have concentrations of about 0.2N in the lungs. Thus, it should be expected that fresh roadway sulfuric acid droplets will have a concentration of 4-25 times greater than aged aerosol.

    For Whitby's measurements, the dry sulfuric acid mass distribution as a function of solution droplet size is shown in Figure 1 for relative humidities of 50% and 99%. Although the increase in relative humidity causes the droplets to grow, there is little effect on the lung deposition, as can be seen in Table 2.

    Because the sensitive tissue of the pulmonary is the receptor of these sulfuric acid droplets, immediate action is warrented to define the extent on health hazard.

6. <u>Publications, Presentations, and Thesis</u>:

       This work was presented at the ACS San Francisco, October, 1976.
   A full report will be published in the ORD series.

7. <u>Plans</u>: Project is complete.

TABLE 1. Concentration of Droplets and Dilution Factors

Mass H_2SO_4 in droplet, g.	Relative Humidity = 50%		Relative Humidity = 99%		Growth Factor $\alpha=$ $\dfrac{\text{Radius at 99\%}}{\text{Radius at 50\%}}$	Dilution Factor
	Radius*, μm	Normality	Radius*, μm	Normality**		
10^{-18}	0.0073	13	0.010	5	1.4	0.13
10^{-17}	0.016	12	0.027	2	1.7	0.20
10^{-16}	0.035	11	0.070	1	2.0	0.12
10^{-15}	0.075	11	0.18	0.8	2.4	0.072
10^{-14}	0.16	11	0.42	0.6	2.7	0.051
10^{-13}	0.35	11	1.0	0.5	2.9	0.041

TABLE 2. Deposition calculated from the 99% and 50% relative
humidity sulfuric acid dry mass distributions.

	Dry Mass H_2SO_4, mg/m^3	
Relative Humidity:	99%	50%

0.01 μm < D < 10 μm

Total inhaled	20	20
Pulmonary deposition	10	12
Tracheabronchial deposition	1	1
Nasopharynx deposition	2	0
Total deposition	13	13

D < 0.1 μm

Total inhaled	13	11
Pulmonary deposition	7	9
Tracheabronchial deposition	1	1
Nasophyarynx deposition	0	0
Total deposition	8	10

APPENDIX A

ARB Projects funded by the Federal Interagency
Energy/Environment Research and Development Program

PROJECT MISTT

Direction of MISTT Field Studies, by W.E. Wilson . . . . . .

Management of MISTT, by W.E. Wilson . . . .

Aircraft Monitoring and Analysis for an Aerosol
   Characterization Study in St. Louis, by D.L. Blumenthal .

Project MISTT Field Program, by R.B. Husar . . . .

Formation of Atmospheric Aerosols--Aerosol Characteristics
   Measured at Glasgow, MO and in the St. Louis Urban Plume
   during the Summer 1975, by K.T. Whitby . . . .

Formation of Atmospheric Aerosols--Coal Fired Power Plant
   Plume Studies in St. Louis, Summer 1976, by K.T. Whitby .

Project MISTT - Synoptic Scale Haziness and Air Pollution,
   by R.B. Husar . . . .

Processing and Analysis of Project MISTT Data, by
   R.B. Husar . . . .

St. Louis Plume Study - Halocarbon and Hydrocarbon
   Measurements, by R.A. Rasmussen . . . .

Application of Statistical and Mathematical Methods
   to Air Pollution Problems, by J.H. Overton . . . .

Atmospheric Boundary Layer Measurements in Project
   MISTT; MISTT-II, by B. Hicks . . . .

Field Sampling and Analysis of Airborne Particulate
   Material in Conjunction with MISTT, by P.T. Cunningham .

Formation of Atmospheric Aerosols--Aerosols Produced
   by Combustion, by K.T. Whitby . . . .

Aerosol Formation and Removal in Plumes, by J.R. Brock . .

Mobile Laboratory Operations in Support of Project MISTT,
   July-August 1975, by T.G. Ellestad . . . .

Gas Calibration Support for 1976 MISTT Summer Field Program,
   July 1976, by T.G. Ellestad . . . .

111

APPENDIX B

PUBLICATIONS, PRESENTATIONS, AND THESIS LISTING INDEX

1970

1. Ensor, D.S. and A.P. Waggoner. 1970. Angular Truncation Error in the Integrating Nephelometer. Atmos. Environ. 4:481-487.

1971

2. Brock, J. 1971. On Size Distributions of Atmospheric Aerosols. Atmos. Envir. 5:833-841.

3. Brock, J. 1971. Models for Asymptotic Size Distributions for Atmospheric Aerosols. J. of Colloid and Interface Sci. 37:907-911.

4. Ensor, D.S., W.M. Porch, M.J. Pilat and R.J. Charlson. 1971. Influence of Atmospheric Aerosol on Albedo. J. Applied Meteor. 10:1300-1306.

5. Friedlander, S.K. 1971. The Characterization of Aerosols Distributed with Respect to Size and Chemical Composition. J. Aerosol Sci. 2:331.

6. Waggoner, A.P. and R.J. Charlson. 1971. Stimulating the Color of Polluted Air. Applied Optics. 10:957.

7. Zeigler, C.S., R.J. Charlson and S.H. Forler. 1971. Mt. Rainier: Now You See It, Now You Don't. Weatherwise. 24:115-119.

1972

8. Brock, J. 1972. Condensational Growth of Atmospheric Aerosols. J. of Colloid and Interface Sci. 39:32-36.

9. Charlson, R.J., D.S. Covert, Y. Tokiwa and P.K. Mueller. 1972. Multi-wavelength Nephelometer Measurements in Los Angeles Smog Aerosol III: Comparison to Light Extinction by NO_2. J. Colloid and Interface Sci. 39:260-265.

10. Covert, D.S., R.J. Charlson and N.C. Ahlquist. 1972. A Study of the Relationship of Chemical Composition and Humidity to Light Scattering by Aerosols. J. Applied Meteor. 11:968-976.

11. Ensor, D.S., R.J. Charlson, N.C. Ahlquist, K.T. Whitby, R.B. Husar and B.Y.H. Liu. 1972. Multiwavelength Nephelometer Measurements in Los Angeles Smog I: Comparison of Calculated and Measured Light Scattering. J. Colloid and Interface Sci. 39:242-251.

12. Harrison, H., J. Herbert and A. Waggoner. 1972. Mie Theory Computations of Lidar and Nephelometric Scattering Parameter for Power-Law Aerosols. Applied Optics. 11:2880-2885.

13. Husar, R.B. 1972. On the Formation of Photochemical Aerosols. In: Proceedings of International Workshop on Nucleation Theory and its Applications. Atlanta, GA, April 10-12, 1972.

14. Husar, R.B., K.T. Whitby, B. Liu and N. Barsic. 1972. The Minnesota Aerosol Analyzing System used in the Pasadena Smog Project. J. Colloid and Interface Sci. 39:211-224.

15. Judeikis, H.S. and S. Siegel. 1972. Particle-Catalyzed Oxidation of Atmospheric Pollutants. The Aerospace Corp. El Segundo, CA. ATR-73(7256)-1.

16. Lin, M.J., D.P. Johnson and J.H. Lunsford. 1972. The EPR Spectra of COS^- and CS_2^- on Magnesium Oxide. Chem. Phys. Letters. 15:412-414.

17. Miller, M.S., S.K. Friedlander and G.M. Hidy. 1972. A Chemical Element Balance for the Pasadena Aerosol. J. Colloid Interface Sci. 39:165-176.

18. Schoonheydt, R.A. and J.H. Lunsford. 1972. An Electron Paramagnetic Resonance Study of SO_2^- on Magnesium Oxide. J. Phys. Chem. 76:323-328.

19. Schoonheydt, R.A. and J.H. Lunsford. 1972. Infrared Spectroscopic Investigation of the Adsorption and Reactions of SO_2 and MgO. J. Catal. 26:261-265.

20. Thielke, J.F., R.J. Charlson, J.W. Winter, N.C. Ahlquist, K.T. Whitby, R.B. Husar and B.Y.H. Liu. 1972. Multiwavelength Nephelometer Measurements in Los Angeles Smog Aerosols II: Correlation with Size Distributions, Volume Concentrations and Broad Band Light Scattering. J. Colloid and Interface Sci. 39:252-259.

21. Waggoner, A.P., N.C. Ahlquist and R.J. Charlson. 1972. Measurement of the Aerosol Total Scatter-Backscatter Ratio. Applied Optics. 11:2886-2889.

22. Waggoner, A.P., R.J. Charlson and N.C. Ahlquist. 1972. Comment on "On the Brown Color of Atmospheric Haze" by H. Horvath. Atmos. Environ. 6:143-144.

23. Whitby, K.T., R.B. Husar and B.Y.H. Liu. 1972. The Aerosol Spectra of Los Angeles Smog. J. Colloid and Interface Sci. 39:177-204.

24. Whtiby, K.T., B.Y.H. Liu and R.B. Husar. 1972. Physical Mechanisms Covering the Dynamics of Los Angeles Smog Aerosols. J. Colloid and Interface Sci. 39:136-164.

25. Wilson, W.E., W.E. Schwartz and G.W. Kinzer. Haze Formation: Its Nature and Origin. EPA-CPA 70-Neg. 172, U.S. Environmental Protection Agency, RTP, NC, 1972. 71pp.

1973

26. Anderson, J.A., D.L. Blumenthal and G.J. Sem. Characterization of Denver's Urban Plume Using an Instrumented Aircraft. Brown Cloud of Denver. The Denver Air Pollution Study, Proceedings of a Symposium. EPA, RTP, NC, 1973.

27. Bhardwaja, O.S., R.J. Charlson, A.P. Waggoner and N.C. Ahlquist. 1973. Rayleigh Scattering Coefficients of Freon-12, Freon-22, and CO_2 Relative to that of Air. Applied Optics. 12:135-136.

28. Brock, J. 1973. Comments of Theories of Aerosol Charging. J. of Colloid and Interface Sci. 39:418-420.

29. Brock, J. and M.S. Wu. 1973. Field Changing of Aerosols. J. of Colloid and Interface Sci. 45:106-114.

30. Crow, L.W. Airflow Study Related to EPA Field Monitoring Program Denver Metropolitan Area Nov., 1973. In: Denver Air Pollution Study-1973. EPA-600/9-76-007a. (1:3-29), U.S. Environmental Protection Agency, RTP, NC, 1976.

31. Frank, R., C.E. McJilton and R.J. Charlson. Sulfur Oxides and Particles: Effects on Pulmonary Physiology in Man and Animals. Presented at: Conference on Health Effects of Air Pollutants, NAS, Washington, D.C., Oct. 3-5, 1973.

32. Friedlander, S.K., 1973. Chemical Element Balances and Identification of Air Pollution Sources. Environ. Sci. Tech. 7:235-240.

33. Hedgpeth, H., S. Siegel, T.B. Stewart and H.S. Judeikis. 1973. Cylindrical Flow Reactor for the Study of Heterogeneous Reactions of Possible Importance in Polluted Atmospheres. The Aerospace Corp. El Segundo, CA, ATR-73(7256)-4. 21pp.

34. Heisler, S.L., S.K. Friedlander and R.B. Husar. 1973. The Relationship of Smog Aerosol Size and Chemical Element Distributions to Source Characteristics. Atmos. Environ. 7:633-649.

35. Johansson, T.B., J.W. Nelson, R.E. Van Grieken, K.R. Chapman and J.W. Winchester. Elemental Composition of North Florida Aerosol Size Fractions. In: American Chemical Society 166th National Meeting. Chicago, August 26-31, 1973. Abstract COLL 059.

36. Johansson, T.B., J.W. Nelson, R.E. Van Grieken and J.W. Winchester. 1973. Elemental Analysis of Aerosol Size Fractions by Proton Induced X-Ray Emission. In: Transactions, American Nuclear Society. 17:103.

37. Jones, P.W. The Analysis of Ambient Denver Air for Organic Vapors Including Carcinogenic POM Compounds. In: Denver Air Pollution Study 1973. EPA-600/9-76-007a. (1:31-50), U.S. Environmental Protection Agency, RTP, NC, 1976.

38. Judeikis, H.S. and S. Siegel. 1973. Efficiency of Gas-Wall Reactions in a Cylindrical Flow Reactor. The Aerospace Corp. El Segundo, CA. ATR-73(7256)-2.

39. Judeikis, H.S. and S. Siegel. 1973. Particle-Catalyzed Oxidation of Atmospheric Pollutants. Atmos. Environ. 7:617-631.

40. Lin, C., M.B. Baker and R.J. Charlson. 1973. Absorption Coefficient of Atmospheric Aerosol: A Method for Measurement. Applied Optics. 12:1356-1363.

41. Lunsford, J.H. and D.P. Johnson. 1973. Electron Paramagnetic Resonance Study of S_3^- Formed on Magnesium Oxide. J. Phys. Chem. 58:2079-2083.

42. McJilton, C., R. Frank and R.J. Charlson. 1973. The Role of Relative Humidity in the Synergistic Effect of SO_2^- Aerosol Mixture on the Lung. Science. 182(4111):503-504.

43. Middleton, P.B. and J.R. Brock. 1973. The Denver Brown Cloud. In: Denver Air Pollution Study-1973. EPA-600/9-76-007a. (1:101-140), U.S. Environmental Protection Agency, RTP, NC, 1976.

44. Miller, D.F., W.E. Schwartz, J.L. Gemma and A. Levy. Haze Formation: Its Nature and Origin. EPA-650/3-75-010, U.S. Environmental Protection Agency, RTP, NC, 1973.

45. Miller, D.F., W.E. Schwartz, P.W. Jones, P.W. Joseph, C.W. Spicer, C.J. Riggle and A. Levy. Haze Formation: Its Nature and Origin. EPA-650/3-74-002, U.S. Environmental Protection Agency, RTP, NC, 1973.

46. Porch, W.M., D.S. Ensor, R.J. Charlson and J. Heintzenberg. 1973. Blue Moon: Is this a Property of Background Aerosol? Applied Optics. 13:34-36.

47. Russell, P.A. and C.O. Ruud. 1973. An Analysis of Particulates From the Denver Urban Plume Using Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry. In: Denver Air Pollution Study-1973. EPA-600/9-76-007a. (1:165-182), U.S. Environmental Protection Agency, RTP, NC, 1976.

48. Stewart, T.B. 1973. Positive Displacement Gas Circulating Pump. The Aerospace Corp. El Segundo, CA. ATR-73(7256)-3. 7pp.

49. Stewart, T.B. 1973. Positive Displacement of Gas Circulating Pump. Rev. Sci. Instrum. 44:1144.

50. Taarit, B.Y. and J.H. Lunsford. 1973. Electron Paramagnetic Resonance Evidence for the Formation of SO_3^- by the Oxidation of SO_2^- on MgO. J. Phys. Chem. 77:1365-1367.

51. VanGrieken, R.E., T.B. Johansson, J.W. Nelson and J.W. Winchester. Charged Particles in Elemental Analysis: X-Ray Emission and Elastic Scattering. In: American Chemical Society 166th National Meeting, Chicago, August 26-31, 1973. Abstract NUCL021.

52. Waggoner, A.P. The Brown Cloud of Denver. In: The Denver Air Pollution Study. Proceedings of a Symposium. EPA-600/9-76-007b, U.S. Environmental Protection Agency, RTP, NC, 1973. (In Press)

53. Waggoner, A.P., M.B. Baker and R.J. Charlson. 1973. Optical Absorption by Atmospheric Aerosols. Applied Optics. 12:896.

1974

54. Akselsson, R., C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufman, K.R. Chapman, J.W. Nelson and J.W. Winchester. 1974. Application of Proton Induced X-Ray Emission Analysis to the St. Louis Regional Air Pollution Study. Advances in X-Ray Analysis. 18.

55. Blumenthal, D.L., J.A. Anderson and G.J. Sem. 1974. Characterization of Denver's Urban Plume Using an Instrumented Aircraft. APCA Paper 74-266. Denver, CO.

56. Brock, J. and N. Marlow. 1974. Calculations of Bipolar Charging of Aerosols. J. of Colloid and Interface Sci. 51:23-31.

57. Brock, J. and N. Marlow. 1974. Charged Aerosol Particles and Air Pollution. Environ. Letters.

58. Brock, J., J. Bricard, G. Madelaine and M. Pourprix. 1974. Repartition de las Charge d'Espace Au Voisinage d'un Faisieau de Particules. C.R. Acad. Sc. Paris. 278:1974.

59. Charlson, R.J., W.M. Porch, A.P. Waggoner and N.C. Ahlquist. 1974. Background Aerosol Light Scattering Characteristics: Nephelometric Observations at Mauna Loa Observatory Compared with Other Remote Locations. Tellus. 26(3):345-360.

60. Charlson, R.J., A.H. Vanderpol, A.P. Waggoner, D.S. Covert and N.C. Ahlquist. 1974. Sulfuric Acid. Ammonium Sulfate Aerosol: Optical Detection in the St. Louis Region. Science. 184(4133):156-158.

61. Grosjean, D. and S.K. Friedlander. 1974. Gas-Particle Distribution Factors for Organic and Other Pollutants in the Los Angeles Atmosphere. Submitted to: APCA J.

62. Hedgpeth, H., S. Siegel, T.B. Stewart and H.S. Judeikis. 1974. Cylindrical Flow Reactor for the Study of Heterogeneous Reactions of Possible Importance in Polluted Atmospheres. Rev. Sci. Instrum. 45:344.

63. Husar, R.B., D.L. Blumenthal, J. Anderson and W.E. Wilson. The Urban Plume of St. Louis. Proc. Div. of Environmental Chemistry, ACS. Los Angeles, CA, March 28-April 5, 1974.

64. Jensen, B. and J.W. Nelson. Novel Aerosol Sampling Apparatus for Elemental Analysis. In: Proc. Conf. Nucl. Techniques in Environ. Research. Columbia, MO, July 29-31, 1974.

65. Johansson, T.B., R.E. Van Grieken and J.W. Winchester. 1974. Interpretation of Aerosol Trace Metal Particle Size Distributions. In: Proc. Conf. Nucl. Techniques in Environ. Research. Columbia, MO, July 29-31, 1974.

66. Johansson, T.B., R.E. Van Grieken and J.W. Winchester. 1974. Marine Influences on Aerosol Composition in the Coastal Zone. J. De Recherches Atmos. 14 pp.

67. Lunsford, J.H. Structure and Reactivity of Adsorbed Oxides of Sulfur. EPA-650/3-74-006, U.S. Environmental Protection Agency, RTP, NC, 1974.

68. Nelson, J.W., I. Williams, T.B. Johansson, R.E. Van Grieken, K.R. Chapman and J.W. Winchester. Elemental Analysis of Aerosols Using Proton Scattering. In: IREE Trans. Nucl. Sci., NS-21: 618-621, February 1974.

69. Rao, K.V. and J.H. Lunsford. 1974. An Electron Paramagnetic Resonance Study of SO_2^- and SO_4^- Ions on Vanadium Oxide Supported on Silica Gel. J. Phys. Chem. 78:649-651.

70. Stewart, T.B. and J.S. Judeikis. 1974. Measurement of Spatial Reactant and Product Concentrations in a Flow Reactor Using Laser-Induced Fluorescence. Rev. Sci. Instrum. 45:1542.

71. Van Grieken, R.E., T.B. Johansson and J.W. Winchester. 1974. Trace Metal Fractionation Effects Between Sea Water and Aerosols from Bubble Bursting. J. De Recherches Atmos. 11 pp.

72. Winchester, J.W., D.L. Meinert, J.W. Nelson, T.B. Johansson, R.E. Van Grieken, C. Orsini, H.C. Kaufman and R. Akselsson. Trace Metals in the St. Louis Aerosol. In: Proc. Conf. Nucl. Techniques in Environ. Research. Columbia, MO, July 29-31, 1974.

1975

73. Blumenthal, D.L. and W.H. White. The Stability and Long Range Transport of Ozone or Ozone Precursors. 1975. APCA Paper No. 75-07.4. Boston, MA.

74. Davidson, C.I., S.K. Friedlander and S.V. Hering. The Deposition of Pb-Containing Particles from the Los Angeles Atmosphere. In: Proceedings of the Intnl. Conf. on Environ. Sensing and Assessment. Las Vegas, NV, 1975. Vol. 1. 3 pp.

75. Desaedeleer, G.G. and J.W. Winchester. 1975. Trace Metal Analysis of Atmospheric Aerosol Particle Size Fractions in Exhaled Human Breath. Environ. Sci. and Tech. 9:971-972.

76. Desaedeleer, G.G., J.W. Winchester, R. Akselsson, K.A. Hardy and J.W. Nelson. Bromine and Lead Relationships with Particle Size and Time Along an Urban Freeway. In: Proceedings of the International Nuclear and Atomic Activation Analysis Conference on Analytical Chemistry in Nuclear Technology. Oak Ridge, TN, October 14-16, 1975.

77. Draftz, R.G. Similarities of Atmospheric Aerosols from Four Major U.S. Cities. Presented at: Eighth Aerosol Technology Meeting. RTP, NC, October 1975.

78. Durham, J.L., W.E. Wilson, T.G. Ellestad, K. Willeke and K.T. Whitby. 1975. Comparison of Volume and Mass Distributions for Denver Aerosols. Atmos. Environ. 9(8):717-722.

79. Fox, D.L., J.E. Sickles, M.R. Kuhlman and P.C. Reist. 1975. Design and Operating Parameters for a Large Ambient Aerosol Chamber. APCA J. 25(10):1050-1053.

80. Gartrell, G. and S.K. Friedlander. 1975. Relating Particulate Pollution to Sources: The 1972 California Aerosol Characterization Study. Atmos. Environ. 9:279-298.

81. Gillani, N.V. and R.B. Husar. Mathematical Modeling of Air Pollution - A Parametric Study. Presented at: Proc. Second Federal Conference on the Great Lakes. Argonne, IL, March 25-27, 1975.

82. Grosjean, D. and S.K. Friedlander. 1975. Gas-to-Particle Distribution Factors for Organic and Other Pollutants in Los Angeles. J. Air Poll. Control Assoc. 25(10):1038-1044.

83. Husar, R.B. Fine Particulate Standard: An Assessment of the need and an attempt of its formulation. Presented at: Proc. ASME Air Pollution Div., Fourth Annual Symp. St. Louis, MO, March 24-25, 1975.

84. Husar, J.D., R.B. Husar and P.K. Stubits. 1975. Determination of Sub-Microgram Amounts of Atmospheric Particulate Sulfur. Anal. Chem. 47(12):2062-2065.

85. Husar, R.B. and W.R. Shu. 1975. Thermal Analyses of the Los Angeles Smog Aerosol. J. Applied Meteor. 14(8):1558-1565.

86. Johansson, T.B., R.E. Van Grieken, J.W. Nelson and J.W. Winchester. 1975. Elemental Trace Analysis of Small Samples by Proton Induced X-Ray Emission. Anal. Chem. 47(6):855-859.

87. Lin, M.J. and J.H. Lunsford. 1975. Photooxidation of Sulfur Dioxide on the Surface of Magnesium Oxide. J. Phys. Chem. 79:892-897.

88. Nelson, J.W. 1975. Application of Proton Induced X-Ray Emission Analysis to the St. Louis Regional Air Pollution Study. Advances in X-Ray Analysis. 18:588.

89. Nelson, J.W. and D.L. Meinert. 1975. Proton Elastic Scattering Analysis-A Complement to Proton Induced X-Ray Emission Analysis of Aerosols. Advances in X-Ray Analysis. 18:598.

90. Nelson, J.W. 1975. Automatic Time Sequence Filter Sampling of Aerosols for Rapid Multi-element Analysis by Proton Induced X-Ray Emission. Advances in X-Ray Analysis. 19:403.

91. Nelson, J.W. 1975. X-Ray Techniques for Aerosol Sulfur Baseline Assessment Along an Urban Freeway. Advances in X-Ray Analysis. 19:415.

92. Vanderpol, A.H., F.D. Carsey, D.S. Covert, R.J. Charlson and A.P. Waggoner. 1975. Aerosol Chemical Parameters and Air Mass Character in the St. Louis Region. Science. 190.

93. Van Grieken, R.E., T.B. Johansson, J.W. Winchester and L.A. Odom. 1975. Micro-Determination of Zirconium-Hafnium Ratios in Zircons by Proton Induced X-Ray Emission. Anal. Chem. 275:343-348.

94. Vaughan, W.M., R. Sperling, N.V. Gillani and R.B. Husar. Horizontal SO_2 Mass Flow Rate Measurements in Plumes: A Comparison of Correlation Spectrometer Data with a Dispersion and Removal Model. In: Proc. 68th Annual Meeting, APCA. Boston, MA, June 1975.

95. Winchester, J.W. 1975. The Ocean as a Source of Particulate Matter. Nat'l Acad. Sci. Report. (In Press).

96. Winchester, J.W. Approaches to Evaluating Dry Deposition of Atmospheric Aerosol Pollutants onto Lake Surfaces. In: Proc. First Specialty Symposium on Atmospheric Contribution to the Chemistry of Lake Waters. Internat. Assoc. Great Lakes Res. September 28-October 2, 1975.

1976

97. Akselsson, K.R., K.A. Hardy, G.G. Desaedleer, J.W. Winchester, W.W. Berg, T.B. Vanderwood and J.W. Nelson. 1976. X-Ray Techniques for Aerosol Sulfur Baseline Assessment Along an Urban Freeway. Advances in X-Ray Analysis. 19:415-425.

98. Boueres, L.C.S., F. Adams, J.W. Winchester, C.Q. Orsini, J.W. Nelson, T.A. Cahill and D.R. Lawsen. Sulfur and Heavy Metals in South American Urban and Nonurban Atmospheres. Presented at: The World Meteorological Organization Technical Conference on Atmospheric Pollution Measurement Techniques. Gothenburg, Sweden, October 11-15, 1976.

99. Brock, J. 1976. Simulation of Aerosol Kinetics. J. of Colloid and Interface Sci. 54:249-264.

100. Brock, J. 1976. Studies in Aerosol Dynamics: The Denver Brown Cloud. Environmental Monitoring Series, EPA. (In Press).

101. Brock, J. 1976. Simulation of Aerosol Dynamics. EPA Ecological Research Series. (In Press).

102. Brock, J. 1976. The Houston Urban Plume Study. EPA Ecological Research Series. (In Press).

103. Brock, J., K. DeBower and S. Suck. Dynamics of Automotive Sulfate Emissions. In: Proceedings of A.C.S. Symposium on Automotive Sulfate Emissions. August 1976.

104. Brock, J. and P.B. Middleton. 1976. Dynamic Model for Urban Particulate Pollution. Submitted to: Atmos. Environ.

105. Cunningham, P.T. and S.A. Johnson. 1976. Spectroscopic Observation of Acid Sulfation Atmospheric Particulate Samples. Science. 191:77-79.

106. Dannevik, W.P., S. Frisella, L. Granat and R.B. Husar. SO_2 Deposition Measurements in the St. Louis Region. Preprint: Third Symp. on Atmospheric Turbulence, Diffusion and Air Quality, AMS, Raleigh, NC, October 19-22, 1976.

107. Desaedeleer, G.G., J.W. Winchester and K.R. Akselsson. Monitoring Aerosol Elemental Composition in Particle Size Fractions for Predicting Human Respiratory Uptake. Presented at: International Conference on Particle Induced X-Ray Emission and its Analytical Application. Lund, Sweden, August 23-26, 1976.

108. Desaedeleer, G.G., J.W. Winchester, J.O. Pillotte, J.W. Nelson and H.A. Moffett. Proton Induced X-Ray Emission Analysis of Roadway Aerosol Time Sequence Filter Samples for Pollution Control Strategy. In: IAEA Conference Proceedings. Vienna, March 1976.

109. Draftz, R.G. Microscopical Analysis of Aerosols Transported from St. Louis. Presented at: American Chemical Society Meeting. New York, NY, April 1976.

110. Draftz, R.G. Aircraft Collection and Microscopical Analysis of Ambient Aerosols from Urban Atmospheres. Presented at: Air Pollution Control Assoc. Meeting. Portland, OR, June 1976.

111. Draftz, R.G. Comparison of Elemental and Microscopical Analysis of Atmospheric Aerosols. Presented at: American Chemical Society Meeting. New York City, NY, April 1976.

112. Draftz, R.G. Morphology of Airborne Dust in Maricopa County, Arizona in preparation for presentation at the 1977 AAAS Symposium on Denver Dust. Denver, CO, February 1977.

113. Farmer, W.M. and J.O. Hornkohl. Environmental Aerosol Measurements Using an Airborne Particle Morphokinetometer. EPA-600/3-76-087, U.S. Environmental Protection Agency, RTP, NC, 1976.

114. Gillani, N.V. and R.B. Husar. Analytical-Numerical Model for Mesoscale Transport, Transformation and Removal of Air Pollutants. In: Proc. 7th Technical Meeting on Air Pollution Modeling and its Applications. NATO/CCMS. Airlie, VA, September 7-10, 1976.

115. Gillani, N.V. and R.B. Husar. Mesoscale Model for Pollutant Transport, Transformation and Ground Removal. Preprint: Third Symp. on Atmospheric Turbulence, Diffusion and Air Quality, AMS, Raleigh, NC, October 19-22, 1976.

116. Gillani, N.V. and R.B. Husar. Synoptic Scale Haziness Over Eastern U.S. and its Long Range Transport. Invited Paper: Proc. 4th National Conf. of Fire & Forest Meteorology, SAF/AMS, St. Louis, MO, November 1976.

117. Graf, J., R.H. Snow and R.G. Draftz. Field Air Sampling Study-Phoenix, Arizona. EPA Ecological Research Series. (In Press).

118. Hardy, K.A., R. Akselsson, J.W. Nelson and J.W. Winchester. 1976. Elemental Constituents of Miami Aerosol as Function of Particle Size. Environ. Sci. and Tech. 10(2):176-182.

119. Husar, R.B. 1976. Therman Analysis of Aerosols. J. of Thermal Analysis. 10(2).

120. Husar, R.B. Determination of Ambient H_2SO_4 and its ammonium salts by 'in situ' aerosol thermal analysis. In: Proc. Symp. on Radiation in the Atmosphere, Garmisch-Partenkirchen. Germany, August 19-28, 1976.

121. Husar, R.B., N.V. Gillani and J.D. Husar. A Study of Long Range Transport from Visibility Observations, Trajectory Analysis and Local Air Pollution Monitoring Data. In: Proc. 7th Technical Meeting on Air Pollution Modeling and its Applications. NATO/CCMS. Airlie, VA, September 7-10, 1976.

122. Husar, R.B., N.V. Gillani, J.D. Husar and C.C. Paley. Large Scale Haziness Over Midwestern and Eastern U.S. Presented at: Symp. on Radiation in the Atmosphere, Garmisch-Partenkirchen. Germany, August 19-28, 1976.

123. Husar, R.B., N.V. Gillani, J.D. Husar, C.C. Paley and P.N. Turcu. Long Range Transport of Pollutants Observed Through Visibility Contour Maps, Weather Maps and Trajectory Analysis. Preprint: Third Symp. on Atmospheric Turbulence, Diffusion and Air Quality, AMS. Raleigh, NC, October 19-22, 1976.

124. Husar, R.B., N.V. Gillani and J.D. Husar. Particulate Sulfur Formation in Power Plant, Urban and Regional Plumes. In: Proc. Symp. on Aerosol Science and Technology, 82nd Nat'l Meeting of AIChE. Atlantic City, NJ, August 30-September 1, 1976.

125. Husar, R.B., J.D. Husar, S.B. Fuller, W.H. White, J.A. Anderson, W.M. Vaughan and W.E. Wilson. 1976. Sulfur Budget in Large Plumes: Pollutant Flow Rate Measurements in the St. Louis Region. Submitted to Science.

126. Husar, R.B., J.D. Husar, N.V. Gillani, S.B. Fuller, W.H. White, J.A. Anderson, W.M. Vaughan and W.E. Wilson. Pollutant Flow Rate Measurement in Large Plumes: Sulfur Budget in Power Plant and Area Source Plumes in the St. Louis Region. In: Proc. American Chemical Society Meeting (Div. of Environmental Chemistry). New York, NY, April 1976.

127. Husar, J.D., R.B. Husar, E.S. Macias, W.E. Wilson, J.L. Durham, W.K. Shepherd and J.A. Anderson. 1976. Particulate Sulfur Analysis: Application to High Time Resolution Aircraft Sampling in Plumes. Atmos. Environ. 10:591.

128. Husar, J.D., E.S. Macias and R.B. Husar. High Sensitivity Flame Photometric Particulate Sulfur Analysis. In: Proc. American Chemical Society Meeting (Div. of Environmental Chemistry). New York, NY, April 1976.

129. Husar, R.B., E.S. Macias and W.P. Dannevik. Measurement of Dispersion with a Fast Response Aerosol Detector. Preprint: Third Symp. on Atmospheric Turbulence, Diffusion and Air Quality, AMS. Raleigh, NC, October 19-22, 1976.

130. Husar, R.B., D.E. Patterson, C.C. Paley and N.V. Gillani. Ozone in Hazy Air Masses. Presented at: Internationl Conference on Photochemical Oxidant and its Control. (EPA) Raleigh, NC, September 12-17, 1976.

131. Husar, R.B., D.E. Patterson, W.H. White, D.L. Blumenthal and T.B. Smith. 1976. Three-Dimensional Distribution of Air Pollutants in the Los Angeles Basin: Average vertical profiles at Hawthorne, El Monte, Ontario and Riverside. Submitted to: J. Applied Meteor.

132. Husar, R.B. and W.H. White. 1976. On the Color of the Los Angeles Smog. Atmos. Environ. 10(3):199-204.

133. Johansson, T.B., R.E. Van Grieken and J.W. Winchester. 1976. Elemental Abundance Variation with Particle Size in North Florida Aerosols. J. of Geophysical Research. 81(6):1039-1046.

134. Judeikis, H.S. and T.B. Stewart. 1976. Laboratory Measurement of SO_2 Deposition Velocities in Selected Building Materials and Soils. Aerospace report No. ATR-76(7498)-1.

135. Judeikis, H.S. and T.B. Stewart. 1976. Laboratory Measurement of Heterogeneous Interactions of SO_2. Submitted to: Atmos. Environ.

136. Judeikis, H.S. and T.B. Stewart. 1976. Lab Measurement of SO_2 Deposition Velocities on Selected Building Materials and Solids. Atmos. Environ. 10:769.

137. Kaufman, H.C., K.R. Akselsson and W.J. Courtney. 1976. A Computer Program for PIXE Spectrum Resolution of Aerosols. Advances in X-Ray Analysis. 19:355-366.

138. Lamb, B.K. and F.H. Shair. 1976. A Limit Model for Determining the Impact of Rural Power Plant Emissions Relative to Urban Emissions Upon Urban Air Quality: Part 1. Model Description and Consideration of Long-term Impacts. Atmos. Environ. (In Press).

139. Lin, M.J. and J.H. Lunsford. 1976. Electron Paramagnetic Resonance Evidence for the Formation of S_2O^- on Magnesium Oxide. J. Phys. Chem. 80:635-639.

140. Lin, M.J. and J.H. Lunsford. 1976. An EPR Study of $H_2S_2^-$ on Magnesium Oxide. J. Phys. Chem. 80:2015-2018.

141. Macias, E.S. 1976. Atmospheric Aerosol Sulfur and Mass Concentration. St. Louis, MO, August and September 1975. (In Press).

142. Macias, E.S., R.A. Fletcher, J.D. Husar and R.B. Husar. 1976. Particulate Sulfur Emission Rate from a Simulated Freeway. In: The General Motors/EPA Sulfate Dispersion Experiment. EPA-600/3-76-035, U.S. Environmental Protection Agency, RTP, NC, 1976. 145 pp.

143. Macias, E.S., R. Fletcher, J.D. Husar and R.B. Husar. Particulate Sulfur Emission Rate from a Simulated Freeway. In: Proc. of Div. of Environmental Chemistry, American Chemical Society. San Francisco, CA, August 29-September 3, 1976.

144. Macias, E.S. and R.B. Husar. 1976. Atmospheric Particulate Mass Measurement with "Two MASS" Beta Attenuation Mass Monitor. Environ. Sci. and Tech. 10:904.

145. Macias, E.S. and R.B. Husar. A Review of Atmospheric Particulate Mass Measurement via the Beta Attenuation Technique. In: Proc. of the Symposium on Fine Particles. Minneapolis, MN, May 28-30, 1975.

146. Macias, E.S. and R.B. Husar. 1975. High Resolution on-Line Aerosol Mass Measurement by the Beta Attenuation Technique. In: Proc. of the Second International Conference on Nuclear Methods in Environmental Research, Vogt, J.R. (ed.) U.S. ERDA, Columbia, MO.

147. McSweeney, A. A Diffraction Technique to Measure Size Distribution of Large Airborne Particles. EPA-600/3-76-073, U.S. Environmental Protection Agency, RTP, NC, 1976.

148. Meinert, D.L. and J.W. Winchester. 1976. Chemical Relationships in the North Atlantic Marine Aerosol. Submitted to: J. Geophysical Research.

149. Miller, D.F. Smog Chamber Studies of Photochemical Aerosol-Precursor Relationships. EPA-600/3-76-080, U.S Environmental Protection Agency, RTP, NC, 1976.

150. Nelson, J.W., B. Jensen, G.G. Desaedeleer, K.R. Akselsson and J.W. Winchester. 1976. Automatic Time Sequence Filter Sampling of Aerosols for Rapid Multi-Element Analysis by Proton-Induced X-Ray Emission. Advances in X-Ray Analysis. 19:415-425.

151. Orsini, C.Q., H.C. Kaufmann, K.R. Akselsson, J.W. Winchester and J.W. Nelson. Variation of Elemental Composition with Particle Size in the St. Louis Aerosol. Presented at: The International Conference on Particle Induced X-Ray Emission and its Analytical Applications. Lund, Sweden, August 23-26, 1976.

152. Pilotte, J.O., J.W. Nelson and J.W. Winchester. Application of. Multi-Station Time Sequence Aerosol Sampling and Proton Induced X-Ray Emission Analysis Techniques to the St. Louis Regional Air Pollution Study for Investigating Sulfur-Trace Metal Relationships. In: Proceedings of ERDA Symposium on X- and Gamma-Ray Sources and Applications. Ann Arbor, MI, May 19-21, 1976.

153. Rasmussen, R.A. 1976. Surface Ozone Observations in Rural and Remote Areas. J. of Occupational Medicine. 18(5):346-349.

154. Rasmussen, R.A., R.B. Chatfield and W.M. Holdren. Transport of Hydrocarbon and Oxidant Chemistries Observed at a Rural Mid-West Site. Submitted for publication in: Proc. of Symp. on the Non-Urban Tropospheric Condition. Miami Beach, FL, November 10-12, 1976.

155. Rasmussen, R.A., E. Robinson and R. Chatfield. An Assessment of the Lower Tropospheric Continental Ozone Budget. Submitted for publication in: Proc. Int. Conf. on Photochemical Oxidant Pollution and Its Control. Section on Causes of Urban, Suburban and Non-Urban Oxidant Pollution. Raleigh, NC, September 12-17, 1976.

156. Richards, J.R., D.L. Fox and R.C. Reist. 1976. The Influence of Molecular Complexes on the Photo-Oxidation of Sulfur Dioxide. Atmos. Environ. 10:211-217.

157. Roberts, P.T. and S.K. Friedlander. 1976. Photochemical Aerosol
      Formation SO_2, 1-Heptene, and NO_x in Ambient Air. Environ. Sci. and
      Tech. 10(6):573-580.

158. Roberts, P.T. and S.K. Friedlander. 1976. Analysis of Sulfur in
      Deposited Aerosol Particles by Vaporization and Flame Photometric
      Detection. Atmos. Environ. 10:403-408.

159. Schwartz, W.E., G.D. Mendenhall, P.W. Jones, C.J. Riggle, A.P. Graffeo
      and D.F. Miller. Chemical Characterization of Model Aerosols.
      EPA-600/3-76-085, U.S. Environmental Protection Agency, RTP, NC, 1976.

160. Schwartz, W.E., P.W. Jones, C.J. Riggle, D.F. Miller and W.E. Wilson.
      1976. Organic Characterization of Cyclohexene/NO_x Aerosol. Environ.
      Sci. and Tech. (In Press).

161. Sheline, J., R. Akselsson and J.W. Winchester. Trace Element Similarity
      Groups in North Florida Spanish Moss: Evidence for Direct Up Take of
      Aerosol Particles. J. of Geophysical Research. 81(6):1047-1050.

162. Van Grieken, R.E., T.B. Johansson, K.R. Akselsson, J.W. Winchester,
      J.W. Nelson and K.R. Chapman. 1976. Geophysical Applicability of
      Aerosol Size Distribution Measurements Using Cascade Impactors and
      Proton Induced X-Ray Emission. Atmos. Environ. 10:571-576.

163. Waggoner, A.P., A.H. Vanderpol, R.J. Charlson, T.V. Larson, L. Granat
      and C. Tragardh. 1976. Sulfate as a Cause of Tropospheric Haze.
      Nature. 261:120-122.

164. Weiss, R.E., A.P. Waggoner, R.J. Charlson and N.C. Ahlquist. Sulfate
      Aerosol, It's Geographic Extent. 1976. Science. (In Press).

165. Wesely, M.L., B.B. Hicks, W.P. Dannevik, S. Frisella and R.B. Husar.
      1976. An Eddy-Correlation Measurement of Particulate Deposition from
      the Atmosphere. Submitted to: Atmos. Environ.

166. Whitby, K.T., B. Cantrell, R.B. Husar, N.V. Gillani, J.A. Anderson,
      D.L. Blumenthal, W.E. Wilson, Jr., Ibid; W.E. Wilson, Jr., R.J. Charlson,
      R.B. Husar, K.T. Whitby and D.L. Blumenthal. Paper No. 76-30-06.
      69th Annual Meeting of Air Pollution Control Assoc. Portland, OR.

167. Whitby, K.T., B.C. Cantrell, R.B. Husar, N.V. Gillani, J.A. Anderson,
      D.L. Blumenthal and W.E. Wilson. Aerosol Formation in a Coal Fired
      Power Plant Plume. In: Proc. American Chemical Society Meeting (Div.
      of Environmental Chemistry). New York, NY, April 1976.

168. White, W.H., J.A. Anderson, D.L. Blumenthal, R.B. Husar, N.V. Gillani,
      S.B. Fuller, K.T. Whitby and W.E. Wilson. Formation of Ozone and
      Light-Scattering Aerosols in the St. Louis Urban Plume. In: Proc.
      American Chemical Society Meeting, (Div. of Environmental Chemistry).
      New York, NY, April 1976.

169. White, W.H., J.A. Anderson, D.L. Blumenthal, R.B. Husar, N.V. Gillani, S.B. Fuller and W.E. Wilson. 1976. Formation and Transport of Secondary Air Pollutants: Ozone and Aerosols in the St. Louis Urban Plume. Science. 194(4261):187-189.

170. White, W.H. and R.B. Husar. 1976. A Lagrangian Model of the Pasadena Smog Aerosol. J. Air Poll. Control Assoc. 26(1):32-35.

171. White, W.H. and R.B. Husar. 1976. Comments on Chu & Seinfeld paper - "Formulation and Initial Application of a Dynamic Model for Urban Aerosols." Atmos. Environ. 10:85.

172. Wilson, W.E., R.J. Charlson, R.B. Husar, K.T. Whitby and D. Blumenthal. Sulfates in the Atmosphere. In: Proc. 69th Annual Meeting of Air Pollution Control Ass'n. Protland, OR, June 27-July 1, 1976.

173. Wilson, W.E., R.B. Husar, K.T. Whitby, D.B. Kittelson and W.H. White. Chemical Reactions in Power Plant Plumes. In: Proc. American Chemical Society Meeting, (Div. of Environmental Chemistry). New York, NY, April 1976.

174. Winchester, J.W. Assessing Air Pollution Particulate Fallout Potential for Water Pollution in Lake Michigan. In: Proceedings of the Second Federal Conference on the Great Lakes. Interagency Committee on Marine Science and Engineering of the Federal Council for Science and Technology. August 17, 1976.

175. Winchester, J.W. Sulfur and Trace Metal Relationships in Non-urban and Marine Aerosols Studied Using Proton Induced X-Ray Emissions. Presented at: International Conference on Particle Induced X-Ray Emission and its Analytical Applications. Lund, Sweden, August 23-26, 1976.

176. Winchester, J.W. and J.W. Nelson. Non-urban Sulfur Aerosol Studies. Technical Progress Report December 1975-August 1976. EPA Grant No. R803887, U.S. Environmental Protection Agency, RTP, NC. (Contract J.W. Winchester for reprints.).

APPENDIX C

PUBLICATIONS, PRESENTATIONS, AND THESIS LISTING INDEX

1. Adams, F.   98

2. Ahlquist, N.C.   10, 11, 20, 21, 22, 27, 59, 60, 164

3. Aksellsson, R.   54, 72, 76, 97, 107, 118, 137, 150, 151, 161, 162

4. Anderson, J.A.   26, 55, 63, 125, 126, 127, 166, 167, 168, 169

5. Baker, M.B.   40, 53

6. Barsic, N.   14

7. Berg, W.W.   97

8. Bhardwaja, O.S.   27

9. Blumenthal, D.L.   26, 55, 63, 73, 131, 166, 167, 168, 169, 172

10. Boueres, L.C.S.   98

11. Bricard, J.   58

12. Brock, J.R.   2, 3, 8, 28, 29, 43, 56, 57, 58, 99, 100, 101, 102, 103, 104

13. Cahill, T.A.   98

14. Cantrell, B.   166, 167

15. Carsey, F.D.   92

16. Cahpman, K.R.   35, 54, 68, 162

17. Charlson, R.J.   4, 6, 7, 9, 10, 11, 20, 21, 22, 27, 31, 40, 42, 46, 53, 59, 60, 92, 163, 164, 166, 172

18. Chatfield, R.B.   154, 155

19. Courtney, W.J.   137

20. Covert, D.S.   9, 10, 60, 92

21. Crow, L.W.   30

22. Cunningham, P.T.   105

23. Dannevik, W.P.   106, 129, 165

24. Davidson, C.J.   74

131.	Van Grieken, R.E.	35, 36, 51, 54, 65, 66, 68, 71, 72, 86, 93, 133, 162
132.	Vaughan, W.M.	94, 125, 126
133.	Waggoner, A.P.	1, 6, 12, 21, 22, 27, 52, 53, 59, 60, 92, 163, 164
134.	Weiss, R.E.	164
135.	Wesely, M.L.	165
136.	Whitby, K.T.	11, 14, 20, 23, 24, 78, 166, 167, 168, 172, 173
137.	White, W.H.	73, 125, 126, 131, 132, 168, 129, 170, 171, 173
138.	Willeke, K.	78
139.	Williams, I.	68
140.	Wilson, W.E.	25, 63, 78, 125, 126, 127, 160, 166, 168, 169, 172, 173
141.	Winchester, J.W.	35, 36, 51, 54, 65, 66, 68, 71, 72, 75, 76, 86, 93, 95, 96, 97, 98, 107, 108, 118, 133, 148, 150, 151, 152, 161, 162, 174, 175, 176
142.	Winter, J.W.	20
143.	Wu, M.S.	29
144.	Zeigler, C.S.	7

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-77-080	2	3. RECIPIENT'S ACCESSION•NO.
4. TITLE AND SUBTITLE AEROSOL RESEARCH BRANCH, ANNUAL REPORT FY1976/76A		**5. REPORT DATE** August 1977
		6. PERFORMING ORGANIZATION CODE
7 AUTHOR(S) W.E. Wilson and C. Danskin, editors		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		**10. PROGRAM ELEMENT NO.** 1AA603, 1AD712, 1AA601
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		**13. TYPE OF REPORT AND PERIOD COVERED** Final
		14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES A complementary report, EPA-600/7-77-076, describes research activities funded by the Energy/Environment program.

16. ABSTRACT

The research program of the Aerosol Research Branch includes research grants and contracts at institutions in many parts of the United States, in addition to an intramural program. The purpose of these projects is to study the chemical and physical properties of aerosols, identify the mechanisms of aerosol formation and removal, and conduct experiments to measure these rates.

The results of the research are being used (1) to establish the contribution of the various sources to the ambient atmospheric aerosol loading, (2) to characterize urban, natural, and primary and secondary aerosols, (3) to develop quantitative descriptions of the generation and removal rates associated with each major aerosol source and sink, (4) to quantify the effects of aerosol on atmospheric chemical reactions, and (5) as a scientific basis for recommending regulatory actions concerned with air quality improvements.

The research projects funded under EPA's base program are described.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Aerosols *Research projects		13B 07D

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 143
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)