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SOUTHERN CALIFORNIA AIR QUALITY STUDY (SCAQS) PROGRAM PLAN

June 1987

STI Ref. 96030-708R Agreement No. A5-157-32

Prepared for:

California Air Resources Board (ARB) P.O. Box 2815 Sacramento, CA 95812

Prepared by Sonoma Technology Inc. (STI) and Desert Research Institute (DRI) with extensive input from the California Air Resources Board (ARB) and other sponsors, participants, and members of the technical community.

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ABSTRACT

This program plan outlines the measurement and management approach and reviews the technical background for the Southern California Air Quality Study (SCAQS). SCAQS is a multi-year, integrated, cooperative study which is funded by many different government agencies, industry groups, and individual corporate sponsors. This plan has been prepared with the input of the sponsors, participants, and potential users of the study data and represents a composite of their ideas.

The overall goal of SCAQS is to develop a comprehensive and properly archived air quality and meteorological data base for the South Coast Air Basin that can be used to test, evaluate, and improve elements of air quality simulation models for oxidants, PM-10, fine particles, toxic air contaminants, and acidic species. In addition, SCAQS will provide a data base which can be used to address specific technical questions regarding the emission, transport, transformation, and deposition of pollutants.

The study is planned to take place in 1987 during six weeks in early summer and four weeks in late fall. Extensive routine measurements and special studies will take place on 18 days during the study. Most of the monitoring will take place at existing air quality monitoring sites. Airborne, meteorological, and tracer measurements are planned at additional locations.

ACKNOWLEDGEMENTS

The preparation of this program plan was funded by the California Air Resources Board (ARB) under Contract #A5-157-32. The planning process has involved a great deal of interaction with the ARB staff and management. The input and guidance of Dr. D. R. Lawson, Mr. F. J. DiGenova, Dr. J. R. Holmes, and Dr. J. K. Suder are particularly appreciated. In addition, Dr. D. R. Lawson played a major role in the conception and design of SCAQS and has been an effective advocate for the study to potential sponsors and participants.

Without the support and financial commitments of the sponsors, this study would not be possible. These sponsors are: the Environmental Protection Agency (EPA), the South Coast Air Quality Management District (SCAQMD), the Coordinating Research Council (CRC), the Electric Power Research Institute (EPRI), the Ford Motor Company, the General Motors Research Laboratories (GMRL), the Motor Vehicle Manufacturers Association (MVMA), Southern California Edison (SCE), and the Western Oil and Gas Association (WOGA).

Many sponsors, participants, and potential users of the program data have contributed their ideas and their time for review and comment during the planning process. The list of such people is too long to include here, but many of them are listed in Appendix A. We gratefully acknowledge their contributions and recognize that the planning effort would have been impossible without their cooperation and efforts.

Several parts of the plan were prepared by other members of the STI or DRI staff and by STI consultants. The staff members and consultants who prepared parts of the plan are: Dr. L. W. Richards, STI; Dr. S. V. Hering, STI; Mr. D. E. Lehrman, STI; Dr. J. C. Chow, DRI; Dr. G. R. Cass, Caltech; and Dr. T. B. Smith.

In addition, members of the Technical Advisory Group for the project contributed ideas to the plan as well as provided continuing review of the planning effort. The members of the technical advisory group were: Dr. R. Atkinson, Dr. G. R. Cass, Dr. S. K. Friedlander, Dr. D. Grosjean, Dr. G. M. Hidy, Dr. W. B. Johnson, Dr. P. H. McMurry, and Dr. T. B. Smith.

Finally, we very much appreciate the exhaustive efforts of M. Howard, S. Duckhorn and S. Hynek who typed the text, prepared the figures, and published the drafts and final version of this plan under tight schedules.

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1. INTRODUCTION

1.1 BACKGROUND AND ISSUES

In recent years in California, the mix and spatial distribution of pollutant emissions have changed substantially, and several new classes of pollutants have gained the public's attention. In the next few years, many difficult regulatory issues relating to these changes will confront the California Air Resources Board (ARB), the Environmental Protection Agency (EPA), and the South Coast Air Quality Management District (SCAQMD). Resolution of these issues and development of effective control strategies to ameliorate California's air quality problems will require a better understanding of the relationships among the sources, receptors, and effects of the pollutants in question. This understanding can only be developed through measurement, data analysis, and modeling in an iterative fashion. Design and evaluation of alternative control strategies must be done using models which embody our best understanding of the above relationships.

This program plan outlines the first steps in a measurement, analysis, and modeling strategy which can ultimately provide the regulatory agencies with tools necessary to make effective decisions. This study, the Southern California Air Quality Study (SCAQS), addresses the following issues: ozone (0_3) , NO₂ and the roles of nitrogen oxides (NO_X), PM-10, fine particles, visibility, toxic air contaminants, and atmospheric acidity. The first five issues are addressed in depth, and adequate information should result from this project for the development and testing of descriptive and prognostic models. Understanding of the latter two issues will be greatly improved by this study, but this study alone will not necessarily provide the information required to develop and test prognostic models.

Although similar problems are faced by most California air basins, the focus of this study will be the South Coast Air Basin (SOCAB) since that is where the problems are most severe. Also, the SOCAB is one of the most well documented and intensively researched airsheds in the world.

Since the scope of the study is beyond the resources of the ARB alone, and since the results of the study could affect the actions of both government and industry, SCAQS has been designed as a cooperative project. Coordinated sponsorship by both government and industry should help assure adequate funding to meet the goals of the study. In addition, development of a protocol which is satisfactory to the parties affected by the results should minimize conflict about technical issues during the regulatory process.

SCAQS is designed to meet the goals and objectives agreed upon by the ARB and other potential sponsors. This program plan is the result of an open planning process which entailed extensive consultation with the modeling and measurement communities. The resulting design is an attempt to satisfy the needs expressed by the technical community to meet the stated objectives. The scope is quite large, and there obviously will be additional changes as the study evolves. The earlier version of this document (Blumenthal et al., 1986) was used as a starting point from which the final study design has been constructed. Feedback from potential sponsoring agencies and data users regarding their relative priorities and levels of resources has been used to refine the design. Lists including most of the people and organizations who have been involved in the planning process to date are included in Appendix A.

SCAQS data will be used to test and evaluate models which predict or describe the ambient distribution of pollutants. These models, in turn, will be used to develop and assess control strategies. The relationship between the SCAQS measurements and their ultimate use in developing control strategies is shown schematically in Figure 1-1. The primary focus of SCAQS is to provide measurements which relate source emissions to ambient pollutant spatial and temporal distributions. SCAQS will also include some source and effects-related measurements and a data analysis component.

The development and use of models can be a controversial subject because the model results have direct implications in terms of emissions controls. To minimize controversy and to expedite the measurements, SCAQS is designed to focus on measurements and data analysis but not directly to include modeling efforts. This modeling will be performed by the sponsors at a later date. However, since SCAQS must serve the needs of the modelers, extensive input has been solicited from the modeling community during the SCAQS design phase. A quantitative analysis of air quality modeling needs for input and testing data was undertaken as part of the SCAQS planning process (Seinfeld et al., 1986), and the SCAQS measurements presented here are consistent with that analysis.

1.2 STUDY GOALS

The overall goals of the study are:

- to develop a comprehensive and properly archived air quality and meteorological data base for the South Coast Air Basin which can be used to test, evaluate, and improve elements of air quality simulation models for oxidants, NO₂, PM-10, fine particles, visibility, toxic air contaminants, and acidic species. The data base should be adequate:
 - to test models proposed for the design of attainment strategies for PM-10, ozone, and NO₂; and
 - to clarify the hydrocarbon/NO $_X/O_3$ relationships so that ozone prediction models can be improved and new strategies to meet federal "reasonable efforts" requirements can be developed and tested;
- 2. to evaluate measurement methods for PM-10, fine particles, acidic species, and important nitrogen and carbon species; and
- 3. to enhance our understanding of the relationships between emissions and the spatial and temporal distributions of pollutants so that air quality simulation models and, ultimately, air quality management strategies can be improved.

The data obtained by meeting these goals should be of utility in the development and testing of air quality models of known accuracy, precision, and validity which can be used to design and evaluate the effect of proposed attainment strategies for O_3 , NO_X , PM-10, and selected toxic air contaminants.



Figure 1-1. RELATIONSHIP BETWEEN MEASUREMENTS, MODELS AND CONTROL STRATEGIES

1-3

1.3 TECHNICAL OBJECTIVES

To meet the goals stated in Section 1.2, a set of program objectives has been defined. Each of these objectives can be accomplished by addressing specific technical issues. The SCAQS objectives and their related technical issues are listed in this section. The origins and importance of the issues are discussed in Section 2. The primary goal of SCAQS is to develop a data base for use by modelers. Although modeling per se is not a part of SCAQS, the modeling community has been surveyed to determine the objectives of some of the groups which will use the SCAQS data. A summary of these objectives is presented to put SCAQS in perspective.

For most modeling activities, knowledge of the physical and chemical characteristics of the emissions from the major source types is required. For many of the source types in the South Coast Basin, the chemical and physical properties of particle and hydrocarbon emissions are not well known. To improve our knowledge of these properties, some emissions characterization studies are being designed which will be complementary to and coordinated with SCAQS. The objectives of these studies are also presented in this section.

1.3.1 SCAQS Objectives and Issues

Objective 1

Obtain a data base representative of the study area and sampling periods, with specified precision, accuracy, and validity, which can be used to develop, evaluate, and test episodic source and receptor models for 0_3 , $N0_2$, PM-10, fine particles, and atmospheric optical properties as well as annual average models for PM-10.

Issues to be addressed:

Data should be obtained which can be used to:

describe the spatial, temporal, and size distributions, and physical and chemical characteristics of suspended particles less than 10 μm diameter;

describe the spatial and temporal distribution of 0_3 and 0_3 precursors including important intermediate species such as OH, $H0_2$, $N0_3$, H_20_2 , and products such as HNO₃ and PAN;

refine the South Coast Air Basin emission inventory for the spatial and temporal distributions of particle, hydrocarbon, NO_X , and SO_X emissions for the study period;

describe the spatial distribution of selected toxic air contaminants;

describe the three-dimensional distributions of wind, temperature, relative humidity and cloud cover in the study area;

describe the initial pollutant spatial distribution and the pollutant concentrations at the boundaries of the SOCAB for the study days;

determine the relationship between the hydrocarbon/NO_X ratios in ambient air and their ratios in current emissions inventories;

determine the organic composition of selected samples of source and receptor region aerosols;

determine the contribution of trace metals to atmospheric aerosols in source and receptor areas as a function of size; and

determine the spatial distribution of nitrogen species. Perform a nitrogen mass balance across the Basin, accounting for total nitrogen species through transformations and deposition.

Objective 2

Identify the characteristics of emissions from specific sources or source types for use in receptor modeling of both gases and aerosols with emphasis on sources of organic and toxic emissions.

Issues to be addressed:

Determine which chemical and physical properties of source emissions are most useful for source attribution of receptor concentrations.

Estimate the changes in the ratios of chemical species as a function of source-receptor travel time, interactions with other species, and meteorological conditions.

Quantify the uncertainty of source attribution by receptor models as a function of the chemical and physical properties used to characterize sources. Select the optimal properties for routine source profile measurements.

Determine the percentages of the PM-10 and fine particles which are primary and secondary. Assess the relative contributions of natural and anthropogenic sources to PM-10 concentrations.

Objective 3

Assess the dependence of particle and 0_3 formation and removal mechanisms upon selected meteorological and precursor variables.

Issues to be addressed:

Assess the importance of water in the vapor and liquid phases for the formation of aerosol in the SOCAB.

Assess the role of aromatic hydrocarbons in the formation of particles and as an ozone precursor.

Assess the formation rates of nitric acid and aerosol nitrate as a function of: (1) the presence of liquid water, (2) altitude, (3) UV intensity, and (4) the presence of 0_3 .

Estimate the rate of ozone removal at surfaces as a function of time of day and atmospheric stability.

Objective 4

Assess how the spatial and temporal distributions of particles, 0_3 , 0_3 precursors, and NO_X depend upon emission height and selected meteorological variables.

Issues to be addressed:

Assess the relative contribution of elevated and ground based emissions to ground level O_3 , NO_X , PM-10, and fine particle concentrations, with emphasis on the influence of elevated source emissions of NO_X on wintertime NO_2 and summertime ozone concentrations.

Assess the importance of various mechanisms for day-to-day carryover of pollutants.

Assess the effects of high temperatures upon evaporative emissions and thus on ambient concentrations of hydrocarbon species.

Objective 5

Quantify the contributions of aerosols in an upwind source region and in an eastern basin receptor region to atmospheric acidity, mutagenicity, and visibility degradation.

Issues to be addressed:

Determine the species contributing to total acidity (aerosol and gas) in source and receptor regions, and estimate the contribution of aerosol and gaseous components to total acidity and to dry deposition.

Determine the relative contributions of primary and secondary aerosol species to visibility degradation in each region.

Assess the mutagenicity of PM-10 and PM-2.5 in each region.

Objective 6

Evaluate the validity of methods of measuring PM-10, fine particles, and precursor species in quantifying atmospheric constituents as they exist in the atmosphere during sampling.

Issues to be addressed:

Determine the concentrations of liquid water in particles in source and receptor areas as a function of relative humidity (RH) and particle size. Assess the change in mass as a function of size when particles are collected on substrates and analyzed under non-ambient environmental conditions. Determine the concentration of particulate organic matter in source and receptor areas as a function of particle size and ambient temperature. Assess the change in mass as a function of particle size, ambient temperature, and ambient pressure when particles are collected on substrates for subsequent laboratory analyses.

Determine the relationship between measurement values obtained at a single station and volume-averages over grid sizes used in prognostic air quality models.

Compare and evaluate various methods for the measurement of nitric acid and other nitrogen species and determine their accuracy, precision, and validity under a range of environmental conditions.

Compare and evaluate various methods for the measurement of carbonaceous species, and determine their accuracy, precision, and validity under a number of environmental conditions.

1.3.2 Modeling Considerations

The input and testing data required by air quality models were quantitatively assessed by a Model Working Group (MWG) as part of the program planning process (Seinfeld et al., 1986, 1987). The expected objectives of future modeling efforts include the following:

Sensitivity Testing

Performing model sensitivity tests to identify the sensitivity of model results to uncertainties in the model input data obtained during SCAQS.

Model Mechanisms Evaluation

Evaluating the physical and chemical bases for air quality models which describe photochemical and aerosol processes in the SOCAB.

Issues to be addressed:

Evaluate objective and fundamental methods of estimating threedimensional wind fields.

Evaluate chemical and physical mechanisms for 0_3 and aerosol formation.

Quantify the uncertainties in model results which are caused by: (1) measurement uncertainties of the model input data and parameters, (2) deviations from model assumptions, and (3) the stochastic nature of the atmosphere.

Compare the ability of alternative mathematical models to represent atmospheric and chemical mechanisms.

Overall Model Performance Evaluations; Performance Comparisons

Testing the performance of air quality models in predicting concentrations of PM-10, ozone, and important precursor and intermediate species as a function of space and time.

Issues to be addressed:

Identify common measures of performance applicable to all models.

Compare model results with corresponding measurements in space and time for each model tested.

Compare performance measures among air quality models.

1.3.3 Emissions Considerations

An Emissions Working Group (EWG) has been established as part of the SCAQS planning process. This group has developed a program plan for preparing the SCAQS inventory (Oliver et al., 1987). This includes procedures for collecting day-specific emission information, recommended special emission characterization studies, and a schedule for inventory delivery. This emissions inventory plan is consistent with the model input needs determined by the Model Working Group (Seinfeld et al., 1986).

1.4 OVERVIEW OF STUDY AND GUIDE TO PROGRAM PLAN

SCAQS includes the following elements:

- a project management and coordination activity;
- planning and preparation;
- measurement methods comparison and evaluation studies;
- a six week summer and a four week fall field measurement program and associated quality assurance activities;
- an emissions inventory assessment and enhancement for the study period;
- data archiving and distribution;
- data analysis and coordination activities;
- complementary emissions characterization studies for important source types; and
- reports and presentations.

Complementary model development and evaluation activities will be funded independently by some of the sponsors. This program plan describes the study elements listed above with the exception of the measurement methods comparison studies. These studies were planned separately and have been completed (Hering and Lawson et al., 1986b and Hering et al., 1987). The results from these studies have been incorporated into the SCAQS measurement program.

The SCAQS field measurement program will take place during early to mid summer and late fall periods. During each study period, several two-day to three-day periods will be studied intensively, for a total of 18 intensive study days.

The field study will include the following elements:

- a network of existing routine air quality monitoring stations (C-sites);
- nine monitoring stations located along typical air trajectories which will measure aerosols and gases routinely on intensive study days (B-sites). B-sites will be collocated with C-sites. B-site measurements will be made by techniques of known precision and accuracy. B-site measurements will be more extensive and have better time resolution than C-site measurements. Nine B-sites will be operated in the summer period and five during the fall period;
- one research station each in a source and receptor region in the summer and one station in a source region in the fall (A-sites). These stations will be collocated with B-sites and will be the base of operations for cooperating investigators. A-site measurements will be more sophisticated and experimental than the B-site measurements;
- a network of meteorological measurements at the surface and aloft to be operated on intensive study days;
- routine upper-air pollutant and LIDAR measurements to be made by aircraft on intensive study days;
- complementary measurements of selected toxic air contaminants to be made at selected sites;
- complementary physical and chemical measurements of fog and clouds on intensive study days;
- "special" studies on selected intensive study days including multiple tracer studies;
- assembly and archiving of complementary data from existing data sources; and
- a quality assurance program including independent systems and performance audits.

The study consists of a number of closely coordinated projects funded by several co-sponsors including the ARB, the Environmental Protection Agency (EPA), the South Coast Air Quality Management District (SCAQMD), the Coordinating Research Council (CRC), the Electric Power Research Institute (EPRI), the Ford Motor Company, the General Motors Research Laboratories (GMRL), the Motor Vehicle Manufacturers Association (MVMA), Southern California Edison (SCE), and the Western Oil and Gas Association (WOGA). The sponsors oversee and provide guidance to the study through a Management Advisory Group (MAG). The study is being coordinated by contractors who are funded by the ARB. The management contractor has prepared a final program plan (this document) which, to the maximum extent feasible, is satisfactory to all of the members of the MAG, and the study will be conducted according to that program plan. The ARB has also funded a Data Manager who will assemble, archive, and distribute to participants all data obtained as part of the study. Agreement to abide by a data management and exchange protocol is a condition of participation in the study.

Details of the program plan are outlined in the subsequent sections. Discussions of prior studies in the SOCAB, the data needs of various types of models, and the existing data resources in the SOCAB are presented in Section 2. Details of the planned measurements and emissions assessments are presented in Section 3, and the approach to quality assurance is discussed in Section 4. The data management activities and protocol are outlined in Section 5. Data analysis and complementary modeling activities are discussed in Section 6, and the program management structure is described in Section 7. The contracts related to the study, and the contributions of various sponsors are discussed in Section 8.

The preparation of this plan has been an iterative process. This fourth and final version of the SCAQS program plan incorporates additions, corrections, and changes in scope which resulted from review of the three previous versions by the ARB, sponsors, participants and the scientific community. As part of the planning process, Emissions, Meteorology, and Model Working Groups were formed to review the plan and to recommend specific measurement and data collection activities which would ensure that the study will meet the needs of the analysts and modelers who will use the data. The plan which has evolved is consistent with the recommendations of the working groups.

2. CURRENT KNOWLEDGE AND INFORMATION NEEDS

2.1 AIR QUALITY MANAGEMENT PLAN

The South Coast Air Basin (SOCAB) comprises 6600 square miles of the non-desert portions of Los Angeles, San Bernardino, Riverside and Orange Counties. Its population of approximately 10.5 million inhabitants is expected to increase to 13 million by the year 2000. This will be accompanied by a 31% increase in the number of dwellings and a 33% increase in employment. It is expected that 10.1 million on-road vehicles in the Basin will travel 234.3 million miles per day by the year 2000 (SCAQMD, 1982). The tremendous growth predicted over the next two decades adds to the even more rapid growth which has occurred since 1950. This growth has been accompanied by deterioration of air quality. Without careful planning and appropriate emissions controls, air quality could become even worse in the future.

The South Coast Air Quality Management District (SCAQMD) is charged with the responsibility for determining compliance with California state and federal air quality standards, proposing plans to attain those standards when they are exceeded, and for implementing those plans to the greatest extent possible. To these ends, the SCAQMD operates a network of sampling sites, illustrated in Figure 2-1, which measure ambient concentrations of carbon monoxide (CO), ozone (0_3) , sulfur dioxide (SO₂), nitrogen dioxide (NO₂), total suspended particulate (TSP) matter, PM-10, and suspended particulate lead. Table 2-1 presents the federal primary and secondary and California state standards for different atmospheric pollutants along with the number of sites and number of days in 1982 which exceeded these standards (Hoggan et al., 1983). Recent data for 1983 (ARB, 1983, and Hoggan et al., 1984) and earlier years are consistent with the number of exceedance cases indicated in Table 2-1. It is evident that the South Coast Air Basin was in violation of every standard, except that for SO_2 , at nearly every one of its sampling sites during 1982. Results for 1983, 1984, 1985 are similar and pollution levels in subsequent years are not expected to change significantly without changes in emissions. There is an obvious need to undertake measures to reduce ambient concentrations of carbon monoxide, nitrogen dioxide, ozone, and suspended particulate matter.

The most recent Air Quality Maintenance Plan (AQMP) (SCAQMD, 1982) proposes several control measures which would be implemented between now and the year 2000. SCAQMD (1982) estimates that these "Short Range Control Tactics" will cost approximately \$800 million to implement, most of which will be borne by petroleum refineries, electric utilities, and motor vehicle manufacturers. The emissions reductions are in addition to control measures which had been mandated prior to the Plan. The largest emission reductions by the year 2000 proposed in this plan result from the following additional control measures:

 Major CO reductions will result from more frequent tuneups to manufacturers' specifications; low emission, high fuel economy vehicles for local government; increased bicycling; ride sharing; modified work schedules; home goods delivery; traffic signal synchronization; electric, methanol-powered and dual-fueled vehicles; and more stringent emissions controls on in-use and new vehicles.



Figure 2-1. Existing Air Quality and Meteorological Monitoring Sites in the South Coast Air Basin. (Site codes are listed in Table 2-3 on pages 2-20 through 2-22.)

2-2

Pollutant	Federal Primary Standard	No. of Sites in Violation	Range in No. of Violation Days per site ^(e)	Federal Secondary Standard	No. of Sites In Violation	Range in No. of Violation Days per site ^(e)	California State Standard	No. of Sites in Violation	Range in No. of Violation Days per site ^(e)
Ozone	0.12 ppm (1 hr)	32	1 to 121	0.12 ppm (1 hr)	32	1 to 121	0.10 ppm (1 hr) ^(a)	33	2 to 160
Carbon Monoxide	9.0 ppm (8 hr) 35.0 ppm (1 hr)	13 0	2 to 50 0	9.0 ppm (8 hr) 35.0 ppm (1 hr)	13 0	2 to 50 0	9.0 ppm (8 hr) 20.0 ppm (1 hr)	13 6	2 to 47 1 to 7
Nitrogen Dioxide	0.05 ppm (aaa ^(f)) 	9	NA ^(c)	0.05 ppm (aaa) 	9	NA 	 0.25 ppm {1 hr}	 11	 1 to 8
Sulfu r Dioxide	0.03 ppm (aaa) 0.14 ppm (24 hr)	0 0	0 0	0.03 ppm (aaa) 	0	0 	 0.05 ppm (24 hr)	 0	 0
Sulfate		••	** #		~-		25 µg/m ³ (24 hr)	14	1 to 3
Lead	1.5 µg/m ³ (calendar qtr.)	1. ^(b)	1 ^(b)	1.5 µg/m ³ (calendar qtr	.) 1 ^(b)	1 ^(b)	1.5 µg/m ³ (per 30 days)	2 ^(b)	1 to 3 ^(b)
TSP	75 μg/m ³ (aga ^(g))	14	NA	60 µg/m ³ (aga)	18	NA	60 µg/m ³ (aga)	18	NA
	260 µg/m ³ (24 hr)	4	1 to 2	150 μ g/m ³ (24 hr)	23	1 to 22	100 µg/m ³ (24 hr)	26	2 to 37
PM-10	50 µg/m ³ (aaa)						30 µg/m ³ (aga)		
	150 µg/m ³ (24 hr)						50 µg/m ³ (24 hr)		

Table 2-1. Federal and California State Standards with Number of Sites^(d) Exceeding them in 1982.

(a) Oxidant instead of ozone

(b) Number of quarters instead of number of days

(c) NA - not applicable for annual average (d) Out of a total of 35 sites for O_3 , 27 sites for CO, 24 sites for NO₂, 21 sites for SO₂, and 27 sites for TSP, lead, and sulfate. (e) Only sites exceeding the standard at least once are included.

(f) aaa = annual arithmetic average

(g) aga = annual geometric average

- Major S0₂ reductions will result from flue gas desulfurization on fluid cracking units, electric utility boiler modifications, weatherproofing of existing homes, insulation standards for new homes, and greater reliance on wind energy.
- Major primary particulate reductions will result from paving roads and vehicular emissions controls.
- Major nitrogen oxides (NO_X) reductions will result from controls on stationary internal combustion engines, truck freight consolidation terminals, additional emissions controls on in-use and new motor vehicles, introduction of electric vehicles, electrification of railroad line haul operations, emissions standards for off-road heavy duty equipment, and improved home insulation.
- Major reactive organic species reductions will result from controls on thermally enhanced oil recovery and wood furniture finishes, changes in aerosol spray can contents and other consumer solvents, ride sharing, modified work schedules, reduction of the number of aircraft engines involved in idle and taxi operations, further controls on in-use and new vehicles, methanol fleet conversion, emissions standards for new boats and pleasure craft, and new source review.

If these measures are implemented, it is anticipated that the SCAQMD will continue to be in compliance with the federal SO_2 standard and will attain the federal NO_2 standard. Though attainment of the CO standard is not predicted by the AQMP analysis, this standard is exceeded at only a few sites, and the proposed emissions reductions bring the total to within 1.5% of the emissions estimated for CO attainment.

However, the reductions in precursor gas and primary particle emissions would be insufficient to predict attainment of the ozone and suspended particulate matter standards. Additional controls with existing technology are problematic, and the AQMP is not expected to yield attainment of these standards by the year 2000.

The AQMP is constantly being changed in response to new information and new standards: "...both the AQMP and the 1982 Revision are interim reports which represent the most complete information which could be gathered within the time and resources available....New approaches and new ways of assessing the problems are required if the region is to meet its air quality goals without serious economic and social disruption." (SCAQMD, 1982). SCAQS will provide these new ways of assessing problems if the objectives stated in Section 1 can be met.

2.2 AIR POLLUTION CHARACTERISTICS OF THE SOUTH COAST AIR BASIN

The key components of air pollution are emissions, transport and transformation, and receptor concentrations. This subsection provides a brief summary of knowledge about these components in the South Coast Air Basin. Emphasis is given to effects of these components on particulate matter and ozone concentrations at receptors. Effects on atmospheric acidity, toxic air contaminants, and visibility are inextricably related to the concerns about ozone and suspended particulate matter.

2.2.1 Emissions

Table 2-2 presents the SOCAB emissions classified into six categories as compiled from the 1983 emissions inventory (ARB, 1986). Total emissions from the state of California are given for comparison. The emissions in several of these categories have changed since the 1979 inventory as the result of the implementation of controls on various sources and fuel switching (from oil to natural gas) in the utility industry.

The first observation from this table is that the SOCAB contained a large fraction of all emissions in the state during 1983, ranging from 26% to 38%. Furthermore, this large fraction of total state emissions was confined to only 4% of the state's land area and is roughly comparable with the area's 44% of the state population. The largest emitters of both reactive organic gases (ROG) and nitrogen oxides in 1983 were on-road vehicles. Light duty passenger vehicles and light and medium duty trucks were the largest contributors within this source category, though heavy duty diesel trucks were significant NO_x emitters. Solvent use was a major emitter of reactive organic gases, with architectural coatings, other surface coatings, and domestic uses being its major sources. Fuel combustion was also a major NO_X emitter, with the electric utilities being the highest contributor within this category. The large total organic gas (TOG) emission rate derived largely from solid waste landfills. Tilling, re-suspended road dust, and light-duty passenger vehicle emissions were the major primary particle emitters, with diesel trucks and mineral processing also of significance.

There are slight seasonal deviations in these Basin-wide emission rates; these changes are typically within the measurement uncertainty of the inventory process (Grisinger et al., 1982). Seasonal differences are related primarily to weather conditions, with higher fuel consumption in the wintertime for heating. Reactive organic emissions are higher in the summer owing to the use of paints in construction. The increased CO and particle emissions from fuel combustion in the winter are somewhat offset by negligible winter emissions from the unplanned fires which take place intermittently during the hot summer months. Thus, while the aggregate emission rates do not vary appreciably over the year, the temporal and spatial detail of these emissions varies significantly. Figures 2-2 and 2-3 show the gridded emissions of TOG, CO, NO_{x} , SO_{x} , and TSP from surface and elevated point sources. These figures illustrate the spatial complexity of emissions in the SOCAB. They represent 1982 emissions projections from 1979 data. The vertical scales of each figure are unequal, so comparisons among Figure 2-2, Figure 2-3, and Table 2-2 must be qualitative. Nevertheless, several inferences can be made. Surface emissions of TOG, CO, and NO_x have similar spatial distributions. These emissions are highest near the center of the Basin and taper off near the coastal areas and toward the eastern extremes. Table 2-2 implies that the major sources of these species are on-road vehicles. Surface SO_x emissions are most concentrated near and southeast of the Palos Verdes peninsula. Table 2-2 implies that petroleum transfer and storage and low-level combustion of sulfur-containing fuels take place in these grid squares. Surface particulate emissions are more uniformly distributed throughout the Basin with several large peaks which are probably attributable to some of the "miscellaneous processes" listed in Table 2-2. The downtown particle peak corresponds to similar patterns on the TOG, CO, and NO_x plots and can probably be attributed

Emissions Source Categories	Location	Total Organic Gases (TOG)	Reactive Organic Gases (ROG)	Carbon Monoxide (CO)	Nitrogen Oxides (NO _X)	Sulfur Oxides (SO _X)	Particulate Matter < 10 um (PM-10)
Fuel	SOCAB	42	17	84	240	22	12
Combustion	Calif.	150	71	470	770	220	88
Waste	SOCAB	1	1	3	0	0	0
Burning	Calif.	96	46	920	2	1	86
Solvent	SOCAB	430	390	0	0	0	1
Use	Calif.	920	850	0	0	0	1
Petroleum Processing, Transfer & Storage	SOCAB Calif.	370 1300	110 600	14 84	14 26	36 95	4 8
Industrial	SOCAB	25	21	80	12	13	15
Processes	Calif.	79	66	200	40	38	85
Misc.	SOCAB	530	64	44	2	0	640
Processes	Calif.	2400	260	300	5	0	2400
On-Road Vehicles Other	SOCAB Calif.	710 1800	670 1700	5300 12000	630 1700	50 130	48 140
Mobile	SOCAB	79	75	460	130	32	12
Sources	Calif.	320	300	1600	460	84	59
All Sources	SOCAB	2200	1400	6000	1000	150	740
(annual)	Calif.	7000	3800	16000	3000	570	2900
Uncertainty(b) SOCAB			<u>+</u> 10%	<u>+</u> 16%	<u>+</u> 11%	<u>+</u> 9%	<u>+</u> 19%

Table 2-2. 1983 Emission Rates(a) in the South Coast Air Basin Compared to Those of California (Emission rates in tons/day based on one year of emissions)

(a) Data from ARB (1986). TOG and ROG in equivalent weights of CH₄, NO_X in equivalent weights of NO₂, SO_X in equivalent weights of SO₂, and PM-10 contains all particles less than 10 um. Note that sums are rounded to two significant figures, since uncertainties don't justify more than that.
(b) Composite relative uncertainty of total emissions derived from subjective estimates

(b) Composite relative uncertainty of total emissions derived from subjective estimates for individual source type emissions which range from +15% to +100% from Grisinger et al. (1982). Uncertainties are much higher for size and time-resolved emissions rates.



Figure 2-2. Spatial Pattern of Surface Emissions (<10 m AGL) in the South Coast Air Basin. These Data are 1982 Projections from the 1979 Emission Inventory for TOG (a), CO (b), NO_X (c), SO_X (d), and TSP (e) (personal communication with Ed Yotter of ARB, (1986).



Figure 2-2. (Continued)



Figure 2-3. Spatial Pattern of Elevated Emissions (>10 m AGL) in the South Coast Air Basin. These Data are 1982 Projections from the 1979 Emission Inventory for TOG (a), CO (b), NO_X (c), SO_X (d), and TSP (e) (personal communication with Ed Yotter of ARB, 1986).



Figure 2-3. (Continued)
to re-suspended road dust. The east Basin peaks could be attributable to agricultural tilling.

The peaks for all pollutant emissions in Figure 2-3 originate from the same point sources, and they are relatively few. Grisinger et al. (1982) list these sources and their location in order of emission rate. These elevated emitters are concentrated along the middle and southern coast with a few located in the east Basin. NO_X appears to be the most widely distributed elevated source, and many of its isolated appearances probably result from natural gas combustion which is accompanied by few other pollutant emissions. The elevated emissions of suspended particulate matter are more isolated in space than are the surface emissions, but their emissions rates are comparable to or greater than the surface rates in corresponding grid squares.

The temporal variations in pollutant emissions are not well documented. Though Grisinger et al. (1982) provide diurnal patterns for on-road vehicle emissions which show peaks during the morning and evening rush hours and lower than average emissions at night, these patterns are inferred rather than measured. SCAQMD receives daily NO_X emission rates from large stationary sources, but these are not formally incorporated into the inventory process. The ambient concentration changes observed during the 1984 Olympics by Davidson and Cassmassi (1985) indicate that temporal emission distributions may have an important effect on the products of those emissions.

The ARB and SCAQMD emissions inventory for the South Coast Air Basin is one of the best of its type in existence. Nevertheless, it contains uncertainties which derive from errors in the vast amount of acquired data, emission factors which are not derived from the specific emissions sources, and variable or undocumented process rates. The emission rates reported in Table 2-2 reflect activities as they were in 1983. Even though SCAQMD (1982) has made projections into 1987, these projections are no substitute for a re-assessment of the emitting sources during the year of concern.

The 1983 inventory may not even present an entirely accurate picture for that year. Emission rates from stationary sources which exceed 10 tons/year are updated with each inventory revision from approximately 65,000 permits filed by 10,000 companies. Emissions from smaller sources are not routinely re-estimated, and these can account for more than 50% of the reactive organic gas emissions from stationary sources. Biogenic and geogenic emissions are not included in the inventory, and these could be significant.

Grisinger et al. (1982) provide semi-quantitative estimates of the uncertainty of emission rates for the 1979 inventory, and the Basin-wide estimates recorded in Table 2-2 are tolerable for most assessment purposes. The individual emissions category uncertainties, however, range from 15% to 100% (these coefficients of variation are one standard deviation centered on the average emission rate estimate). Uncertainties for ROG rates from major emission categories such as surface coatings and gasoline hot soak and evaporation are especially large (30% to 40%). Uncertainties associated with smaller spatial scales and time intervals probably are much higher than these estimates.

One specific concern involves the uncertainty of the ratio of reactive hydrocarbons to nitrogen oxides (NO_x) emissions which is used in the EKMA

modeling (Liu, 1982) for the AQMP. The Basin-wide ratio for these emissions is approximately 3.5 while ambient measurements in the downtown area yield an average ratio of 10.3. (The ROG/NO_x ratio is based on volumetric concentrations of these gases. The mass emission rates in Table 2-2 must be converted by a factor equal to the ratio of their molecular weights.) This inconsistency can be explained by (1) inaccurate ROG or NO_x emission rates, (2) ROG and NO_x chemical reactions in the atmosphere, including different deposition rates, or (3) inaccurate measurements of ambient ROG and NO_x . Oliver and Peoples (1985) re-examined the 1979 inventory with respect to hydrocarbon and NO_x emissions from stationary and off-road mobile sources. They found some evidence of double counting, missing sources, and inconsistent use of emissions factors. Their corrections to the 1979 inventory amounted to 0.2%, 1.0%, and -3.0% adjustments to the Basin-wide rates for TOG, ROG, and NO_x , respectively, being emitted by stationary and off-road mobile sources. However, the relative adjustments within specific source categories were larger.

The PM-10 particulate emissions in Table 2-2 are also highly uncertain. In fact, the 1983 inventory is the first complete inventory to include sizespecific emissions information. Improved size-specific emissions measurements are being made as part of the AQMP process and as part of the 1987 major inventory update.

Grisinger et al. (1982) also call attention to the need to add ammonia emissions, better hydrocarbon profiles, and chemical speciation of emitted particulate matter (including hazardous substances) to the inventory. Ammonia is needed because of its potential involvement in the secondary fraction of PM-10. The hydrocarbon profiles are needed to separate ROG into reactivity categories. Several of these categories have been proposed and compared (e.g. Trijonis et al., 1978a) and others have been defined for air quality modeling. These hydrocarbon profiles can also be combined with other properties of the emissions to apportion ambient concentrations to their sources (e.g. Mayrsohn and Crabtree, 1976, Mayrsohn et al., 1977; Feigley and Jeffries, 1979). Chemical speciation of particulate matter is also necessary to apportion sources (e.g. Friedlander, 1973) and because of the roles of certain species in sulfur oxidation and atmospheric acidity. Abatement of toxic material concentrations will also require chemical-specific inventories for these species. Though Taback et al. (1979), Parungo et al. (1980), Rodes and Holland (1981), Dzubay et al. (1979), Miller et al. (1972), and Oliver and Peoples (1985) have made several chemically-specific measurements of source emissions in the SOCAB, no comprehensive data of the important components are yet available for any SOCAB source category.

2.2.2 Transport, Transformation, and Deposition

Transport, transformation and deposition are treated together because of the large effects which meteorological conditions have on the movement and changes of pollutants. These phenomena have been, and continue to be, subjects of intensive research on which volumes have been written. The intent here is to identify the subject areas of importance for particle and oxidant concentrations in the South Coast Air Basin. The data acquired in SCAQS will be used to elucidate these transport and transformation phenomena.

Southern California is in the semi-permanent high pressure zone of the eastern Pacific. It experiences hot summers, and rainfall is sparse and occurs

mostly during winter. Frequent and persistent temperature inversions are caused by subsidence of descending air warmed by compression settling over the cool, moist marine air. These inversions often occur during periods of maximum solar radiation (SCAQMD, 1982). Relative humidities can vary, depending on the origin of the air mass. RH typically exceeds 50% throughout the basin, being higher near the coast than farther inland (Smith et al., 1984).

As illustrated in Figure 2-1, the SOCAB is surrounded on the north, east, and west by mountains, some of which rise above 10,000 feet. The Basin opens to the Pacific Ocean on the southwest. The topography of the Basin combined with the land/sea interface introduces important mesoscale effects which are superimposed on the synoptic weather patterns.

Figures 2-4 and 2-5 from Smith et al. (1972) illustrate the diurnal evolution of surface flow patterns in the SOCAB for summer and winter months respectively. Similar patterns were found by Keith and Selik (1977). In the summertime, the sea breeze is strong during the day and there is a weak land-mountain breeze at night. Because of the high summer temperatures, the land temperature does not usually fall below the water temperature at night, and the nocturnal winds are slow and weak. The opposite is true during the winter, when the mountain-land breeze at night yields strong ventilation, and a mild sea breeze is only established late in the day when temperatures approach their maxima.

The predominant trajectories are from the west and south during summer mornings, switching to predominantly westerly flows by the late afternoon and early evening. These summertime trajectories become difficult to discern at night owing to the generally stagnant conditions. As shown in Figure 2-5, the prevailing wintertime trajectories are from the east and north at night, switching to westerly trajectories by late afternoon. In both cases, there is strong propensity for the transport of emissions from the western and southern parts of the SOCAB to the eastern and northern parts, with this propensity being higher during the summer months than in the winter months. Aircraft (e.g. Blumenthal et al., 1978; Calvert 1976a, 1976b), tetroon (e.g. Angell et al., 1976), and tracer (e.g. Shair et al., 1982) studies provide results which are qualitatively consistent with the trajectories illustrated in Figures 2-4 and 2-5.

The land/sea breeze circulation can cause air to transfer back and forth between the Basin and the Pacific Ocean. Cass and Shair (1984) estimated that up to 50% of the sulfate measured at Lennox was attributable to backwash of emissions which had been transported to sea on the previous day. During the daytime, emissions from coastal sources are advected inland by the sea breeze. At night, these polluted air masses are swept back toward the coast to await their re-entry to the Basin on the following day. There is ample evidence (e.g. Kauper and Niemann, 1975; 1977), however, that a good portion of these pollutants which pass the coastline can be transported to neighboring air basins.

Air from the Basin can exit through a number of routes other than the sea. Smith and Shair (1983) found transport routes through Soledad Canyon, Cajon Pass, and San Gorgonio Pass when they released tracer gases in the South Coast Air Basin. Smith and Shair (1983) also showed evidence of transport aloft from the San Fernando Valley into eastern Ventura County. Godden and



Figure 2-4. Summer Variation in Surface Wind Flow Patterns throughout the Day in the South Coast Air Basin (Smith et al., 1972).



Figure 2-5. Winter Variation in Surface Wind Flow Patterns throughout the Day in the South Coast Air Basin (Smith et al., 1972).

Lague (1983) note, however, that tracer experiments also provide "...circumstantial evidence...that pollutants can be transported both from Ventura County through the Simi Hills and along the coast to West Los Angeles...".

Smith et al. (1984) have made a comprehensive study of air pollution climatologies in California. In addition to the above observations, Smith et al. (1984) note the potential for slope flows and convergence zones in the SOCAB. Slope flows provide a mechanism for the transport of pollutants from below the inversion to above. They occur when the mountains absorb solar radiation and heat the surrounding air, making it more buoyant. Smith et al. (1984) comment that "In areas such as the South Coast Air Basin, this transport mechanism provides one of the more effective methods of removing pollutants from the Basin." This upslope flow can result in high pollutant concentrations at elevated locations. These locations would not normally experience such pollution due to their own local emissions.

Convergence zones occur where terrain and pressure-gradients direct wind flows in opposite directions; the convergence results in an upwelling of air, and a consequent transport of pollutants to higher elevations. These convergence zones can also restrict the transport of pollutants from one basin to another. Smith et al. (1984) plot SOCAB convergence zones at Elsinore (McElroy et al., 1982; Smith and Edinger, 1984), the San Fernando Valley (Edinger and Helvey, 1961), El Mirage, the Coachella Valley, and Ventura.

Several of these meteorological features (upslope flow, convergence zones, marine air intrusions, transport into the stable layer, and plume rise from elevated sources) inject pollutants above the mixed layer. As the mixing depth increases during the day, some of these elevated pollutants can become re-entrained in the mixed layer and advected to ground level.

Smith et al. (1984) comment that "... The primary source of uncertainty in defining meteorological air pollution potential in the state lies in the description of mixing height behavior, particularly in the coastal areas where mixing height changes significantly with distance inland." Smith et al. (1984) believe that current SOCAB upper air measurements should be supplemented with additional soundings in the San Bernardino/Riverside area. While these complex meteorological phenomena affecting pollution potential are qualitatively simple, their quantitative description is much more difficult.

In addition to atmospheric movements, temperature, insolation, and relative humidity affect the transformations of precursor gases to ozone and suspended particulate matter. Photochemical transformations are probably the most important of these, and they have been recognized as important since the days of Haagen-Smit in the early 1950s. Ozone plus the sulfate, nitrate and organic fractions of the aerosol are influenced by photochemical processes.

The photochemical influence on ozone formation is well established in the SOCAB in laboratory studies (e.g. Kopczynski et al., 1972), in semi-coherent air parcels sampled with airborne platforms (e.g. Calvert, 1976a, 1976b; Feigley and Jeffries, 1979; Spicer et al., 1983) and at fixed ground stations (e.g. Spicer, 1977; Reynolds et al., 1974; McRae and Seinfeld, 1983; Godden and Lurmann, 1983) which represent SOCAB atmospheres. Measurements in these studies all show a morning buildup (or high initial concentration) of NO from fresh emissions, followed a few hours later by a dramatic decrease in NO and peak of NO₂, which is in turn followed by a peak in ozone concentrations in the early to late afternoon (depending on the location of the sampling site). While these qualitative features are well-established and reproducible, the chemistry and physics describing them is not. Dunker et al. (1984), Leone and Seinfeld (1984a, 1984b), and Killus and Whitten (1983) have compared the most recent photochemical reaction mechanisms applied to similar situations. Though all mechanisms exhibit the same qualitative features of reactant and end-product concentrations with time, the peak values and the time of occurrence of those peaks are mechanism dependent. The practical mechanism which is most representative of reality is still open to judgment.

Photochemical sulfate formation in the Los Angeles atmosphere typically follows a diurnal cycle with a daytime maximum rate near 6% per hour (Roberts, 1975; Cass, 1981). Nitrogen dioxide is converted to nitric acid by hydroxyl radicals at rates five to ten times faster than sulfur dioxide is converted to sulfate (Forrest et al., 1981). Nitrogen dioxide is also converted to peroxyacetyl nitrate (PAN), and the proportions depend on the initial ROG/NO_x ratios (Spicer et al., 1983). Russell et al. (1985) found that over a 24 hour trajectory simulation, 7% of NO_x emissions were transformed to airborne HNO₃. Though both nitric acid and PAN are gases, nitric acid is also present in liquid particles. The photochemical formation of organic aerosol is less well understood (Pitts et al., 1978; Hidy and Mueller, 1979), but is the subject of much current work. Studies of organic aerosol formation are inconclusive because of the plethora of precursors and the volatilities of their products. Theoretical mechanisms for the photochemical conversion of gases to particles are still in their formative stages.

The differences between inventoried and ambient ROG/NO_x ratios can be explained, at least in part, by these theoretical reaction mechanisms. Haney and Seigneur (1985) re-examined the ambient ROG and NO_X concentrations generated by a recent application of the SAI urban airshed model to the SOCAB which used an initial ROG/NO_x emissions ratio of 2.86. They found that the ROG/NO_X ratios at Anaheim and Downtown L.A. reached values of 7 to 9 during the hours just past noon and dropped to values of 3 to 5 at night. The afternoon values correspond to the period of maximum ozone production, when a large portion of the ambient NO_X is reduced by photochemical reactions. Photochemistry ceases after sunset, allowing the NO_X to be replenished. Calculations for Riverside show ratios ranging from 4.5 to 61.7 because the pollutants have undergone longer photochemical reaction times and ambient NO_{x} levels are much lower than those at the downtown sites. Haney and Seigneur (1985) conclude that the faster oxidation of NO_X with respect to ROG during photochemical smog formation can account for the difference between inventoried and ambient ROG/NO_X ratios and that neither the inventory nor the ambient measurements are necessarily in error.

Though photochemical transformation processes are of greatest importance for the production of ozone, gases can be transformed into suspended particulate matter by a number of other processes. Husar et al. (1976) show direct evidence of the condensation of gaseous species on solid or liquid particles. Relative humidity changes affect the water content of aerosols, which have consequences with respect to their size and their propensity to scatter light (Charlson et al., 1969; Covert et al., 1972; Tang et al., 1981). This effect tends to be important at relative humidities above 70% when many dry, ionic particles deliquesce. Sulfate formation rates increase when small particles in solution are present in the atmosphere (Cass, 1975; Dittenhoeffer and dePena, 1978; Gillani and Wilson, 1983; Gillani et al., 1983). Under these conditions, the growth of relatively large particles can be favored (McMurry and Wilson, 1980; Hering and Friedlander, 1982).

Particles can also form in fog and clouds because soluble particles are preferentially activated during the formation of clouds and fog, and ionic species formed in fog or cloud water will become part of these particles when the fog or clouds evaporate. This mechanism has been inferred from models (e.g. Chameides and Davis, 1982; Seigneur and Saxeena, 1984; Young et al., 1983; Jacob and Hoffmann, 1983), from rain chemistry (Lazrus et al., 1983), and cloud measurements (Richards et al., 1983a, 1983b; Daum et al., 1983). Catalysis by trace metals such as manganese and iron may be important in sulfate formation in fog and clouds (Martin, 1983; Young et al., 1983; Jacob and Hoffmann, 1983; Seigneur and Saxeena, 1984; Seigneur et al., 1985). Nitric acid has been shown to be rapidly scavenged by fog or clouds (Levine and Schwartz, 1982).

The non-photochemical particle formation mechanisms may be especially influential at night and during winter periods. Richards (1983) proposes a mechanism in which ozone aloft reacts with NO_X to form nitrate. Richards (1983) speculates that this mechanism may explain the high morning concentrations of large particle nitrate which were observed by Appel et al. (1978). Recent theoretical formulations of these particle formation mechanisms have been developed for incorporation into the comprehensive mathematical models describing the SOCAB (e.g. Russell et al., 1983; Bassett and Seinfeld, 1983; Heisler and Friedlander, 1977; Bassett et al., 1981; Seigneur et al., 1985).

Wet and dry deposition of atmospheric constituents in the SOCAB are not well understood, even though Roberts (1975) estimated that nearly 50% of the sulfur oxides are removed at the ground within the Basin and Morgan and Liljestrand (1980) estimated that the dry deposition of pollutants may exceed wet deposition by an order of magnitude. Most theoretical formulations of deposition describe the flux to the surface as a product of an ambient concentration and a deposition velocity. These deposition velocities are functions of turbulent diffusion near the ground, molecular motions at the ground-air interface, and the reaction of the pollutant with the surface. McRae et al. (1982b) mathematically described the turbulent diffusion mechanisms and found that the deposition rates are extremely sensitive to atmospheric stability. They noted that there are no satisfactory theoretical treatments of mass transfer close to the surface and that field data on pollutant uptake by surfaces are inadequate. Dry deposition samples in the SOCAB have been collected on surrogate surfaces (as summarized in Shikiya et al., 1984), but these are not considered to be accurate estimates of drv deposition fluxes.

2.2.3 Receptor Measurements

Figure 2-1 shows the sampling sites which have been acquiring routine air quality monitoring data in the South Coast Air Basin. Though several of these sites have changed from time to time, the basic network has remained essentially the same since 1965. Ludwig et al. (1983) have examined the spatial distribution of this network with respect to its adequacy in determining ozone standard violations. They found that as few as ten of the SCAQMD stations would provide an accurate estimate of the number of exceedances per site. The coverage of this network is such that coastal, inland, and valley areas are represented. All EPA siting criteria and shelter requirements are complied with at all sites.

Table 2-3 identifies the routine measurements which are made at existing sampling sites in the South Coast Air Basin. Carbon monoxide by non-dispersive infrared spectrophotometry, ozone by ultraviolet photometry, nitric oxide and nitrogen oxides by chemiluminescence, sulfur dioxide by pulsed fluorescence, total hydrocarbons by flame ionization detector, and total suspended particulate matter by standard HiVol samplers are measured at most sites. Gas concentrations of one-hour duration are acquired continuously and suspended particle samples of 24-hour duration are acquired on an every-sixth-day schedule. Mass, sulfate, nitrate, and lead measurements are made on most of the HiVol samples. Size-classified particulate matter in the 0 to 10 μ m size range is currently being collected at 11 sites, as indicated in Table 2-3, using automatic mass flow controlled high volume samplers with Sierra-Anderson 321A size-selective inlets. This monitoring is being performed in anticipation of the promulgation of a new national ambient air quality standard for particulate matter (Federal Register, 1984) and to determine compliance with California's size-selective particulate matter standard. Mass, sulfate and nitrate measurements are currently being made on these samples.

Table 2-3 also shows the distribution of surface meteorological monitoring networks which acquire wind speed, wind direction, temperature, relative humidity, and insolation data. Goodin et al. (1979, 1980) have examined the adequacy of this network for replicating a known surface wind field and have found it adequate when the proper interpolation and adjustment schemes are used. The network is not adequate, however, for determining a three-dimensional wind field.

Ambient air quality data acquired from this network over many years show the following general features taken from the 1982 Summary of Air Quality (SCAQMD, 1983; Hoggan et al., 1983):

- Ozone. Coastal stations experience the lowest concentrations and the lowest number of standard exceedance cases. Concentrations increase sharply from the coastal to the inland valley portions of the Basin. The area with the highest ozone levels extends from the San Fernando Valley through the San Gabriel Valley and into the Riverside-San Bernardino area and adjacent mountains. In 1982, Azusa, Pico Rivera, Los Angeles, and Norco exhibited hourly ozone concentrations in excess of 0.35 ppm. The highest value of 1982 was 0.40 ppm which occurred at the downtown Los Angeles site between noon and 1 p.m. on September 2, 1982. Figures 2-6a, b, c, and d show long-term trends, monthly averages, and the diurnal pattern of ozone concentrations at Azusa which are typical of the patterns at most inland sites in the network. Highest ozone dosages tend to occur at elevated sites in the San Gabriel and San Bernardino Mountains. NO values are very low at these sites, and there is little opportunity for the 03 which reaches them to be scavenged.
- <u>Carbon Monoxide</u>. More than half of the SOCAB stations are in compliance with the CO standard. The highest concentrations are observed during the

Site	Sampling Site					Pollutants Monitored					<u> </u>		Meteorological Measurements			
Code		03	NO/NOx	CO	sous SO2	тнс(а)	MMHC (b)	TSP	Рb	S04	NO3	TOF (C) PM10	Temp	Humidity	ws/wd(d)	Radiation
	LOS ANGELES	BASIN	ſ													,
	SURFACE		-													
1	Alhambra														x	
2	Anaheim	X	X	X	X			X	X	X	X				Ŷ	
3	Azusa	X	X	X	X	X		X	X	X	X	X	X		Ŷ	
4	Banning	X						X	X	X	X	X			. Ŷ	
5	Burbank	X	X	X	X							X			Ŷ.	
6	Burbank AP												X	X	Ŷ	
7	Cajon														Ŷ	
8	Chino	X.													Ŷ	
9	Compton AP														Ŷ	
10	Costa Mesa	X	X	X	X										Ŷ	
11	El Toro	X	X					X	X	X	X	X			Ŷ	
12	El Toro MB												¥	¥	Ŷ	
13	Fontana	X	X	X	X			X	X	X	X	X	~	~	Ŷ	
14	Glendora	X			• -						~	~			Ŷ	
15	Hawthorne AP														Ŷ	
16	Hemet	X													Ŷ	
17	John Wayne A	P											¥	Y	ŷ	
18	La Habra	X	X	X	X	X		X	X	Y	Y		~	~	Ŷ	
19	Lake Gregory	X						Ŷ	x	Ŷ	Ŷ				Ŷ	
20	Lennox	X	X	X	X	X		X	Ŷ	X	ÿ				Ŷ	
21	Long Beach	X	X	X	X	X.		Ŷ	Ŷ	Ŷ	Ŷ	Y			Ŷ	
22	Los Alamitos	X			X			Ŷ	Ŷ	Ŷ	Ŷ	Ŷ			Ŷ	
23	Los Angeles	X	X	X	X	X	X	Ŷ	Ŷ	. X	Ŷ	Ŷ	X		Ŷ	
24	LAX										~	~	Ŷ	Y	Ŷ	
26	Lynwood	X	X	X	X	X		X	X	Y	Y		~	^	Ŷ	
27	Malibu							~	~	~	A				Ŷ	
28	March AFB												Y	¥	Ŷ	
29	Mission Hill	s											~	^	Ŷ	
30	Newhall	¯χ													Ŷ	
31	Norco	X													Ŷ	
32	Norton AFB	~				•							v	¥	÷.	
33	Ontario AP							Y	Y	Y	¥	Y	Ŷ	÷	÷	
34	Pasadena	X	x	X	X			Ŷ	Ŷ	Ŷ	Ŷ	^	÷.	^	Ŷ	
35	Perris	Ŷ		~				Ŷ	Ŷ	Ŷ	Ŷ		^		÷	
36	Pico Rivera	Ŷ	Y	¥	Y			Ŷ	Ŷ	Ŷ	Ŷ				÷.	
37	Pomona	Ŷ	Ŷ	Ŷ	~			•	•	•	•				X	
39	Redlands	Ŷ	Ŷ	ⁿ				Y	v	v	v		*		Š	
30	Redondo Rose	กิ	~					*	•	•	*				X	
53	Airport														Y	
40	Reseda	X	X	X	¥	¥		Y	¥	¥	Y				Ŷ	
41	Rialto		**	~	n			~	~	^	~				Ŷ	
42	Riverside			x				Y	¥	¥	¥				Č.	
42	Rubidowy	X	¥	Ŷ	¥	¥		Ŷ	Ŷ	Ŷ	Ŷ	v			X	
40		~	~	~	~	~		~	~	~	•	^				

Table 2-3. Air Quality and Meteorologica	Routine Measurements at Existing S	ites in	the	South	Coast	Region
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Table 2-3. (continued)

						Pol	ollutants Monitored			·			Meteorological Measurements				
Site <u>Code</u>	Sampling <u>Site</u>	03	NO/NO×	6as C0	eous S02	THC ^(a)	NMHC (b)	TSP	РЬ	S04	NO 3	TOF ^(C) PM10	Temp	Humidity	WS/WD ^(d)	Radiation	
44 45	San Bernardino San Juan	X	x	x	x			X	x	X	x	X			X		
46 47	Santa Monica Torrance AP	AP											X X	X X	X X X		
48 49 50	Upland Van Nuys Venice Vernon	X	X	Χ.	X	. X		X	X	X	X		X	X	X X X		
51 52 53 54 55 56	W. LA Whittier Zuma Beach Beaumont Fullerton AP	X X	X X	X X	X X	X X	X	X	X	X	X		X X	X X	X X X X		
57 58	Mt. Wilson Pomona AP														X		
	UPPER AIR																
25	Loyola- Marymount												¥	Y	Y		
33	Ontario AP	X											x	Δ	~		

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Site	Sampling			6		Po1	lutants	s Monitored				··	4	Meteorological Measurements			
Code	Site	03	NO/NOx	CO	SO2	тнс (а)	NMHC (b)	TSP	Pb	S04	NO 3	TOF (C) PM10	Тетр	Humidity	WS/WD ^{(d}	Radiation	
	VENTURA COUNT	<u>Y</u>															
	SURFACE																
	Anacapa Is Contine Page	X						X					X	X	x	x	
	El Rio	x	X	X				X					X	X	X X	X	
	Djai	x						X					X	X X	X X	X	
59	Dxnard AP Piru	X						X					X X	X X	X	X	
60	Pt. Mugu Rocketdyne	x											X X	X	X X		
-	San Miguel Is Santa Barbara	Is											X X	X X	X X		
	Santa Cruz Is Santa Rosa Is												X X	X	X X		
61 62	Simi Valley Thousand	X	X	X	X	X		X	X	X	X	X	X	X	x	X	
	Oaks Upper Ojat	X													x		
	Ventura	X	X	X		X	X	X					X	X	X	X	
	UPPER AIR																
	Pt. Mugu												x	x	x		
	San Nicolas Is	. <u>.</u>	<u> </u>										x	X	x		

Table 2-3. (continued)

(a) THC = total hydrocarbon

(b) NMHC = non-methane hydrocarbon

(c) TOF = total benzene extractable organic fraction

(d) WS/WD = wind speed and wind direction

2-22



Figure 2-6a. Sixteen Year Trend in the Annual Average of Daily Maximum 1-Hour Ozone Concentration from 1965 to 1980 at Azusa, San Bernardino, and La Habra. (SCAQMD, 1981)



Figure 2-6b. 1982 Ozone Monthly Average of Daily 1-Hour Maximum at Azusa, CA. (Hoggan et al., 1983)



I-RANGE WITHIN WHICH 95% OF MEASUREMENTS FALL (+-2 S.D.)

Figure 2-6c. 1982 Winter Average Ozone for Each Hour at Azusa, CA. (Hoggan et al., 1983)

2-25







winter at Lennox, Lynwood, Burbank, and Reseda. The highest one-hour value of 27 ppm in 1982 occurred at Lynwood on December 17, 1982. The diurnal distribution of CO follows the morning and evening rush hours. This pollutant is particularly useful in identifying the presence or absence of motor vehicle emissions at each receptor.

- Sulfur Dioxide. SO_2 concentrations are generally low throughout the Basin, except when the monitor encounters a plume. Daytime concentrations are generally higher than nighttime concentrations. This is consistent with SO_2 emissions from elevated sources being injected above the nighttime mixing layer. For the most part, the presence of this pollutant indicates the influence of nearby elevated source emissions. The maximum twenty-four hour average SO_2 concentration in 1982 was 36 ppb at Lennox on December 7.
- <u>Nitrogen Oxides</u>. Highest concentrations were found in 1982 at Los Angeles, West Los Angeles, Lennox, Long Beach, and Whittier. NO2 concentrations do not show consistent patterns across the Basin, probably owing to the multitude of possible interactions of this pollutant with other pollutants, nearby emissions, and meteorological variables. The maximum hourly average NO2 concentration in 1982 was 410 ppb measured at Los Angeles on September 3. This followed closely on the maximum ozone concentration which was measured at the same site on the preceding day.
- Total Suspended Particulate Matter. The highest 24 hour TSP levels are detected in an area extending from the eastern San Gabriel Valley, through the Pomona Valley and into the Riverside-San Bernardino area. Seasonal averages vary from location to location, indicating the multiplicity of factors affecting TSP concentrations. The sulfate, nitrate, and lead fractions of TSP provide some insight into the contributors to these pollutant levels. Sulfate typically comprises 7%-13% of TSP and the highest levels are consistently found downwind of major SO₂ emission sources. Highest sulfate levels generally occur during the late summer under conditions of high humidity, while the lowest concentrations are evident in the winter. Nitrate typically comprises 12%-20% of TSP. Highest levels are experienced in the San Bernardino -Riverside area in the summer and fall. Lead concentrations ranged from 0.3% to 1.1% of TSP in 1982 and are decreasing as lead is phased out of use in the motor vehicle fleet (Hoggan et al., 1978). Highest lead levels in 1982 were found in the densely populated areas of Lennox and Lynwood. In 1982, the highest TSP value of 272 μ g/m³ occurred at Fontana on July 16 and the highest daily sulfate value of 37.3 μ g/m³ occurred at Lennox on December 7, though most other high values were found in the September/ October time-frame. The highest annual average nitrate of 21.3 μ g/m³ occurred at Riverside and the highest monthly average lead level was 1.7 $\mu g/m^3$ at Lennox in October. SCAQMD has estimated PM-10 annual averages from 1984 TSP data (Figure 2-7). These averages are likely to exceed 50 $\mu g/m^3$ at nearly all SOCAB sampling sites, with the sites in the San Bernardino/Riverside areas having the highest values. Measured PM-10 values at seven sites show that Downtown L.A., Rubidoux, Azusa, Burbank, Long Beach and Los Alamitos exceed the new annual PM-10 standard. Only Rubidoux exceeded the new 24 hr PM-10 standard of 150 μ g/m³ with a high concentration of 208 $\mu g/m^3$.



Figure 2-7. Estimated PM-10 Annual Arithmetic Averages (●) from 1984 TSP Data (Based on TSP x 0.59 = PM-10) and Measured PM-10 Annual Averages (▲) from October 1984 to October 1985 (personal communication, Art Davidson, SCAOMD, 1985). While most historical monitoring has focused on 0_3 , C0, $S0_2$, $N0_2$, and TSP owing to their regulation by National Ambient Air Quality Standards, it has been recognized that particulate and gaseous organic material, nitrogenous substances, trace metals, atmospheric mutagens, acid deposition, and visibility are also phenomena of public concern. Both short-term and long-term monitoring programs have been implemented to study these issues. Typical concentrations and ranges for several of these measurements are summarized in Section 3.

A major concern in the interpretation of receptor measurements has been the extent to which these measurements are representative of actual concentrations in the atmosphere. The limitations of measurement technology have repeatedly clouded the interpretation of data used to elucidate cause and effect relationships between variables.

Oxidant measurements taken in the SOCAB prior to 1974 indicated that the major problem areas were confined to the eastern cities in the Basin, and scrutiny of mid-Basin cities, such as Pasadena, was minimized. Pitts et al. (1976) reexamined the oxidant measurements taken between 1955 and 1974 after applying corrections for different calibrations (buffered and unbuffered KI calibrations were converted to an ultraviolet absorption standard) used in Los Angeles County and other counties of the SOCAB. Their re-interpretation of the corrected data concluded that "...oxidant levels do not increase along a west to east axis across the basin [as was previously believed]....they do increase along a southwest to northeast axis across the basin, which roughly matches the orientation of the prevailing onshore sea breezes." Hydrocarbon interferences with the current ultraviolet absorption ozone measurement method must be considered in interpretation of ozone measurements derived from it.

Winer et al. (1974) have quantified the interference of PAN and several other organic nitrates in the chemiluminescent monitoring of NO_2 . Nitroethane and nitric acid were found to interfere, but only semi-quantitative estimates are given by Winer et al. (1974). Grosjean (1983) observed that "On smoggy days...NO₂ can be seriously overestimated if the response of chemiluminescent instruments to PAN and HONO is not taken into account." He found that NO_2 was overestimated by as much as 33%, 56%, and 65% in three different smog episodes. Godden and Lurmann (1983) found that many of their model predictions of NO and NO_2 could easily fall within the range of uncertainties caused by the unknown degree of measurement interference caused by other nitrogenous species. These measurement interferences clearly affect the interpretation of these data and the determination of compliance with standards.

The particle size ranges and chemical composition of routine TSP measurements have been shown to be uncertain. The standard HiVol sampler has a 50% sampling effectiveness between 30 and 50 um, depending on wind speed and sampler orientation with respect to the wind direction (McFarland et al., 1979). The glass fiber filters used for SOCAB measurements in the recent past yielded higher sulfate and nitrate concentrations than were actually present in the atmosphere (Witz and MacPhee, 1977; Witz and Wendt, 1981; Witz et al., 1982). Spicer (1977) warns that "...some of the extreme particulate nitrate levels recorded in Southern California [in ACHEX] during 1-2 hr afternoon sampling periods may be attributable in part to collection of artifact nitrate." Grosjean (1975) found that the benzene-soluble organic fraction of TSP, which has been measured for years on SOCAB samples, is a variable fraction of the total organic content which is not relatable to any significant phenomena.

These particle measurement concerns have not been abated by the proposed PM-10 reference method. Watson and Rogers (1985) have evaluated the proposed California Method P for PM-10 mass measurement and have semi-quantified the potential effects of different sampler inlets, filter media, flow measurement and control, sample handling and other environmental variables. Each of these variables has a measurable effect on the mass and chemical species concentrations, though not all of these effects are quantifiable in a specific application. The greatest controversy involves the size-selective properties of PM-10 inlets (Rodes et al., 1985; Wedding et al., 1985; McFarland and Ortiz, 1985; Wedding et al., 1986).

A portion of the difference between ROG/NO_X ratios in ambient air and in the emissions inventory may result from the ambient ROG measurements. Liu (1982) compared measured ROG/NO_X ratios acquired for every day of June, 1981, by three different monitoring methods. Several adjustments were applied to the ROG and NO_X values to account for interferences. These average ratios obtained by the different methods ranged from 1.7 to 41, a range which surely includes the 3.5 ratio yielded by the Basin-wide emissions inventory. The ROG/NO_X ratio of 10.3 which was finally selected for EKMA modeling must, therefore, be used with due consideration of its large uncertainty.

These recognized measurement limitations and their effects on the data interpretation apply to routine measurement methods which have been in place for years. Limitations to several of the measurements proposed for SCAQS in Section 3 are only partially known, or are totally unknown, at this time. Past history suggests that a portion of SCAQS resources should be dedicated to the quantification of these measurement limitations, and that the uncertainties derived from this quantification must be integral to the data interpretation process.

2.3 PAST AIR QUALITY STUDIES IN THE SOUTH COAST AIR BASIN

The South Coast Air Basin has probably been subjected to more air pollution analyses than any other location in the world. Much of the generally applicable and fundamental knowledge regarding emissions, air pollution meteorology, air pollution chemistry, and receptor concentrations has been derived from these studies. The combination of outstanding scientific expertise in California universities, interest from local and national industries located in the SOCAB, community concerns about air quality; and cooperation and financial support from local, state, and federal regulatory agencies has encouraged this high level of productivity. Table 2-4 identifies a fraction of these studies, categorized by specific problem areas. Though this list is far from complete, it conveys the long historical record and the intense scientific interest which are characteristic of air pollution research in the SOCAB.

Most of these studies were of short duration and of small geographical extent. Though they provide evidence of cause-effect relationships among emissions, meteorological, and receptor variables, this evidence is rarely conclusive. These studies have proposed novel measurement, modeling and data interpretation methods, but the modeling efforts have usually had to settle Table 2-4. Previous Air Quality Related Studies Undertaken in the South Coast Air Basin

EMISSIONS INVENTORY AND CHARACTERIZATION:

ARB (1986) Cass et al. (1982a) Chass and George (1960) Dzubay et al. (1979) Grisinger et al. (1982) Huang and Head (1978) Mayrsohn and Crabtree (1976) Mayrsohn et al. (1977) Oliver and Peoples (1985) Parungo et al. (1980) Pitts et al. (1984) Pueschel et al. (1979) Richards et al. (1976, 1977) Rodes and Holland (1981) Rose et al. (1965) Taback et al. (1979) Tombach (1982) METEOROLOGY, WIND FIELDS AND DISPERSION: Ackerman (1977) Angell et al. (1975, 1976) Blumenthal et al. (1978, 1979) Cass and Shair (1984) Chang and Norbeck (1983) Crane et al. (1977) Drivas and Shair (1974a, 1974b) Drivas (1975, 1982) Edinger (1959) Edinger and Helvey (1961) Edinger et al. (1972) Farber et al. (1982b) Gloria et al. (1974) Goodin et al. (1979) Goodin and Lague (1983) Hanna (1977) Hidy et al. (1971) Hinds (1970) Husar et al. (1977) Kauper and Niemann (1975, 1977) Keith and Selik (1977) Lissaman (1973) McElroy et al. (1982) McRae et al. (1981) Pack and Angell (1963) Panofsky (1975) Reible et al. (1982)Sackinger et al. (1982) Schultz and Warner (1982)

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Table 2-4. (continued)
Shair et al. (1982)
Shettle (1972)
Smith et al. (1972, 1976, 1984)
Smith and Edinger (1984)
Smith and Shair (1983)
Vaughn and Stankunas (1974)
Wakimoto and Wurtele (1984)
White and Husar (1976)
Zak (1982)
Zeldin and Meisel (1977)
MULTICOMPONENT, SIZE-CLASSIFIED AEROSOL MEASUREMENT AND SOURCE APPORTIONMENT:
Cass (1978a)
Cass and McRae (1981, 1983)
Colucci et al. (1969)
Friedlander (1973)
Gartrell and Friedlander (1975)
Giauque et al. (1974, 1979)
Grisinger (1982b)
Hammerle and Pierson (1975)
Heisler et al. (1973)
Hidy (1972)
Hidy and Friedlander (1972)
Hidy et al. (1974, 1975)
Hidy and Mueller (1979)
Ho et al. (1974)
Hoggan et al. (1978)
Huang et al. (1982, 1983)
Husar et al. (1972, 1976)
Ludwig and Robinson (1968)
Lundgren (1971)
MacPhee and Bockian (1967)
Miller et al. (1972)
Mueller et al. (1972)
Neiburger and Wurtele (1949)
Novakov et al. (1972a, 1972b)
Porch and Ellsaesser (1977)
Saltzman et al. (1985)
Stelson and Seinfeld (1981)
Tiao and Hilmer (1978)
Trijonis et al. (1975a)
Volz (1973)
Wadley et al. (1978)
Whitby et al. (1972)
White et al. (1973)
Witz and Wadley (1983)
VISIBILITY:
Alkezweeny and Lockhart (1972)
Appel et al. (1983)
Barone et al. (1978)
Cass (1979)
Charlson et al. (1968, 1969)
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Table 2-4. (continued)

Charlson and Pierrard (1969) Charlson (1972) Covert et al. (1972) Ensor et al. (1972) Noll et al. (1968) Pratsinis et al. (1984) Thielke et al. (1972) Thomas (1962) Trijonis (1982a, 1982b) White and Roberts (1977)

SULFATE AND NITRATE MEASUREMENTS AND RELATIONSHIPS TO SOURCES:

Appel et al. (1977a, 1977b, 1978, 1982) Baboolal and Farber (1982) Cass (1975, 1978b, 1981) Grisinger (1982a) Grosjean (1982a) Harker et al. (1977) Heisler et al. (1980) Henry and Hidy (1979) Hering and Friedlander (1982) Novakov et al. (1972a, 1972b) Richards (1983) Roberts and Friedlander (1975) Russell et al. (1983) Russell (1985) Russell et al. (1985) White et al. (1978) Witz and MacPhee (1977) Witz and Wendt (1981) Witz et al. (1982) Zeldin et al. (1983)

CARBONACEOUS, ORGANIC, HYDROCARBON, AND HALOCARBON MEASUREMENTS (including toxic organics):

Altshuller and Bellar (1963) Altshuller and McPherson (1963) Altshuller et al. (1966) Appel et al. (1976, 1977a, 1979) Brenner et al. (1980) Cass et al. (1982b) Cronn et al. (1977) Duval and Friedlander (1981) Ellis et al. (1984a, 1984b) Ellis and Novakov (1982) Gordon et al. (1968)Gordon and Bryan (1973) Gordon (1976) Gray et al. (1985) Grosjean and Friedlander (1975) Grosjean et al. (1983)

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Table 2-4. (continued)
Grosjean (1975, 1982b, 1984)
Grosjean and Fung (1984)
Gundel and Novakov (1984)
Hester et al. (1974)
Kotin et al. (1954)
Lonneman et al. (1968)
Madar et al. (1952)
Miguel and Friedlander (1978)
Neligan (1962)
Novakov (1982)
Pitts et al. (1981, 1982, 1985)
Rosen et al. (1982)
Schuetzle et al. (1973, 1975)
Singh et al. (1985)
Wolff et al. (1982)
DETERMINISTIC PHOTOCHEMICAL AND AEROSOL MODELS AND APPLICATIONS:
Feigley (1978)
Godden and Lurmann (1983)
Gutfreund et al. (1981)
Haney and Seigneur (1985)
Heisler and Friedlander (1977)
Killus and Whitten (1983)
Liu and Roth (1973)
Liu and Grisinger (1982a, 1982b)
Liu (1982)
Liu et al. (1982)
Llovd et al. (1979)
Lurmann et al. (1979, 1982)
Martinez (1971a, 1971b)
Martinez et al. (1983)
McRae et al. (1982a, 1982b)
McRae and Seinfeld (1983)
Renzetti and Bryan (1961)
Reynolds (1979)
Reynolds et al. (1973, 1974, 1976, 1978)
Roth (1972)
Roth et al. (1974, 1983a, 1983b)
Seigneur et al. (1981a, 1981b, 1983a, 1983b, 1983c, 1984, 1985)
Sklarew et al. (1972)
Tesche (1983)
Tesche et al. (1983a, 1983b)
Tiao et al. (1976)
Wayne et al. (1971)
PHOTOCHEMICAL MEASUREMENTS AND EMPIRICAL MODELS:
Altshuller et al. (1971)
Aron and Aron (1978b)
Aron (1980)
Bailey (1975)
Calvert (1976a, 1976b)
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Table 2-4. (continued) Caporaletti et al. (1977) Chang et al. (1980a) Chock (1982, 1985) Chock and Levitt (1976) Chock et al. (1982) Coyne and Bingham (1977) Davidson and Cassmassi (1985) Decker (1972) Edinger et al. (1972) Edinger (1973) Eldon and Trijonis (1977) Elkus and Wilson (1977) Estoque (1968) Evans (1977) Farber et al. (1982a) Feigley and Jeffries (1979) Fontjin et al. (1970) Grosjean (1982a) Grosjean et al. (1983) Grosjean and Fung (1984) Hamming and Dickinson (1966) Hanst et al. (1982)Harris et al. (1982) Johnson and Singh (1976) Kok (1983) Kopczynski et al. (1972) Lawrence (1972) Lea (1968) Levitt and Chock (1976) Lin (1982) Littman et al. (1956) Ludwig et al. (1981, 1983) McKee (1976) Merz et al. (1972) Miller and Ahrens (1970) Mosher et al. (1970) Paskind and Kinosian (1974) Phadke et al. (1977) Pitts et al. (1976) Platt et al. (1980) Renzetti and Romanovsky (1956) Reviett (1978) Rogers et al. (1956) Russell et al. (1985) Schuck et al. (1966) Severs (1975) Simmonds et al. (1974) Spicer (1977) Spicer et al. (1983) Stephens (1968, 1969) Tiao et al. (1975a, 1976) Tombach (1982) Trijonis and Eldon (1978) Trijonis and Mortimer (1982)

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Table 2-4. (continued)
Trijonis et al. (1978b)
Tuazon et al. (1978)
Tuazon et al. (1981)
Winer et al. (1983)
Zafonte et al. (1977)
ATMOSPHERIC ACIDITY:
Brewer et al. (1983)
Broadbent et al. (1985)
Ellis et al. (1984c)
Hansen et al. (1982)
Hering et al. (1986a)
Hoffmann et al. (1983)
Hoffmann(1984)
Jacob et al. (1985)
Kawamura and Kaplan (1983, 1986)
Kok (1980)
Liljestrand and Morgan (1978, 1981)
Marsh and Bregman (1984)
Morgan and Liljestrand (1980)
Munger et al. (1983)
Richards et al. (1983a, 1983b, 1985)
Riggan et al.(1985)
Seigneur and Saxeena (1984)
Seigneur et al. (1985)
Shikiva et al. (1984)
Tombach and Pettus (1982)
Waldman et al. (1982)
Waldman (1984)
Waldman et al. (1985)
Walker (1985)
Wall et al. (1984)
Yoong (1981)
Young et al. (1983)
Zeldin and Ellis (1984)
EFFECTS OF EMISSIONS CONTROLS:
Atkinson et al. (1983)
Chock et al. (1981)
Costanza and Seinfeld (1982)
Glasson (1981b)
Hamming et al. (1973)
Kauper and Hopper (1965)
Killus et al. (1981)
Leonard et al. (1976)
Oliver et al. (1983)
Pitts et al. (1983)
Roth et al. (1983a, 1983b)
SCAQMD (1982)
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Table 2-4. (continued)

Seigneur et al. (1983c) Tesche and Burton 1978 Tesche et al. (1984) Trijonis (1972, 1974, 1983) Trijonis and Arledge (1975) Trijonis et al. (1978a)

CARBON MONOXIDE AND PRIMARY NITROGEN DIOXIDE:

Aron and Aron (1978a, 1978b) Chang et al. (1980b) Colucci and Begeman (1969) Hamming et al. (1960) Horie and Mirabella (1982) Liu and Goodin (1976) Neuroth (1979) Pandolfo and Jacobs (1973) Pandolfo et al. (1976) Rogers (1958) Tiao et al. (1975b) Trijonis et al. (1975b) Ulbrich (1968) Witz and Moore (1981) Witz et al. (1982) for whatever data were available. The measurements have rarely been coordinated in such a way that they were compatible with each other or with the models. This brief survey of studies leaves the impression that had these projects been coordinated with one another, and had they been designed around a set of common and inclusive objectives, their value would have been substantially increased.

Important field measurement studies which did involve a degree of this coordination were the Pasadena Aerosol Study (Hidy and Friedlander, 1972), the Aerosol Characterization Experiment (Hidy et al., 1975; Hidy and Mueller, 1979), the Three Dimensional Gradient Study (Blumenthal et al., 1978), the Los Angeles Reactive Pollutant Program (Feigley and Jeffries, 1979), the Los Angeles Catalyst Study (Tiao and Hilmer, 1978), and the Air Quality Maintenance Plan (SCAQMD, 1982). Several of these studies are summarized in Appendix B. Each of these studies involved a planned acquisition of data with the goal of using those data for interpretive purposes. Each study resulted in reports and papers which drew generalized conclusions concerning source-receptor relationships, physical and chemical mechanisms, and the potential effects of emissions changes.

Three of these studies are worthy of further scrutiny in the design of the SCAQS:

- The California Aerosol Characterization Experiment (ACHEX), because it is the predecessor to the SCAQS and it resulted in many of the hypotheses to be tested by the SCAQS.
- The Los Angeles Reactive Pollutant Program (LARPP), because it provided extensive data for model development and testing.
- The Final Air Quality Management Plan Analysis (AQMP), because it serves as the basis for proposed emissions reductions in the SOCAB.

ACHEX was an exploratory study aimed at developing a basic understanding of the sources and compositions of California aerosols. It was successful at describing the size distribution and the major elemental components of the suspended particles. Much was learned about the spatial distribution and composition of the aerosol, and the general sources of particulate matter concentrations were identified. The specific mechanisms for homogeneous and heterogeneous aerosol formation and the composition of the organic component of the aerosol were left as major unresolved issues. The role of water in aerosol formation, composition, and visibility was indicated to be important (Ho et al., 1974), but this role was not defined. The major conclusions of ACHEX were summarized by Hidy and Mueller (1979) as follows:

- the mass concentration of aerosol in California varies widely and is heavily influenced by sulfate, nitrate, and organic carbon formed from gas-phase precursors;
- aerosol concentrations in the eastern part of the SOCAB exhibit marked diurnal variations in concentration and composition. Two-hour average concentrations were substantially higher than 24-hour averages, reaching 450 μ g/m³ for mass, 70 μ g/m³ for sulfate, 70 μ g/m³ for nitrate, and 50 μ g/m³ for non-carbonate carbon;

- the multimodal aerosol size distribution was confirmed, with a submicron fraction dominated by aerosol formed from anthropogenic emissions and a supermicron fraction derived from dust and natural sources;
- sulfate, nitrate, and organic species were primarily in the submicron size range. Sulfate was more effective, per unit mass, than any other species in reducing visibility;
- the portion of aerosol attributable to photochemical processes was consistently in the 0.1 to 1.0 μ m size range;
- the photochemical mechanism was a major contributor to the formation of sulfate, nitrate, and organic particles. Heterogeneous formation pathways were also inferred to be important;
- ammonia has an important influence on the formation of photochemical aerosol, and these particles may contain a large fraction of water;
- though many sources contribute to the aerosol, sulfate is mainly linked to stationary sources using fuel oil; organic materials result from transportation using gasoline; and nitrates derive from both of these sources;
- more than half of the total suspended particulate material in the SOCAB measured during ACHEX was due to atmospheric chemical reactions. The remaining half was attributed to primary emissions from stationary and transportation sources and background materials such as sea salt and soil dust; and
- the aerosol sources and constituents primarily responsible for visibility reduction varied over the Basin, with sulfate and transportation sources being generally of greatest importance.

ACHEX was a state-of-the-art study for its time. Many of the instruments in common use today were developed for and tested in this study. Since ACHEX, much has been learned via laboratory experiments and field studies regarding the interactions of atmospheric variables, and this knowledge has been incorporated into complex and computationally intensive models which simulate these interactions. In hindsight, and with this additional knowledge, a study to address the issues raised by the above-stated conclusions would be designed quite differently from ACHEX. This hindsight does not detract from the value provided by measurements and data interpretation provided by these researchers more than a decade ago. Of particular note are the large number of publications and fundamental theories which resulted from ACHEX. These results are a direct consequence of the participation of a variety of experts, the open planning process and the free data exchange protocols established at its outset. Several subsequent air quality studies have cost more but were less influential because they neglected these important features.

The Los Angeles Reactive Pollutant Program (LARPP) consisted of airborne meteorological and pollutant sampling of coherent air parcels as they moved along a trajectory. Thirty-five days of sampling were conducted between September and November of 1973. Tetroons and tracer releases were used to locate the positions of air parcels, and instrumented helicopters continuously measured ozone, nitrogen oxides, total and non-methane hydrocarbons, carbon monoxide and air temperature. Ground-based LIDAR and mobile van measurements were also taken. The data were used in the development and testing of the ELSTAR Photochemical Air Quality Simulation Model (Lloyd et al., 1979). This was one of the first studies which involved industrial (Coordinating Research Council), federal (Environmental Protection Agency and the National Oceanic and Atmospheric Administration) and state (Air Resources Board) sponsors. It provided a model for cooperation among different sponsors to achieve common goals.

While ACHEX and LARPP were primarily research studies which did not focus on pollution control objectives, the AQMP provides a management analysis of more current (1979) emissions and air quality levels with the objective of determining those emissions reductions which are required to reduce air quality concentrations by a certain amount. Three analysis methods applied to routine emissions and ambient data were used by SCAQMD:

- Linear rollback (e.g. Barth, 1970; deNevers and Morris, 1973) was used for CO, SO₂ and NO₂. The total emissions in the Basin are to be reduced by the proportional reduction required of the highest non-background concentration to meet the standard.
- Species fractionation rollback was used for suspended particulate matter. Proportional reductions in Basin-wide primary particulate emissions are prescribed for non-sulfate and non-nitrate fractions of TSP in excess of the ambient standard. Proportional reductions in SO₂ and NO_x emissions are prescribed for the sulfate and nitrate fractions of TSP.
- City-specific EKMA (U.S. EPA, 1981) was applied to 27 station days selected from worst-case situations observed in 1977-1980. Trajectory-specific EKMA was applied to 17 of these cases. Individual back trajectories were plotted for each case and only hourly NO_X and hydrocarbon emissions along those trajectories were considered. Assuming that NO_X emissions will be 23% less in 1987 than they were for 1979, the necessary reductions in Basin-wide hydrocarbon emissions were calculated. Assumptions and sensitivity analyses results are given by SCAQMD (1982) and are too lengthy to repeat here.

The AQMP conclusions are plagued by great uncertainty. There is still controversy concerning whether or not NO₂ emissions reductions will increase or decrease ozone levels (Glasson, 1981a, 1981b; Chock et al., 1981; Pitts et al., 1983; Roth et al., 1983a). Davidson and Cassmassi (1985) provide convincing empirical evidence that shifting emissions schedules may significantly affect ozone concentrations, an option which has not been considered by the AQMP. Given the likelihood that a large fraction of the suspended particle concentrations may be composed of photochemical aerosol, linear rollback may not be an adequate approximation of the effects of emissions on this variable. The large variability in particle composition from site-to-site also calls into question the assumption that Basin-wide emissions reductions will affect the most highly loaded samples in a linear manner. The AQMP presumes a 23% reduction in NO_X emissions by 1987 and a corresponding reduction in suspended particulate matter, ozone, and NO₂ concentrations during that year. The effectiveness of the methods used to arrive at the proposed control measures are amenable to testing.

Contrasting ACHEX and LARPP to the AQMP, it is evident that the research and regulatory needs are complementary. While the regulatory process must continue with the information it has, regardless of the imperfection of that information, it can nevertheless identify where more precise information is needed to make effective decisions. Research efforts can then include, and possibly even focus on, those information needs.

2.4 CONTEMPORARY AND FUTURE AIR QUALITY STUDIES IN THE SOCAB

There is an obvious need for further research to address the cause and effect relationships between emissions, meteorology, and ambient concentrations of precursors and products for ozone and suspended particulate matter. Knowledge of the distributions of other pollutants (such as acidic species and toxic air contaminants) and of their effects on human health, visibility, and materials, is still sparse in the SOCAB. Basic information on the values attained by these observables and their spatial and temporal distributions is needed before these important relationships can be established. The sources, emission rates, and locations of species other than particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, and ozone need to be determined. Little is known about PM-10 in the SOCAB and how it is similar to and differs from TSP. With the advent of a new PM-10 standard, and the necessity to create an implementation plan within nine months of promulgation of that standard (Federal Register, 1985), this information becomes even more topical.

Several air quality studies have recently been completed, are currently taking place, or are in the planning stages, which address measurement and modeling issues which are relevant to SCAQS. Some of these have been used in the design of, or made an integral part of, SCAQS.

- The ARB is currently taking samples of benzene, carbon tetrachloride, chloroform, ethylene dibromide, ethylene dichloride, methyl chloroform, perchloroethylene and trichloroethylene gases in Tedlar bags for gas chromatographic analysis. HiVol samples are also being taken with total chromium, lead, manganese and nickel being measured by X-ray fluorescence. The state-wide network includes the Los Angeles, El Monte, Rubidoux, Long Beach, and Upland sites from the SOCAB.
- The SCAQMD and the ARB sponsored a PM-10 sampling network, run by the California Institute of Technology, to measure PM-10 between December 1985 and August 1986. Carbon, ions, and elements have been quantified on the samples. Sampling sites were Burbank, Los Angeles, Lennox, Long Beach, Anaheim, Riverside, and San Nicolas Island. PM-2.5 was measured at the Los Angeles site. Chemical characterizations of particle emissions were also completed. The SCAQMD will apply source and receptor models to these data to estimate source contributions to PM-10.
- Dr. Glen Cass of the California Institute of Technology has recently completed a 15-day measurement program which acquired four-hour aerosol samples between 11 a.m. and 3 p.m. at Pasadena during the summer of 1984. These fine and coarse samples have been chemically characterized and are accompanied by detailed EAA, OPC, nephelometer, RH, T, HNO₃, NH₃, impactor, and SCAQMD gas data. The interpretation of these data is not planned for the near future, owing to lack of sponsorship.

- Project BASIN (Wakimoto and Wurtele, 1984), which was sponsored by the ARB, provided intensive upper air measurements at numerous sites throughout the SOCAB for three days in August of 1984. Mountain wind stations, additional upper air soundings with four-hour resolution, airborne lidar, tracer release, and acoustic sounder measurements were made simultaneously. Though some of these data are being interpreted by scientists at the California Institute of Technology and UCLA, a thorough examination has not been sponsored.
- The Electric Power Research Institute (EPRI) has created a flexible emissions inventorying system covering the entire United States, including the SOCAB (Heisler, 1985). Some of the contents, such as alkaline emissions, nine reactive hydrocarbon classes, and ammonia emissions, are not easily available in other inventories. The inventory system allows rapid updating and regridding for modeling purposes. The current contents are for a base year of 1982, and an update is scheduled for 1987.
- The Southern California Edison Company (SCE) has conducted, and intends to continue, numerous studies in the SOCAB which characterize inorganic and organic components of the aerosol near source dominated as well as photochemically influenced, downwind receptor areas. Over sixty sampling events have been completed at Lennox and Duarte. Inorganic composition has been measured, and detailed organic analyses are being performed on selected samples (Singh et al., 1985).
- SCE released SF6 from the Ormond Beach Generating Station and took airborne and ground-based tracer and air quality measurements during August, 1985. This study was designed to characterize the chemistry in the plumes of gas and oil powered combustors when coupled with coastal meteorology. The 1985 data are being examined to elucidate the nitrogen chemistry in the plume during periods of elevated ozone concentrations. Additional tracer studies are planned for future years to explore power plant influences on atmospheric acidity. These studies will use soluble tracer species and remote sensing devices, if practical.
- SCE is conducting empirical and objective analyses of air quality and meteorological data to relate aerosol concentrations to meteorological regimes. Source apportionment methods are being developed and tested.
- The Coordinating Research Council (CRC) is sponsoring laboratory and field investigations by researchers at the University of Minnesota to improve size-selective aerosol sampling. Positive and negative biases in the sampling process are being quantified, and steps are being taken to correct them.
- CRC is sponsoring an investigation of the atmospheric chemistry and aerosol-forming potential of aromatic organic substances via experiments in the California Institute of Technology's outdoor smog chamber. These experiments are intended to: (1) identify and quantify the gas-phase reaction products and aerosol molecular composition, (2) measure evolution of aerosol size distributions resulting from atmospheric photo-oxidation of aromatic hydrocarbons in the presence and absence of primary particles, and (3) develop more realistic aromatic gas-phase

photochemical reaction mechanisms for air quality models used in the SOCAB.

- CRC is sponsoring the development of a tunable diode laser to measure NO, NO₂, HNO₃, and HCHO at levels as low as 0.5 ppb. The builder of this instrument, Unisearch Associates, will field test it under polluted conditions typical of those in the SOCAB.
- CRC is sponsoring a project to develop a vehicle evaporative emissions model which estimates emissions from contemporary motor vehicles over a realistic range of operating and ambient temperature conditions. The model will produce more accurate estimates than current methods because it will include diurnal temperature profiles, individual fuel system component temperatures, control system-use pattern interactions, and weathering of tank fuel. This model is applicable to improvements of ROG emission rates in the SOCAB.
- CRC is sponsoring a study of the effects of oxygenates used in gasoline blending on evaporative emissions, with emphasis on ethanol and methanol-gasoline blends. A companion study is intended to determine the effects of fuel volatility, dispensed fuel temperature, and initial tank temperatures, dispensed fuel rate, and vehicle fuel system design on the magnitude of vehicle refueling emissions. Results are applicable to improvements of ROG emission rates in the SOCAB.
- The SCAQMD has recently completed a 1983 emissions inventory update for the SOCAB. The ARB is compiling a 1984 point source inventory and a 1985 planning inventory for the National Acid Precipitation Assessment Program which will include ammonia emissions. The next comprehensive inventory for the SOCAB is scheduled for 1987 with availability by mid-1990. This will be the basis for the SCAQS inventory.
- The Electric Power Research Institute (EPRI) is studying alternatives to the contrast method for determining light extinction in the atmosphere. The assumptions of visibility measurement methods have been examined and alternatives have been developed to eliminate several of the assumptions which are not met in normal situations. Modifications to the integrating nephelometer which minimize the alteration of suspended particles with respect to water, organic content, and size distribution have been explored. The results of these studies can be applied to visibility measurements in the SOCAB.
- EPRI is examining alternatives for the measurement of the liquid water content of suspended particles and constructing a calibration and audit standard for these methods. These methods are applicable to the quantification of liquid water in the SOCAB aerosol.
- EPRI has developed quality assurance and standard operating procedures as part of its regional air quality studies. These procedures have optimized maintenance and performance test schedules and contain appropriate data forms. They are available to be combined with other procedures for the development of a SCAQS procedures manual.

- The ARB sponsored wet and dry deposition measurement networks in the SOCAB. The purpose is to estimate deposition fluxes in the region and to determine the acidity of fog. An estimate of the dry deposition velocities of sulfur and nitrogen species using the profile method (Businger et al., 1971) is included in these measurements.
- The ARB is sponsoring studies of atmospheric mutagens and the role of nitrogenous pollutants in their formation (e.g. Pitts et al., 1981).

These studies and others can help to provide the technical bases for decisions which must be made in the near and distant future. Their results will be even more valuable if they can be coordinated with each other and can be supplemented with additional emissions, meteorological, and air quality measurements which will allow cause-effect relationships to be established.

2.5 DATA NEEDS FOR MODELS

The approach taken in the design of SCAOS has been to start not with the measurements, but with the data interpretation methods. Methods applicable to the air pollution situation in the South Coast Air Basin, including both source and receptor models, have been identified from the references in Table 2-4. These references were reviewed, and, where appropriate, the creators and users of these methods were contacted to determine which measurements would be needed as input data, to determine parameters, to evaluate, and to estimate the uncertainties of these methods. Both research and regulatory applications were considered. Since most data interpretation approaches have been designed around existing data bases, and since they often contain many assumptions or calculational schemes which act as surrogates for non-existent measurements. the recommendations for additional measurements ranged from "nothing" to "everything measured at every point at all times." When reasonable compromises were made, and when past experience with models and data interpretation methods applied to the SOCAB was exploited, several common data needs were identified, irrespective of the data interpretation approach considered.

The most input intensive data interpretation methods are source and receptor models which quantitively relate ambient concentrations to source emissions. Data which are acquired for these models can also be used for less quantitative data interpretation methods, such as case-studies, statistical summaries, and correlation analysis.

Source models are those which explicitly describe the movement of constituents in the atmosphere and the interactions between them to predict the concentrations of key species at selected receptors which result from source emissions. Receptor models are those which measure numerous variables at selected receptors and infer the source contributions and transport and transformation mechanisms from those data. The data needs of several of these models specific to the South Coast Air Basin are briefly outlined in the following subsections. These models are extremely complex, and volumes have been written to describe them, their assumptions, their data requirements, and the compromises which have been made to accommodate existing data resources. It is not possible for this planning process to summarize all of the information about these models nor to consider the merits of each. This plan will not select "the model" most appropriate for describing the situation in the SOCAB. Model building is an iterative process which attempts to include those mechanisms and measurements which have the greatest influence on model output. The adequacy of those choices is then tested through focused experiments. The results of those experiments then feed back into the model-building process. The models described here are in evolution even as this is written, and the perceived importance of the data they require will certainly change as new knowledge is gained.

To reiterate: no attempt is made here to prefer one model over another. By polling the modeling community, a common set of measurements has been defined which should be of utility to the future development of several modeling approaches and their ultimate use in making pollution control decisions.

2.5.1 Regression on Principal Components (RPCA)

The RPCA establishes an empirical relationship between atmospheric end-products, such as ozone and constituents of PM-10, by determining rotated eigenvectors of correlations among the causative variables. Linear regressions of the dependent variables on these factors are calculated. RPCA was first applied by Henry and Hidy (1979) to routine air quality data from the South Coast Air Basin, and they found photochemical, relative humidity, and dispersion/stagnation components to have varying influences on ambient sulfate levels. Since that application, several other studies have been published (e.g. Henry and Hidy, 1982; Lioy et al., 1982; Wolff and Korsog, 1985; Malm, 1985; Chow and Spengler, 1985) which show the potential of this method. Chow (1985) provides the most recent summary of these applications and testing of this method.

The RPCA model produces mathematical factors which must be interpreted as physical factors based on the atmospheric variables included in the analysis. These variables need to be selected such that they will be surrogates for the important physical factors. Past applications of RPCA have been limited because these important variables have not always been available.

The important physical factors which are expected to affect oxidant and PM-10 concentrations in the South Coast Air Basin are: (1) primary and precursor emissions of particulate matter, NO_2 , reactive hydrocarbons and SO_2 , (2) photochemical transformation mechanisms, (3) heterogeneous transformation mechanisms, (4) transport and stagnation, (5) temporal variability of all factors, (6) emissions injection height, and (7) previous day carryover.

The observables which have been deemed important by their users for these RPCA models applied to oxidant and PM-10 concentrations are:

- sequential samples (of four to six hour maximum duration on consecutive days) of size segregated and chemically speciated particulate matter. Important species are geologically-related elements (Al, Si, Fe, Ti), other tracer components (e.g. Pb, Br, V, Ni, Cl, Na, elemental carbon, K), secondary products (e.g. total organic carbon, polar organics, sulfate, nitrate), and in situ liquid water content of the aerosol;
- hourly average oxidant, PAN, speciated reactive hydrocarbons, and NO_x/NO₂ concentrations;

- four to six hourly estimates of mixing depth, ventilation, atmospheric stability, relative humidity, and components of wind direction;
- four to six hourly estimates of fog and cloudwater, when fog exists;
- four to six hourly emission rates in the vicinity of sampling sites, classified by ground-level and elevated injection heights, for primary particles, reactive hydrocarbons, NO_X , and SO_2 . Day of the week variability may be adequate;
- nighttime ozone and PM-10 concentrations off the coast and above the inversion layer; and
- light scattering and extinction measurements which correspond with particle and gas measurements.

The RPCA methods require at least fifty (and preferably over one hundred) sets of measurements which cover the entire range of variability expected to occur. It is not yet known whether or not these methods can be used in a predictive mode nor if they will be able to extract better relationships between causative factors and ozone and PM-10 levels because the data required to test them have not been previously available. The results obtained in the cited studies show promise operating on routine data, however.

Several related models, such as objective analysis methods (e.g. Aron and Aron, 1978a, 1978b; Davidson and Cassmassi, 1985), multiple linear regression (e.g. Pratsinis et al., 1984; White and Roberts, 1977) and time series analysis (e.g. Tiao et al., 1975a, 1975b; Trijonis et al., 1975b) make use of the same data as that required for the RPCA model. Watson et al. (1985) observe that a detailed physical explanation of the processes which are likely to affect the atmospheric end-products, and identification of the variables which are likely to be indicative of those processes, is a pre-requisite for a RPCA application. Though Watson et al. (1985) provide such an explanation for factors affecting fine particulate concentrations in the San Joaquin Valley, their analysis is not complete enough to cover the more complex situation in the SOCAB.

2.5.2 Chemical Mass Balance Receptor Model

The chemical mass balance (CMB) receptor model (e.g. Friedlander, 1973) has been used as the basis for control strategies related to total suspended particulate matter (e.g. Cooper et al., 1979). However, the major contributors in these previous applications have been related to primary emitters. Since previous measurements have shown that major contributors to TSP in the SOCAB are of secondary origin, this model may not be directly applicable to the apportionment of these aerosols to sources. Nevertheless, this model is being incorporated into EPA's PM-10 assessment guidelines (personal communication, Tom Pace, U.S. EPA Office of Air Quality Planning and Standards, August, 1985) and has been shown (Watson, 1979) to put an upper limit on the secondary aerosol contribution and to apportion some of the precursors (Mayrsohn and Crabtree, 1976; Tombach, 1982; Feigley and Jeffries, 1979) of secondary aerosol to their sources. If the fractionation among species from various sources as a result of transport and transformation can be measured (e.g. Houck et al., 1982) or estimated (e.g. Duval and Friedlander, 1981), then the
CMB might be an appropriate method for apportioning PM-10, and possibly the precursors of ozone, to their sources.

The CMB model consists of solutions to a set of equations which describe receptor concentrations of selected constituents as linear sums of the fraction of each constituent in source emissions times the total mass contribution of that source to the receptor. The receptor concentrations and source compositions are given to the model and the contribution from each source to each atmospheric constituent is calculated. Chow (1985) provides the most recent compilation of past applications while Watson (1979) presents the model assumptions and testing results. Other test results are reported by Currie et al. (1984) and Dzubay et al. (1984).

A recent evaluation of this model sponsored by the Electric Power Research Institute (Harold Javitz, SRI International, personal communication, September, 1985) concludes that although the CMB formulation is adequate for accurately determining many source contributions, even aggregate secondary contributions and the contributions to their precursors, this adequacy is extremely sensitive to the available observables and their random variability. The accuracy of current applications has been controlled more by the inadequacy of source profile measurements than by ambient measurements. There is no set of common source profile measurements in which all emitted species are characterized for all important sources. Chow (1985) and Edgerton (1985) have recently shown the value of including gaseous as well as particulate species measured in both the source and receptor samples. This increases the accuracy and precision of source apportionment and allows the gaseous species to be apportioned to their emitters. Very few current source profile measurements include the gaseous as well as particulate chemical constituents.

Although the CMB model can be applied to single samples of any duration, samples taken over shorter time periods provide more precise results in that they allow a better definition of contributing sources and a more accurate estimate of fractionation factors.

The important input data needs for the chemical mass balance model are:

- receptor particle measurements of key elements (Al, Si, Pb, Br, K, Cl, Na, V, Ni, Fe), ions (SO¹/₄, NO³/₃, NH⁴/₄), organic and inorganic carbon, speciated organic materials, and individual particle characteristics in O to 2.5 and 0 or 2.5 to 10 µm size ranges;
- receptor gas measurements of NO_X , SO_2 , CO, reactive and nonreactive hydrocarbons;
- source profiles for power plant, motor vehicle, refinery, resuspended dust, and marine aerosol which include gaseous and particulate observables specified above for all sources; and
- estimates of fractionation factors (after Stafford and Liljestrand, 1984) between source and receptor.

2.5.3 Photochemical and Aerosol Models

Many grid and trajectory models have been proposed for describing the relationships between emissions and receptor concentrations. Each of these involves transport and transformation mechanisms. Godden and Lurmann (1983). McRae et al. (1982a), Killus et al. (1985), and U.S. EPA (1981) describe photochemical mechanisms which have been incorporated into deterministic modeling packages. Each of these models has been applied to the June 26 and 27, 1984 smog episode and the 0_3 , NO, and NO₂ concentrations have been compared with those at downwind monitoring stations. Though these "model validation" studies are not strictly comparable, the comparisons of model results and ambient measurements are qualitatively equivalent, regardless of the model used. A model/model comparison is not justified based on the individual reports, however, because these applications were never coordinated in such a way that objective performance measures could be calculated. While much emphasis has been placed on model performance (i.e. a one-to-one match in model end-product with a corresponding measurement in place and time), little emphasis has been placed on model diagnostics (i.e. the comparison of intermediate model calculations with measurements of reactive species and independent measurements of transport variables in space and time). Sensitivity and uncertainty analyses (e.g. Seigneur et al., 1981a; Tilden and Seinfeld, 1982) have shown that model end-product values vary substantially. even with small variations in selected input data. The sensitivity of intermediate calculations, and the extent to which input errors compound upon each other, have not yet been compared to real measurements outside of a smog chamber.

Work is underway to better represent other aerosol formation processes in these models (Seigneur et al., 1985, Russell et al., 1983). The ultimate goal is to produce comprehensive treatments which can estimate receptor concentrations of PM-10, ozone, and other constituents with specified accuracy and precision. These are currently the only types of models which are capable of estimating the effects of a hypothetical change in emissions on air quality. Receptor models can only be used when they are applied before and after such an emissions reduction has taken place.

These models require precise definitions of wind fields, initial values of pollutant and precursor concentrations of the atmospheric constituents, reaction rates, vertical and horizontal fluxes into and out of the volume being modeled, temporal and spatial distributions of gaseous and particulate precursor and primary emissions, and deposition rates at surfaces. It is technically impossible to measure all of these variables with the spatial and temporal resolution required of the models; therefore, simplifying assumptions regarding their values are used to estimate them.

The most important measurements which are not currently being made, but which are feasible, are the following:

 emission rates with a three hour minimum time resolution. The photochemical precursors, NO_X, and speciated hydrocarbons, are the most important species. These are needed as input data for photochemical and aerosol models;

- improved speciation for both gaseous and particulate emissions. The same types of measurements should be made on all major source types and should include elements, ions, organic and inorganic carbon, sulfur dioxide, nitrogen oxides, ammonia, carbon monoxide, speciated gaseous and particulate organic species. Exhaust gases should be cooled, diluted and preferably aged prior to sample collection to approximate their compositions in the environment. Aggregate samples of area sources (e.g. motor vehicle emissions) are preferable to measurements of single sources. These measurements should be sufficient to determine ROG/NO_X ratios for all sources. These speciations are needed both as input data for source models and for receptor models. Ammonia emission rates are also needed for aerosol models;
- accurate wind fields which account for the complex meteorological phenomena described earlier. These are critical to the establishment of effective cause-effect relationships between emissions and receptor concentrations. Additional locations and more frequent upper air measurements are needed to supplement and verify surface measurements;
- boundary and initial concentrations of oxidant and particulate species, and their precursors. These are needed to determine their evolution over a period of time. Of critical importance are the concentrations above the mixed layer during nighttime and morning periods. Concentrations over the ocean are required, and these may be at levels lower than those detected by conventional instruments which have been used previously. Hydrocarbon speciation and free radical concentrations are also needed at various sites to serve as initial concentrations and to verify model predictions throughout a simulated event; and
- intermediate reaction products. These are required to verify that chemical mechanisms are reproducing the multitude of chemical constituents which are actually observed during an episode.

2.6 SUMMARY

It is impossible to do justice to the wealth of information available regarding air quality in the South Coast Air Basin in a survey of this type. The emphasis here has been placed on learning from the past in order to gain in the future. The subsequent parts of this program plan have been influenced by these lessons, which can be summarized as follows.

- The value of simultaneous measurements of emissions, transport, transformation and receptor variables is far greater than the value of any of these measurements acquired at disparate places and times, and the cost effectiveness of simultaneous data collection exceeds that for separate studies.
- The physical and chemical understanding of the atmospheric processes affecting pollutant concentrations in the SOCAB is sufficient to define the observables which need to be measured, their averaging times, and the characteristics of episodes which are conducive to high pollutant concentrations.

- Measurement technology is capable of determining the values of most observables, but each measurement method has a set of assumptions which must be met. Provisions must be made to test those assumptions for each measurement period, and to consider deviations from them in the data interpretation process.
- Potential data interpretation methods, including models, must be identified prior to taking the first measurement and their data requirements must be specified. These requirements include testing as well as input data.

"3. MEASUREMENT APPROACH

This section describes the planned SCAQS field measurements. The measurement approach has been revised since the last version of the program plan (Blumenthal et al., 1986). Recommendations from participants, sponsors, and several working groups which were set up to design and review specific aspects of the study have been taken into account in the revised design. The planning activities, the role of the Field Manager, the measurement recommendations of the modeling community, and the rationale for selection of the sampling periods are summarized in Sections 3.1 through 3.3. The study includes a series of "core" measurements along with several complementary studies which address specific issues. The core measurements are described in Sections 3.4 through 3.7. Most of the special studies are described in Section 3.8; however, some of them are included in the list of A-site measurements in Section 3.4.

3.1 PLANNING AND MANAGEMENT

3.1.1 Planning Activities

The suggested program plan prepared in June, 1986 (Blumenthal et al., 1986) has been revised based upon three types of input. First, the suggested plan was widely distributed to the technical community and potential participants for their review and comment. Second, Emissions, Meteorology, and Model Working Groups were formed to review the plan and to recommend specific measurements and data collection activities which would meet the needs of the analysts and modelers who will use the data. Finally, the sponsors negotiated work statements with the participants who will perform the measurements listed in this section.

In light of the finite resources of the sponsors and limited technical feasibility of some of the measurements, compromises were made to arrive at the consensus program plan presented here. The final design process was an iterative effort with continual review by the Working Groups and the sponsors. Numerous meetings were held, and all points of controversy were pursued until a consensus was reached between the measurements participants, the working groups, and the sponsors. The detailed recommendations of the working groups are discussed in the remaining parts of Section 3 and are reflected in the study design.

3.1.2 Field Management

The SCAQS field program will be coordinated by a Field Manager who will perform the following tasks:

- determine the power, space, and logistical needs of all field participants;
- arrange for access to the AQMD sites to be used during SCAQS;
- arrange for additional power and other necessary facilities;

- coordinate the activities of all measurement personnel and provide support as necessary. The sites will be operated by a contractor whose activities will be coordinated by the field manager;
- prepare the field measurement protocols;
- disseminate daily meteorological forecasts and sampling decisions to the participants;
- coordinate the distribution, exposure, labeling, and transportation to the laboratory of all routinely collected samples; and
- document field activities for progress reports.

3.2 MODEL WORKING GROUP RECOMMENDATIONS

To aid in the planning process, a Model Working Group was established. Members of the Model Working Group are listed in Appendix A. The sampling sites and specific measurements suggested for SCAQS in the Suggested Program Plan (Blumenthal et al., 1986) were based on initial discussions with potential sponsors, participants, and modelers. To assure that the measurements will meet future model and data analysis needs, some preliminary modeling and data analysis activities were performed by members of the Model Working Group to analyze the adequacy of the various components of the SCAQS measurement plan. The results of these activities were considered in this revision to the program plan.

The general question underlying the Model Working Group's analysis is --If the SCAQS program were completed and the planned measurements were all successful, how would the data be used to test, evaluate and improve air quality models? Conversely, can the proposed measurements be planned such that the optimal amount of information can be obtained to meet the goals of the study.

The analyses performed by the Model Working Group and their recommendations are presented in a MWG report (Seinfeld et al., 1986) and are summarized below.

3.2.1 Gas-Phase Chemical Measurements

Lurmann et al. (1986) carried out an extensive set of chemical mechanism trajectory calculations in an effort to determine those gaseous species measurements that would aid most in elucidating $ROG/NO_X/ozone$ chemical reaction mechanisms. The conclusions arising from this study relevant to the choice of gas-phase measurements are as follows:

 <u>Reactive Hydrocarbon Measurements</u>: The total level and speciation of reactive hydrocarbons have the strongest influence on predicted ozone species. Therefore, it is extremely important that reactive hydrocarbons be measured as planned (see Section 3.4). In addition to gas chromatography measurements, it is recommended that occasional gas chromatograph/mass spectrometer measurements be made to ensure proper identification of the peaks.

- Free Radical Measurements: The Working Group studied in detail the question of which free radicals provide the most opportunity for evaluating our knowledge of the gas-phase chemistry and for discriminating among rival chemical reaction mechanisms. The conclusion arising from the studies is that measurements of peroxy radicals, namely, HO₂ and RO₂, will provide the greatest amount of information concerning the detailed behavior of chemical mechanisms. Separate measurements of HO₂ and RO₂ would be best, but, if that is not possible, measurement of the sum of HO₂ and RO₂ is also of value. Although hydroxyl radical measurements have been proposed, these measurements are most useful in assessing the overall OH level in comparison with predicted levels. They will not allow differentiation of chemical reaction mechanisms since all mechanisms predict essentially the same OH levels.
- Hydrogen Peroxide Measurements: Hydrogen peroxide is a very sensitive indicator of HO₂ levels and is an important species in its own right. Measurements of H₂O₂ are viewed as essential.
- Formic Acid: Formic acid measurements would provide an important test of our understanding of the olefinic portion of reaction mechanisms. These measurements are encouraged.

The Working Group places a substantially lower priority on continuous nitric acid measurements than those listed above. However, as noted below, nitric acid measurements on the same time resolution as the aerosol nitrate and ammonia gas-phase measurements are essential.

In commenting additionally on the hydrocarbon measurements, the Working Group deems it very important to determine the total hydrocarbon cloud surrounding the Basin, namely, how far out and how high it extends. The question of marker compounds was discussed. It is important that the incoming air from the ocean be characterized with respect to its hydrocarbon level and composition.

Pilinis and Seinfeld (1986) used an air quality aerosol model to determine the sensitivity of the size and chemical composition of a simulated receptor aerosol to various input variables. Their studies result in the following recommended gas-phase measurements:

- $\underline{SO_2}$ Aloft: Since more than 50% of the SO₂ is emitted aloft from various point sources, upper-air SO₂ concentration measurements are very important. Of special importance is the concentration of SO₂ above the mixed layer overnight. This can be fumigated to the ground when the inversion layer grows the next day.
- <u>NH₃ and Nitric Acid</u>: Aerosol nitrate and nitric acid exist in equilibrium, and the aerosol nitrate concentration is dependent on the amount of ammonia present in the atmosphere. An increase of only 10% in the amount of ammonia can result in a substantial increase in NH₄NO₃ in the aerosol phase.
- Temperature and Relative Humidity: Perturbations of 5 degrees C and 30%
 RH are common during the day in the Basin. Such perturbations can result

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in substantial changes in aerosol mass and physical state, which affect the composition and size distribution of the aerosol.

3.2.2 Aerosol Measurements

Pilinis and Seinfeld (1986) used an air quality aerosol model to determine the sensitivity of the size and chemical composition of a simulated receptor aerosol to various input variables. Their studies result in the following recommendations for the general aerosol measurements:

- Organic and Inorganic Aerosol Concentrations: Coarse (by difference) and fine aerosol loadings should be measured on a routine basis for both organics and inorganics.
- Particle Absorption and Scattering: Both integrating plate particle absorption and particle scattering by nephelometer should be measured on a routine basis.
- <u>Time Resolution</u>: The routine aerosol measurements at the B-sites should be every four hours during the daytime, and could be longer at night. The four-hour samples should start at 0600 local time to coincide with the morning rush hour.

For the impactors and aerosol physical measurements, they recommend the following:

- <u>Impactors</u>: A minimum of five size cuts are needed for aerosol size and chemical composition modeling. Organic and inorganic size distributions are needed. Specifically, elemental and organic carbon size distributions should be measured using the MOUDI impactor; inorganic ion size distributions should be made with the Berner impactor.
- <u>Time Resolution</u>: Twelve-hour averaging for inorganic ion impactor measurements are of little value for aerosol modeling, since temperature and relative humidity changes over 12 hours will change the aerosol substanially. Also, organic aerosol concentrations probably peak on short time scales, just like ozone concentrations. Thus, these measurements should be as short as possible, probably four hours long during the daytime and six hours at night. A 12-hour nighttime sample could replace the two 6-hour samples if necessary.
- <u>Impactor Sites</u>: Aerosol size-composition distributions for inorganic ions are needed for aerosol modeling at both the beginning and the end of a trajectory. However, it is unlikely that a given trajectory will begin at Long Beach and end at Claremont. Also, the predicted aerosol mass and chemical composition are significantly different when the trajectory is Long Beach-to-Claremont, versus Anaheim-to-Rubidoux. At least two receptor measurement sites are needed in order to allow interpolation where data are not available. Thus, the Berner impactor measurements should be made at more than the two A-sites; Rubidoux is the recommended third site. Also, the two receptor sites will allow a comparison between the aerosol at an ammonia-poor site (Claremont) and an ammonia-rich site (Rubidoux).

• <u>Aerosol Physical Measurements</u>: Detailed aerosol size distributions are needed for aerosol modeling. A combination of an electrical mobility analyzer, an optical particle counter, and a large-particle counter could supply hourly-averaged size-distribution data. It is most critical that these measurements be made at the source site (Long Beach) and the two receptor sites (Claremont and Rubidoux). These measurements could be supplemented with a classifier/CNC at the receptor sites.

3.2.3 Meteorological Measurements

Kessler et al. (1986) carried out a number of wind field generation calculations for the South Coast Air Basin. The first conclusion from those studies is that one cannot construct a good three-dimensional wind field from surface measurements alone; upper air data are crucial. The second major conclusion is that the current surface network proposed for SCAQS is adequate for generating a surface level wind field. With approximately six upper air measurements, the question is -- Where should these be made and how frequently? It was generally agreed that measurements in the interior of the SOCAB will be more useful than measurements in the outlying areas, for the purposes of data analysis.

3.2.4 Emissions Inventory

The ROG speciation of the inventory should be consistent with the two types of chemical mechanisms used today in photochemical modeling. The recommended compound classes for the two types of mechanisms are:

Surrogate Species Mechanisms Carbon Bond Mechanism

C4-C5 Alkanes >C5 Alkanes Ethene Terminal Alkenes Internal Alkenes Mono-alkylbenzenes Di-alkylbenzenes Tri-alkylbenzenes Formaldehyde Acetaldehyde Other Carbonyls Nonreactive Paraffinic Bonds

Ethene Olefinic Bonds

Mono-alkylbenzene Bonds Di-alkylbenzene Bonds

Formaldehyde

Other Carbonyls Nonreactive

The Systems Applications, Inc. Urban Airshed Model (UAM) has been applied extensively in the South Coast Air Basin utilizing a horizontal grid resolution of 5 km (Reynolds et al., 1973; Roth et al., 1984). Seigneur et al. (1981) demonstrated a significant deterioration in model performance in the SOCAB when the grid size was increased to 10 km; based on this result, 5 km should be considered to be the minimum resolution required for effective application of the UAM in this region.

The standard temporal resolution of UAM emissions inventories has been one hour. In general, data on point and mobile source emissions can be obtained with this temporal resolution. Frequently, only yearly rates are available for area sources; in this case, day-to-day and hourly variations must be either inferred or ignored. Seigneur et al. (1981) indicate relative insensitivity of the UAM to detailed diurnal resolution of area source emissions. However, the use of yearly information on area sources can introduce significant uncertainty into UAM predictions in cases where seasonal variability in area source emissions is significant. Thus, an effort should be made to obtain daily, monthly or seasonal resolution of area source emissions.

Various UAM applications have indicated that emissions uncertainties of the order of 5-10% would not have significant effects on peak ozone concentrations predicted by the model, while uncertainties of the order of 30-50% in emission rates may produce major uncertainties in predicted ozone peaks.

Primary aerosol particles, emitted directly into the atmosphere, consist principally of elemental and organic carbon and various inorganic species. The primary carbonaceous particles will presumably be chemically inert with respect to the inorganic system; their presence, though, does affect the predicted aerosol size distribution, as well as the total suspended mass. Due to this importance, the aerosol emissions inventory should include both PM-2.5 and PM-10 size fractions for aerosol mass and for both elemental and organic carbon.

3.3 SELECTION OF STUDY PERIODS

The two study periods have been chosen to be representative of the worst oxidant and aerosol periods in the South Coast Air Basin. In addition, these periods will document three substantially different types of pollutant conditions.

The first study period will take place from June 15 to July 26, 1987. The first part of this summer period is typically a period of high humidity in the South Coast Air Basin and should be a period which favors heterogeneous aerosol formation. During June, the percentages of days with low morning stratus clouds and poor afternoon visibility in the inland areas are the highest of any month, as indicated in Table 3-1. The highest average suspended particulate concentrations in the Basin typically occur in June, July, and December. The second half of the summer study period typically experiences the highest concentrations of photochemical pollutants of the year. High ozone concentrations generally occur in the Basin when the 850 mb temperature is greater than 20 °C. Figure 3-1 indicates that July includes the most consistently high 850 mb temperatures of the summer. Figure 3-2 indicates that July also experiences consistently high maximum ozone concentrations. During mid-to-late July, the inland visibility is consistently low (Table 3-1), and there are stratus clouds along the coast about 1/3 of the time. Inland stratus is much less common. Thus, the summer sampling period should produce periods of primarily homogeneous chemistry as well as periods when coastal pollutants interact with water droplets which subsequently dry out as they travel inland. Twelve intensive sampling days, covering episodes of two or three days duration, will be selected from this six-week period on a forecast basis as described in Section 3.7.

	Cet1	ing	Visibility		
	(0800	PST)	(1400 PST)		
	LAX	0NT	LAX	ONT	
	<1800 ft.	<1000 ft.	<6 miles	<6 miles	
May 1 - 15	19%	16%	12%	49%	
16 - 31	37	27	20	65	
June 1 - 15	40	25	36	75	
16 - 30	33	21	12	63	
July 1 - 15	27	8	17	44	
16 - 31	33	9	33	71	
August 1 - 15	40	13	27	55	
16 - 31	32	8	18	53	
Sept 1 - 15	15	12	31	49	
16 - 30	21	3	20	41	
0ct 1 - 15	36	12	37	51	
16 - 31	18	9	33	44	

Table 3-1. Percentage of Days for 1978-83 with Early Morning Clouds and Low Afternoon Visibility.

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The second study period will take place from November 16 to December 13, 1987. This period was chosen to measure late fall stagnation conditions. NO_2 and CO episodes tend to occur at this time, and low inversions and cool temperatures tend to favor the accumulation of primary pollutants. The average daily maximum NO_2 concentrations for September-December in the SOCAB for a six-year period are plotted in Figure 3-3. This sampling period is early enough to avoid the probability of substantial numbers of down days due to winter storms. Six intensive sampling days covering episodes of two or three days duration will be selected on a forecast basis as described in Section 3.7.

The lengths of these sampling periods minimize the probability of missing synoptic conditions of interest due to periods of unusual weather. The choice of the study periods was reviewed and endorsed by the staff of the SCAQMD (Liu, 1986).

3.4 SURFACE AIR QUALITY MEASUREMENTS

3.4.1 Measurement Site Locations

The study region includes the South Coast Air Quality Management District (SCAQMD), the upwind portions of Ventura County, and adjacent offshore regions. Three types of pollutant measurement sites, identified as A-, B-, and C-sites, will be operated in this region. The characteristics of the sites are described below. The C-site locations are shown in Figure 2-1 and identified in Table 2-3; the B- and A-site locations are shown in Figure 3-4.

C-Sites

C-sites include the existing monitoring stations of the SCAQMD, the Ventura County Air Pollution Control District, and other stations at which air quality data are routinely collected and reported. Data from these sites will be routinely acquired and archived by the Districts and integrated into the SCAQS data base after the measurement program.

B-Sites

B-sites are located along typical SOCAB air trajectories and acquire more measurements with greater frequency than the C-sites. These enhanced measurements will be made on the intensive sampling days selected by the forecast strategy described in Section 3.7. During the summer sampling period, the Anaheim, Azusa, Burbank, Downtown Los Angeles, Hawthorne, and Rubidoux sites are collocated with C-sites and a regional-scale background B-site is located at San Nicolas Island. The Long Beach and Claremont B-sites are also A-sites. The Claremont, Long Beach, and Rubidoux sites are termed B+ sites because their measurements are further enhanced with high-resolution particle size and chemistry monitors. During the fall sampling period, the number of B-sites will be reduced to five located at Anaheim, Claremont, Downtown Los Angeles, Hawthorne, and Long Beach. Long Beach and Claremont will be B+ sites for this fall period.

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A-Sites

A-sites will be the base of operations for selected intensive measurements, special experiments, and individual investigators. Long Beach and Claremont are the A-sites for the summer sampling period. These sites represent source and receptor regions respectively. Only the Long Beach source-oriented site is a A-site during the fall sampling period. A-site instruments are operated primarily on intensive study days, but some researchers will operate their equipment continuously.

3.4.2 SCAQS Air Quality Measurements and Measurement Methods

The observables to be measured at the A-, B-, and C-sites, the averaging times, and measurement frequencies are presented in this section.

C-Site Measurements

The C-site measurements consist of those air quality and meteorological variables which are normally measured by the Air Quality Management Districts. Table 3-2 summarizes these measurements, and the specific measurements at each station are identified in Table 2-3. The measurements methods and procedures at the C-sites are already in place and are quality assured by the Districts and the ARB on a regular basis. These data will be extracted from the Districts' data base for the SCAQS summer and fall sampling periods and integrated with the rest of the SCAQS measurements.

B-Site Measurements

. روج چهه ا All of the C-site measurements will also be made at B-sites throughout the summer and fall periods. The measurements to be made at the B-sites are identified in Tables 3-3a through 3-3f. The continuous measurements will be made on all days during the study period. The other measurements will be made only on the intensive sampling days. The measurement methods were selected after extensive evaluation of different alternatives with respect to reliability, sensitivity, cost, availability, and compatibility with existing measurements. Only brief reasons for selecting each method are given in the tables, since the entire selection rationale is too involved for presentation in this program plan. Table 3-3a also includes estimates of the ambient concentration, lower quantifiable limit, and precision for each measurement. In all cases the lower quantifiable limits are sufficient to measure the expected concentrations of the stated variables.

Detailed protocols for field and laboratory operations at B-sites are being prepared. The B-site field operations are summarized below. B-sites will be manned for 24 hours per day on intensive sampling days. Technicians will verify that all continuous monitoring instruments are operating properly and will change canisters and substrates on a defined schedule. A speciallydesigned gas and aerosol sampler (the SCAQS Sampler) has been constructed and tested for HNO₃, NH₃, SO₂ and the PM-2.5 and PM-10 chemically speciated sampling at B-sites. Media in the SCAQS Sampler will be changed at 0600, 1000, 1400 and 1800 hours local time (PDT in the summer, PST in the fall) and midnight standard time (0100 PDT in the summer, 2400 PST in the fall). The changes beginning at 0600 will help match these samples to the morning rush hour during both summer and fall. The change at midnight will allow these

	<u># days</u>	Time duration	Analytical Method
03	all	hourly	UV absorption
NO	all	11 H	Chemiluminescence
NO _X	all	10 01	Chemiluminescence
CO	all	н п	NDIR
so ₂	all	11 I I	Pulsed fluorescence
Wind speed	all	lt bi	Cup anemometer
Wind direction	all	11 11	Wind vane
Total suspended particles	6th day	24 hrs	HiVol sampler
PM-10	6th day	24 hrs	HiVol with Size Selective Inlet
Tracer Samplers (selected sites)	all tracer days	s 1 hr integration	Automated bag or syringe samplers

Table 3-2. C-Site Measurements

Table 3-3a, Network Measurements at B-Sites (See Table 3-3f for abbreviations)

6/6/87	Dum	No nor	····	Amblant	concentrations	<u> </u>	Lower quantifiable		Basson for	References
Observable	ation	site-dav	Meas, method	typical	rance	Units*		Precision**	selection	and Dotas
METEOROLOGY					·····					
Wind speed	Cont.	24	Cup anemometer	3	0 to 20	m/sec	0.25	0.25	A	
Wind direction	Cont	24	Vane	IA	0 to 360	degrees	IA	3	A	
Temperature	Cont	24	Thermistor	IA	0 to 45	degrees C	IA	0.5	A	
Dew point	Cont	24	Dew cell	IA	-10 to 25	degrees C	IA	0.5	A	
UV radiation	Cont	24	UV radiometer	30	0 to 60	watts/m2	0.5	0.25	A	
GASES (continuou	18)									
O3	Cont	24	UV absorption	30	1 to 400	ppb	2	15%	A	
NO	Cont.	24	Chemiluminescence	30	0 to 300	ppb	2	15%	A	
NOx	Cont.	24	Chemiluminescence	50	0 to 350	ppb	2	15%	A	
SO2	Cont	24	Pulsed fluorescence	6	0 to 320	ppb	2	15%	A	
co	Cont	24	NDIR	2	0.5 to 30	ppm	0.5	15%	A	
GASES (Integrated	i sample)									
SO2 in the	4 to 7 hr.	5	Impreg. filter	6	0 to 320	ppb	0.2	7%	C,E	1
NH3 SCAOS	4 to 7 hr.	5	Denuder tube	5	0 to 150	ppb	0.3	10%	D	2
HNO3 Sampler	, 4 to 7 hr.	5	Denuder diff & Nylon	7	0 to 25	ppb	0.4	10%	D	3
Carbonyls	1 hr.	3	DNPH absorber	3-7	1 to 30 (HCHO)	ppb	0.5	10%	C	4
C1-C10 HC	1 hr.	3	Canisters and GC/FID	0.1 to 50	2	ppbC	0.1	10%	B	5
PAN	1 hr.	24	In-situ GC/EC	5-10	0-50	ppb	0.5	15%	c	· 6
H2O2†	1 to 7 hr.	. 8	POHPAA fluorescence	5 (est.)	0 to 25	ppb	6.5	3%	С	7
AEROSOL PHYSK	CAL PROP	PERTIES								
Size dist.††	Cont	24	OPC(Climet 208, PMS ASASP-X)	IA I	IA	IA			В	8
Size dist ††	Cont	24	EAA	IA	A .	, IA	Hesolves diameter ratio	o of 1.8	E,F	8
Light scattering	Cont	24	Integrating nephelometer	350	15-1500	Mm-1	10	10%	B	9
Data acquisition	Cont.		Micro-computer	iA	IA	IA	IA	5mV for 10V f.s.	G	10
AEROSOL CHEMR	STRY (In t	he SCAQS	Sampler)							
PM-10/PM-2.5:	4 to 7 hr.	. 5	SA-254/Bendix 240						8	11
Mass	4 to 7 hr.	. 5	Gravimetric	40	5 to 220	µg/m3	5.8	7%	В	
SO4=	4 to 7 hr.	. 5	IC .	5	0.5 to 25	µg/m3	0.06	7%	В	
NO3-	4 to 7 hr.	. 5	IC	8	0.5 to 30	µg/m3	0.09	7%	В	
Cł	4 to 7 hr.	. 5	IC	3	0.1 10 10	µg/m3	0.1	7%	В	
NH4+	4 to 7 hr.	. 5	AC	5	0 to 20	μg/m3	0.05	7%	8	
Elements	4 to 7 hr.	. 5	WDXH			ng/m3	See 120ke 3-35	5 to 20%	B,G,H	
Elemental C	4 to 7 hr.	. 5	Thermal combustion	2.5	.1 10 10	µg/m3	0.08	10 to 25%	D	
Organic C	4 to 7 hr.	. 5	I hermal combustion	20	1 10 50	µg/m3	1.5	10 10 25%	D	
Fine Babs	4 to 7 hr.	. 5	LASER Int. plate on Nuclepore					10 to 25%	C,G	
HM-10		1	SA-321A , quartz filt.	50	5 050	to a fear	FO	70/	A	12
Mass	24 hr.	1	Gravimetric	50	3-250	μg/m3	8.0	/%	Ą	
S04=	24 hr.	1	KC .	5	0.5-25	µg/m3	0.06	7%	Ą	
NC3-	24 hr.	1	AC	8	0.5-30	µg/m3	0.09	1%	A	
AEROSOL SIZE R	ESOLVED	CHEMIST	RYH	-	A AF 23				-	
SO4=	4 to12 h	r. 4	Berner LPI & IC	2	0.25 10 10	μg/m3	U.4***	/%	• D	
NO3-	4 to 12 h	r. 4	Berner LPI & IC	2	0.25 10 10	µg/m3	0.8***	7%	D	
CH-	4 to12 hi	r. 4	Berner LPI & IC	2	0.25 to 10	µg/m3	0.8***	7%	D	
H+	4 to12 h	r. 4	Berner LPI & electode	NA	NA A OCTO A	μg/m3	NA	NA	D	
NH4+	4 to 12 h	r. 4	Berner LPI & AC	2	0.25 10 10	µg/m3	0.8***	(%	D	
Na+,K+	4 to12 h	r. 4	Berner LPI & IC	2	0.25 10 10	μg/m3	0.08***	/%	D	
Elemental carbon	4 1012 h	r. 4		0.5	V.2 10 4	µg/m3	U.8	101025%	U U	13
Organic Carbon	4 to12 h	r. 4	MOUDI & therm, comb.	1.5	1108	μg/m3	U.Z." Cimiles in Table 0.61	10 10 25%	Ð	
Hements	4 10 7 hr	: 5	URUM & PIXE			no/mis	OUTHER TO 18DIE 3-3D	5 1D 2U%	15.F	14

* Units apply to both ambient concentrations and the lower quantifiable limit. * Precision for values well above the lower quantifiable limit. *** µg/m3 per stage

†Measurements made only at Claremont, Downtown L.A., Long Beach, and Rubidoux. ††Measurements made only at Claremont, Long Beach, and Rubidoux.

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Element symbol	Lower Quantifiable Limit (ng/m ³)*
Na	91
Mg	5
AĬ	7
Si	8
Р	3
S	12
C1	5
к	5
Ca	10
Ti	5
V	8
Cr	58
Mn	12
Fe	25
Ni	14
Cu	25
Zn	12
As	19
Se	27
Br	24
Sr	49
Мо	117
Cd	2
Ba	7
Hg	52
РĎ	96

Table 3-3b. Lower Quantifiable Limits for EPA's Wavelength Dispersive X-ray Fluorescence Analysis of Aerosol Deposits on Teflon Membrane Filters.

*Assumes 34 lpm flow for 4 hrs. through 47 mm diameter filter. Detection limits are twice the standard deviation of several blank filter background spectra. Excitation is with: Cr anode, 54 KeV, 46 ma, 30mm diameter analysis area, and 20 to 100 sec. count times.

Table 3-3c. C_1 to C_{10} Hydrocarbons Measured by GC/FID

Ethane Ethylene Acetylene Propane Propene i-Butane i-Butane 1-Butene n-Butane trans-2-Butene 2,2-Dimethylpropane cis-2-Butene 3-Methy1-1-butene i-Pentane 1-Pentene 2-Methyl-1-butene n-Pentane Isoprene trans-2-Pentene cis-2-Pentene 2-Methy1-2-butene 2,2-Dimethylbutane Cyclopentene 4-Methyl-1-penetene Cyclopentane 2,3-Dimethylbutane 2-Methylpentane 3-Methylpentane 2-Methyl-1-pentene 1-Hexene n-Hexane trans-2-Hexene 1,3,5-Trimethylbenzene 1,2,4-Trimethylbenzene cis-2-Hexene Methylcyclopentane

2,4-Dimethylpentane Benzene Cyclohexane 2,3-Dimethylpentane 3-Methylhexane 2,2,3-Trimethylpentane n-Heptane Methylcyclohexane 2,4-Dimethylhexane 2, 3, 4-Trimethylpentane Toluene 2,3-Dimethylhexane 2-Methylheptane 3-Ethylhexane n-Octane Ethylcyclohexane Ethylbenzene p-Xylene m-Xylene Styrene o-Xylene n-Nonane ∝-Pinene i-Propylbenzene n-Propylbenzene 3-Ethyltoluene 2-Ethyltoluene 1, 3, 5-Trimethylbenzene 1-Ethyltoluene **β-Pinene** Myrcene 1,2,4-Trimethylbenzene & sec-Butylbenzene ∆³-Carene ∝-Terpinene d-Limonene *v***-Terpinene** Terpinolene

- A Already available at the B-sites.
- B Method in general use because of its sensitivity, accuracy and relative freedom from interferences. Accuracy and precision have been evaluated with field data.
- C Only method available with adequate sensitivity.
- D ARB Nitrogen and Carboneous Species Methods Comparison Studies showed consistent results.
- E Method has been evaluated in previous field studies.
- F Equipment cost-effectively available.
- G Other criteria being equal, initial and operating costs are minimized.

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H Method to be provided by a sponsor.

- 1. Na₂CO₃/glycerine impregnated Whatman 541 cellulose fiber filter for sulfur dioxide. The lower quantifiable limit is small and the method has been characterized (Forrest et al., 1981) and used in the field.
- 2. Oxalic acid coated denuder tube with backup filter impregnated with oxalic acid (Ferm, 1979).
- 3. MgO-coated denuder difference method for nitric acid (Appel, Tokiwa, and Haik, 1981).
- 4. 2,4-dinitrophenylhydrazine (DNPH) absorbing cartridge for carbonyls (Levin et al., 1985; Fung and Grosjean, 1982).
- 5. Hydrocarbons are pumped into canisters for later laboratory analysis by GC/FID. There is less adsorption and desorption of hydrocarbons in electropolished stainless steel canisters than in bags (Grosjean and Fung, 1984).
- 6. Electron capture gas chromatography (EC-GC) for PAN (Stephens, 1969b). Units are calibrated and operated continuously in the field.
- 7. Para-hydroxy phenylacetic acid horseradish peroxidase method for gas phase hydrogen peroxide (Lazrus et al., 1986; Kok et al., 1986; Heikes et al., 1985). Samples are collected in bubblers.
- 8. Climet optical particle counter, PMS ASASP-X, and electrical aerosol analyzer (EAA) determine aerosol size distribution data in the 1 to 10 μ m, .09 to 3 μ m, and 0.003 to 1 μ m size ranges, respectively.
- 9. Integrating nephelometer measures scattering of light by particles.
- 10. Microcomputer data acquisition system. Flexible and cost effective. Data can be recorded in a format which can be read by most laboratories, so adding data from other experiments is possible.
- A specially designed aerosol sampling system has been constructed for SCAQS. The SA-254 size selective inlet is for <10 μm particles (Olin and Bohn, 1983) and the Bendix 240 cyclone is for <2.5 μm particles (Chan and Lippman, 1977) at 113 l/min flow rates.
- 12. Hi vol sampler with SA-321A 10 μ m inlet. This inlet may pass some large particles.
- 13. The MOUDI Impactor (Marple and Rubow, 1984) collects submicron particles in defined size ranges on aluminum foils for subsequent carbon analysis.
- 14. The DRUM Impactor acquires submicron-sized samples on mylar films which are submitted to PIXE analysis.

AA	- Atomic Absorption Spectroscopy
AC	- Automated Colorimetry
Bendix 240	- Cyclone with 2.5 μ m cut-point at 113 1/min flow rate
DNPH	- 2,4 dinitrophenylhydrazine
DRUM	- Davis Rotating Universal Multistage Impactor
EAA	- Electrical Aerosol Analyzer
GC/EC	- Gas Chromatography with Electron Capture Detection
GC/FID	- Gas Chromatography with Flame Ionization Detection
IA	- Inapplicable
IC	- Ion Chromatography
LPI	- Low Pressure Impactor
MOUDI	- Multi-Orifice Uniform Deposit Impactor
NA	- Not Available
NDIR	- Non-Dispersive Infrared Absorption
OPC	- Optical Particle Counter
PIXE	- Proton-Induced X-ray Emission Spectroscopy
SA-254	- Sierra Andersen size-selective inlet with 10 μm cut-point at 113 l/min.
SA-321A	- Sierra Andersen two-stage size-selective inlet with 10 µm cut-point at 1130 1/min.
WDXRF	- Wavelength Dispersive X-ray Fluorescence

samples to match the every sixth-day 24 hour PM-10 samples, which are changed at midnight standard time year round. Carbonyl absorbers and hydrocarbon canisters will collect one hour samples starting at 0700, 1200, and 1600 local time; and hydrogen peroxide samples will correspond to the particle sampling schedule except that hourly samples will be taken from 1400 to 1800. High volume PM-10 samples will be of 24-hour duration and will be changed at midnight. MOUDI and Berner LPI samples will be changed at 0600, 1000, 1400, and 1800. The sample durations and changing times have been selected as a compromise between: 1) the amount of time needed to obtain a detectable deposit, 2) minimizing the number of samples to reduce costs, 3) manpower deployment among the different instruments, 4) correspondence of measurement periods, and 5) temporal resolution required for modeling and data interpretation. Though the schedule cited above is not perfect, it is a reasonable compromise between these five requirements.

The B-site stations can be operated by one trained technician. For intensive study days, two technicians working overtime will operate the stations continuously. Having the stations manned full time will enable immediate identification of problems and rapid correction. In addition, it removes the requirement for automatic sequencing of filter sample devices. The technicians will primarily perform the routine station operations and will not be responsible for repairs. A separate, highly knowledgeable technician will be on call for repairs, and spares for critical components will be available at a central location.

A data acquisition system is included in Table 3-3a under the Aerosol Physical Property heading. A personal computer-based system has been designed to control the aerosol equipment and to record all continuous data.

A simplified flow diagram of the SCAQS Sampler is shown in Figure 3-5. This sampler has been designed to meet the specific requirements of SCAQS for integrated fine- and coarse-particle chemistry measurements and coordinated gas-phase measurements of low-level ammonia, sulfur dioxide and nitric acid. The sampler has also been designed to make it easy for the technician to change media for sequential samples and to document all necessary parameters for each sample. Two sets of sampling cassettes will be available at each site so that the technicians can load cassettes between sampling periods and can quickly switch cassettes at sample change times. The cassettes and media holders used for sampling and transport are all color coded, and an extensive media documentation scheme has been developed to minimize problems from sample handling errors.

A-Site Measurements

The primary measurements planned for the A-sites during the summer are summarized in Tables 3-4a through 3-4c. The fall A-site measurements will be finalized later. Many of the measurements listed are quite experimental in nature and are really special studies in themselves. Some of the measurement methods indicated in the table are unique to one investigator or group. Table 3-4a is organized in the same fashion as Table 3-3a for the B-sites, except that ambient concentrations, lower quantifiable limits, and precision are not included, since most of the techniques are still experimental. The measurements listed in Table 3-4 were suggested by the sponsors and technical reviewers and were refined to reflect the consensus of SCAQS participants. The



Figure 3-5. SCAQS Sampler for Gas and Size-Selective Aerosol Sampling.

Table 3-4a.	Additional Measurements at A-Sites During the Summer
5 C	(See Table 3-4b for abbreviations)

6/6/87		,			
Observable	Dur- ation	No. per site-day	Site(s)*	Potential meas. method	Reason for Selection
GASES					
C1-C10 HC	1 hr.	3 more, 6 total	C. LB	Canister & GC/FID	A
C2-C12 HC	3 hr	1:2	LB. LA: C	Canister & GC/FID	E
Halocarbons	6 hr	4	, <u>-</u> ,, C	GC/EC	Ē
Carbonvis	t hr	3 more 6 total	C I B	DNPH absorber	Ā
Carbonyis	3 hr	1:2	LB. LA: C	DNPH absorber	Ä
Methyl & ethyl alcohol	4 to 7 hr.	5	C LB	Charcoal absorber/thermal/impinger/GC-EC	F
Formic, acetic acid	4hr	8	-,	Impreg. filter - IC	Ē
HONO HCHO NO2	15 min	80	CIB	DOAS	BCF
HNO3	A to 7 hr	5	C C	DDM/IC TER/IC luminol detection	E,0,1
H2O2 HNO3	Cont	24	č	TDIAS	8 F
PAN NO2	∆/br	24	č	GC/Umipol	3,0
HNO3, HNO2	_4 to 7 hr.	5	č	Annular denuder, IC	Ē
545444 G					
RADICALS	4 m		0 L D	0040	•
NO3	15 min.	15	C. LB	DOAS	C .
но	Cont.	24	С	Chem. ampliner	E'F
ORGANIC AEROSOL					
EC, OC	2 hr.	12	С	Filter & thermal-optical	F
Carbon 14 (PM-2.5)	24 hr.	1**	C, LB, R	Accelerator mass spec.	E
Carbon 14 (PM-10)	24 hr.	1***	C, LB	Accelerator mass spec.	E
Organics	4 to 7 hr.	5	С	LPI & FTIR	E
INORGANIC AFROSOL					
Water			C.R	TDMA: heated neohelometer	F
Acidity, SO4-	4 to 7 hr	5	C C	Titration & IC	F
S speciation	Cont	24	- EB	Thermal/NH3 & FID	F
SO4- NO3-	4 in 7 hr	5	č	Annular depuder & IC	Ē
PM-10 ions	12	2	č		5
Br Pb	5 hr	1	č	WNYRF	
Elements: EC. OC: SO4- NO3-	4 to 7 br	5	č	Dicote & WDXRE: thermal combustion: IC	C E
SOA_ MO2-	15 min		č	I Pl & fash vacor /EPD_IC	E .
Flomente	A to 7 hr	5	CIRP	IMPROVE & DIVE	FF
Dry deposition	12 5 4		0, LD, H	IC on surrousts surfaces & vegetation	E , F
	04 hr	<u>د</u>	č	Deposition plato/gravimetric: IC	Ē
Coorco mose: SO4=, NO3-	24 IU.	5	č	Botani impactor/gravimetric; IC	с С
Coarse mass; SO4=, NO3-	4 10 7 111.	5	C	Hotary impactor/gravimetric, ic	E
AEROSOL PHYSICAL PROPERTIES	•		_		_
Light absorption	Cont.	24	Ç	Spectrophone	E
Light absorption	4 hř.	6	С	Filter reflectance	E,F
Light absorption, abs. vs. RH	Cont.	24	С	Filter transmission (Aethalometer)	E,F
Path transmittance & radiance	Cont.	13	С	Radiance difference	E
Light extinction	Cont.	13	С	Telephotometer	E
Size vs. RH, vs. reactive gas	15 min.	3	С	TDMA	E,F
Light scattering vs. RH	-15 min.	3	C, R	Heated nephelometer	E,F
Detailed fine part. size distribution			C	Electical classifier	E
INDIVIDUAL PARTICLES					
Size & chem. comp.				Electron microscopy; microprobe; GC/MS	C,F
071/00					
UINER	016-		<u>^</u>		F
Mutagens	24 Df	1		Contains & Today have COTO	С (г
I DXIC AIR CONTAMINANTS	24 Nr.	1	U, LB, LA, H	Canister & regiar bags- GC/FID	E ·
Call. Dry Deposition Sampler	12 hr.	2	U A		5
Operational Evaluation Network Sampler	12 hr.	2	C		E

*For sites, C is Claremont, LB is Long Beach, LA is Los Angeles, R is Rubidoux. **Analyze only 24 of 36 samples. ***Analyze only 7 of 24 samples.

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AA	- Atomic Absorption Spectroscopy
AC	- Automated Colorimetry
DDM	- Denuder Difference Method
DNPH	- 2,4 Dinitrophenylhydrazine
DOAS	- Differential Optical Absorption Spectroscopy
EC	- Elemental Carbon
FPD	- Flame Photometric Detector
FTIR	- Fourier Transform Infared Spectroscopy
GC/EC	- Gas Chromatography with Electron Capture Detector
GC/FID	- Gas Chromatography with Flame Ionization Detector
GC/Luminol	- Gas Chromatography with Luminol Detector
GC/MS	- Gas Chromatography/Mass Spectroscopy
IC	- Ion Chromatography
LPI	- Low Pressure Impactor
OC	- Organic Carbon
PIXE	- Proton-Induced X-ray Emission Spectroscopy
TDLAS	- Tunable Diode Laser Absorption Spectroscopy
TDMA	- Tandem Differential Mobility Analyzer
WDXRF	- Wavelength Dispersive X-ray Fluorescence

Table 3-4c. Key to Reasons for Selection

A	Extension of measurements already made at B-sites.
В	This species also measured by instrument chosen to measure another species.
С	Method has adequate sensitivity, accuracy, freedom from interferences.
D	To increase the variety of elements determined.
Ε	Method provided by a sponsor.
F	Equipment availability.

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criteria for selection of measurement methods were similar to those for the B-sites, even though many of the methods are quite experimental. Most A-site measurements will be made by individual investigators.

Since the A-sites are collocated with B-sites, the B-site measurements from Table 3-3 will also be performed at the A-sites. Two of the A-site measurements will be augmented. Three extra one hour C_1-C_{10} hydrocarbon and carbonyl samples will be obtained each day. The six total sets of samples will be collected starting at 0500, 0700, 0900, 1200, 1400, and 1600 local time on intensive study days.

In addition to the measurements listed in Table 3-4, many investigators are planning studies which are complementary to the primary SCAQS measurements and which will be located at the A-sites. A list of participants which includes those investigators identified by May 8, 1987 is included in Appendix A.

Complementary Toxic Air Contaminants Measurements

Toxic air contaminants will be measured at four SCAQS sites (Claremont, Long Beach, Los Angeles, and Rubidoux) during the summer field intensives. Two of these sites (Los Angeles and Rubidoux) are part of the ARB toxic network. These 24-hour samples will be taken in both stainless steel canisters and in tedlar bags. The compounds which will be measured are listed in Table 3-5. Also included as part of this project are replicate samples for analysis by multiple groups and an exchange of toxic gas standards.

3.5 AIRBORNE AIR QUALITY AND LIDAR MEASUREMENTS

Airborne measurements are required to determine the pollutant distributions in the vertical dimension. They are especially important for documenting initial and boundary conditions, pollutant carryover, mixing layer height, representativeness of surface measurements, and nighttime chemistry aloft.

During the summer, two aircraft will be operated during the intensive study days. The spiral aircraft will measure the three dimensional pollutant distribution in the Basin. It will be instrumented with continuous fast response monitoring equipment, as shown in the top of Table 3-6. It will perform three flights per day, in early morning (0500-0800 PDT), mid-day (1000-1300 PDT), and afternoon (1500-1800 PDT). Its flight pattern will include vertical spirals at Burbank, El Monte, Fullerton, Hawthorne, Riverside, Upland, and offshore. The flights will take about 2.5 to 3 hours.

The orbit aircraft will be used in the summer to obtain integrated samples for later chemical analysis as shown in the bottom of Table 3-6. It will also be instrumented with most of the same types of continuous monitors as the spiral aircraft. This aircraft will make one or two flights per day. On one day of each intensive sampling period, it will sample in the early morning (0400-0800 PDT) and in the afternoon (1400-1800 PDT). On other days it will make only a morning flight. Its flight pattern will include about four sampling orbits at constant altitude, and the flights will take 3-4 hours. In the morning, orbits will be made over Long Beach, El Monte, and at two locations offshore. In the afternoon, the offshore orbits will be replaced by inland orbits over Pomona and Riverside. One set of samples will be Table 3-5. Toxic Air Contaminants to be Measured in the Study Region.

Benzene	Methyl bromide
Carbon tetrachloride	Methyl chloroform
Chloroform	Methylene chloride
Chlorobezene	Perchloroethylene
Ethylene dibromide	Trichloroethylene
Ethylene dichloride	Xylene (o-, m-, and p-)

Aircraft Measurements	Time dur/freq	Analytical Methods
03	Continuous over spirals and orbits. Spirals from surface to 5000'	Chemiluminescence
NO		Chemiluminescence
NOX		Chemiluminescence
so ₂		Flame photometric
Light Scattering (multi-wavelength)		Integrating Nephelometer
Temperature		Thermister
Dewpoint		Cooled mirror
Turbulence		Pressure fluctuation
Position		LORAN
Altitude		Pressure sensor
Aerosol Size Distribution	Ļ	OPC (PMS ASASP-X)
Hydrocarbon	In orbits and at selected spiral locations	Canisters - GC/FID
PAN	In orbits only	Impregnated filter, GC/EC
PM-2.5 mass SO4, NO3, C1-; NH4; Na+ SO2 Carbon (elemental and or	ganic)	Bendix 240 cyclone Gravimetric IC; AC; Atomic absorption Impregnated filter Thermal combustion
HNO3		Cyclone/denuder difference
NH3		Oxalic acid impregnated filter
Carbonyls		DNPH absorber
Tracer Samples	Ļ	Mylar bag - GC/EC

obtained for about 30-40 minutes in each orbit. Typically, the samples will be obtained in the inversion layer above the surface layer (about 1000' ag]) in the morning and in the middle of the mixed layer in the afternoon (about 1500'-2000' ag]).

For the fall sampling, one aircraft will collect integrated samples in addition to its continuous measurements. It will perform two flights per day in the morning (0500-0900 PST) and in the afternoon (1300-1700 PST). It will focus its measurements in the western portion of the Basin, performing spirals at about five locations as well as collecting integrated samples in orbits at two locations. The occurrence of fog will restrict some flights. Occasional night flights could be made when fog is not a problem.

In addition to the in-situ airborne measurements, airborne LIDAR measurements will document the three-dimensional pollutant distribution, especially along the slopes and offshore. In conjunction with the surface and upper air winds, the LIDAR will provide useful information on the fluxes into and out of the basin at the boundaries and on pollutant ventilation and carryover processes. LIDAR flights will be made in early morning and in mid-afternoon during intensive study days. The morning flight will document layers carried over from the previous day and will map the offshore boundary conditions. The afternoon flights will document the boundary conditions and ventilation processes.

3.6 EMISSIONS

Our discussions with the modeling community have indicated that the quality of the available emissions data is one of the limiting factors in improving model accuracy. For three-dimensional grid models, an accurate, gridded, time- and species-resolved inventory will be necessary for each day to be modeled. For receptor models, detailed characterizations of the emissions from different sources will be needed for source identification (especially organics and trace metals).

To address the overall emissions issue, an Emissions Working Group (EWG) was formed. The group consists of university, industry, and government members and is responsible for providing the SCAQS emissions inventory. The EWG will design and execute studies to examine the accuracy of existing inventories and will coordinate special studies to improve these inventories. The EWG members are listed in Appendix A.

Emphasis will be on those species most important for oxidant and aerosol formation including organic and inorganic gases and size-resolved particulate matter. The basis for the SCAQS inventory will be the scheduled 1987 inventory update for the South Coast Air Basin to be prepared by the SCAQMD and the ARB. This inventory will be refined as necessary to include the results of special inventory characterization studies and emissions information specific to the intensive days of the SCAQS field program. The characterization studies are aimed at quantifying and reducing the uncertainties in the inventory, and thus obtaining a more accurate characterization of emissions in the Basin. The EWG will work closely with both the SCAQMD and CARB during this process. The overall plan for compiling the SCAQS inventory is contained in a planning study (Oliver et. al., 1987) which identifies procedures and a schedule for developing the emissions data base. Two primary objectives were associated with the planning study:

- 1) To analyze available options and techniques for compiling emissions data and developing the data base; and
- 2) To develop a detailed work plan and schedule for establishing the SCAQS inventory data base.

The planning study focused greatest attention on 17 specific topics in four general areas:

- Day-specific emissions data needs.
- Procedures for estimating on-road motor vehicle use and emissions.
- Data base schedule.
- Hydrocarbon and particulate speciation.

The 17 specific topics are listed in Table 3-7.

The purpose of collecting day-specific emissions data is to focus on operating conditions and other characteristics that might lead to a significant difference in expected emissions from the average day. Much of the future air quality modeling for the Basin will center on specific days using meteorological and air quality data from SCAQS intensive periods. The EWG's objective is to construct a set of emission inventories that are as representative as possible of actual emission levels on the selected days. Therefore, using the day-specific emission-related data, the average inventory will be modified to represent the particular days in 1987 to be modeled. Since all sources cannot be "monitored" during the intensive periods, the major emission sources will receive primary emphasis under the day-specific data collection effort. In particular, the data will include traffic counts and monitoring of traffic flow, hourly power plant emissions, non-routine operating conditions at major stationary sources (including refineries and airports), a review of source data at the SCAQMD, and checks for unusual natural phenomena during intensive days (such as high winds, fog, storms, and fires).

The EWG planning study (Oliver et al., 1987) recommends a number of special studies to evaluate and reduce uncertainties in the 1987 SCAQS inventory. The details of these special studies and their priorities will be reviewed and refined by the EWG.

The EWG is working with the ARB and the SCAQMD on the details of the SCAQS inventory development schedule. The recommended schedule calls for the completion of the 1987 inventory update by the second quarter of 1990. The SCAQS inventory will then be ready for modeling applications by the third quarter of 1990. This four year overall schedule and its intermediate milestones represent a more aggressive but still realistic approach for completing the inventory than would exist in the absence of the SCAQS program.

Table 3-7. Emissions Working Group Planning Study Topics

- 1. Data Base Schedule
- Emission Inventory Preparation Process
 Results from Model Sensitivity Runs
- 4. Motor Vehicle Emission Factors
- Stationary Source Emissions 5.
- 6. Aerosol Characterization Data
- Uninventoried Sources 7.
- Small Hydrocarbon Sources 8.
- Area Source Gridding 9.
- Vehicle Use Data 10.
- 11. Evaporative Emissions
- 12. Road and Soil Dust Emission Factors
- Temporal Resolution 13.
- 14. HC/NO_X Ratio
- 15. Two Versus One Data Bases
- 16. Day-Specific Data Needs
- 17. Inventory Uncertainties

Meeting this schedule will likely require modifying some priorities in the SCAQMD and ARB inventory preparation programs.

3.7 METEOROLOGICAL MEASUREMENTS AND FORECASTING

A Meteorology Working Group was formed to address the ground and upperair meteorology measurements that are needed for SCAQS, to develop a forecasting team and protocol, and to help design the proposed tracer studies. Members of the Meteorology Working Group are listed in Appendix A. The meteorology measurements described below reflect the recommendations of the working group.

3.7.1 Surface and Upper Air Measurements

A major concern of the modeling community is that adequate characterization of the three-dimensional wind field be performed. Extensive routine surface data exist in the study area as indicated in Figure 2-1, but upper air data are quite limited. Also, the meteorology of the offshore regions should be characterized to document offshore ventilation, carryover, and re-entrainment processes. New offshore measurements are expensive, but data from existing offshore sources will be acquired and included in the data base. Additional measurements will be made on Catalina and San Nicolas Islands. Some offshore meteorology measurements will also be avaliable from the aircraft.

The routinely-available surface and upper air meteorology data for the study period will be acquired by the data management contractor and included in the data archives. The special SCAQS meteorology measurements during the summer study include:

- one doppler acoustic sounder on intensive study days at the Long Beach A-site;
- airsondes six times per day on intensive study days at Glendora and near Anaheim;
- rawinsondes six times per intensive study day at Burbank, El Monte, Hawthorne, Long Beach, Loyola-Marymount University, Ontario, and Riverside;
- surface wind stations at elevated locations on all study days at Catalina Island, Henninger Flats, Kellogg Hill, and Palos Verdes; and
- time-lapse cameras at Mount Wilson and Palos Verdes.

The upper air measurement sites are shown in Figure 3-4. The airsonde and rawinsonde soundings will be made at 0500, 0800, 1100, 1400, 1700, and 2200 PDT in the summer. The measurement sites for the fall program have not yet been selected. The fall sounding times will be the same as the summer times in PST, i.e. the first sounding will be at 0400 PST.
3.7.2 Forecast and Decision Protocol

The forecasting team will issue a meteorology and air quality forecast each afternoon for the following two-day period. The forecast of PM-10 and ozone concentrations will be in terms of three categories, low, medium, and high, based on the historical distribution of ozone daily maxima and PM-10 24-hour average concentrations. The categories, with their associated cut points, are:

	High (75th percentile)	Medium (50th percentile)	Low
PM-10 (24 hr. avg.)	>105 µg/m ³	>88 µg/m ³	<88 µg/m ³
Ozone (max. hr.)	> 24 pphm	>19 pphm	<19 pphm

Days when either PM-10 or ozone are predicted to be in the high category, or when both are predicted to be in the medium category will be considered as acceptable for sampling.

The decision to start intensive sampling will be made by the Program Coordinator, based on the forecast and on the logistical readiness of the investigators and equipment. Nominally, the sampling periods will be for two days, but one- or three-day periods are possible. There will be at least a one day rest period between intensive sampling periods.

The decision to sample will be made after the afternoon forecast (about 1600 local time) for the sampling period which starts at 0000 PST the next night (about 32 hours later). If a decision to sample is made, the intensive sampling may be cancelled the next day after the forecast in the afternoon before the sampling is to start (~ 8 hours in advance).

For each intensive study day, meteorological summaries will be prepared which document cloud locations, bases, thicknesses, and durations; mixing height and inversion strength as available from temperature, wind, and acoustic sounder data; the synoptic conditions; and any unusual weather occurrences.

3.8 SPECIAL STUDIES

Some of the stated project objectives cannot be met with the monitoring data alone. Several special studies will be performed to address specific questions. Some of these are outlined below, but the details of their designs are not included in this plan. Most of these special studies are either selfcontained data acquisition and intepretation projects or are enhancements to the existing SCAQS measurements.

3.8.1 Perfluorocarbon and SF₆ Tracer Releases

Two types of tracer tests will be performed during the SCAQS summer sampling period. One series of tests will evaluate the relative impact of elevated and ground-level emission sources on ground-level concentrations of ozone, NO_2 and PM-10. Four unique perfluorocarbon tracers will be used for these tests. Simultaneous releases will be made from a 200 foot stack at a coastal generating station near Long Beach and from ground level near the stack. One pair of tracers will be released from 0400-0900 PDT during offshore flow and the other pair during onshore flow from 0900-1600 PDT. Perfluorocarbon concentrations will be measured at 50 sites throughout the Basin during the next 36 hours. Three tests will be made to examine periods with high PM-10, high ozone, and moderate ozone.

The second series of tests will involve shorter time scale releases and measurements of SF6. These SF6 releases are designed to provide data to test and evaluate the dispersion and windfield components of air quality simulation models. One of these tests will involve a one hour release during conditions of light offshore flow and a low inversion. The release will be made during the early morning traffic peak in an area of high mobile source emissions in the western portion of the Basin. Hourly average measurements will be made at about 25 sampling locations for the next 12 hours. Grab samples will be taken in a series of automobile traverses to map the plume as it transports downwind.

A second SF₆ test is designed to determine the effect of aged ozone layers aloft on surface ozone concentrations later in the day. SF₆ will be released into an ozone reservoir above the surface mixed layer in the early morning. The release will probably be in the vicinity of El Monte. Sampling will take place at 25 surface sites for 12 hours or more after the release. If the first two SF₆ tests work out and sufficient funds are available, a third SF₆ release will be made into a late evening stagnant air mass in the western basin, and sampling will be conducted overnight and into the next day.

3.8.2 Fog Chemistry Measurements

Fog is known to play an important role in the formation of aerosol in the SOCAB. To better understand the interactions of fog and smog, fogwater samples will be obtained during SCAQS. Active strand cloudwater collectors will be located in fogs to acquire enough sample to quantify the liquid water content, anions and cations, aldehydes, organic acids, S(IV), and hydrogen peroxide. These intermittent measurements may not correspond to SCAQS sampling days because fogs may not occur on these days. The geographical and temporal distribution of these measurements in fogwater can be used with other SCAQS measurements in support of the chemical mechanism modeling project.

3.8.3 Effects of Relative Humidity on Aerosol Composition and Visibility

The liquid water content of suspended particles, as noted in Section 2, has an important influence on secondary aerosol formation mechanisms as well as on visibility reduction. A tandem differential mobility analyzer (TDMA), a nephelometer thermidograph, and a varying humidity aethalometer will be operated during the SCAQS program to determine the effects of changes in relative humidity on aerosol properties. The TDMA will determine changes in the aerosol size distributions at different relative humidities. The difference in computed particle mass for zero and ambient humidities is an approximation of the liquid water content of the aerosol. These measurements will be made at the Claremont A-site. The thermidograph will be used to quantify the influence of ammonia emissions on the hydroscopic properties of SOCAB aerosols. These measurements will be made at the Rubidoux and Claremont sites. The aethalometer will be used in conjunction with a variable dew-point humidification chamber and size selective aerosol sampling to determine the response of carbonaceous species to changes in relative humidity. A reference which produces known quantities of liquid water will be available as a standardization and audit device for these measurements.

3.8.4 Deposition Fluxes

Large particles deposit at the ground by gravitational sedimentation, while small particles and gases deposit by turbulent transport to and absorption at the ground. A rotary impactor will be operated at the Claremont site to determine the concentrations of large particles (greater than ten microns) which are potentially present for deposition. This will be accompanied by a greased deposition plate to measure the quantity of particles which actually reach the ground. Sedimentation velocities can be calculated from these two measurements for use as parameters in particulate modeling. Deposition fluxes of small particles and acidic gases will also be determined by measurements on aerodynamic surrogate surfaces and vegetation at the Claremont site. These deposition fluxes can be combined with the ambient concentrations to infer deposition velocities for fine particles and gases.

3.8.5 Acidic Species Sampler Methods Evaluation

The ARB has conducted measurement method comparisons for nitrogenous and carbonaceous species. The acidic species comparison will be the third in this series of method evaluations. The B-site SCAQS observables include several which are also being incorporated into national and state dry deposition monitoring networks. Several non-SCAQS sampling and analysis systems will be compared during the SCAQS summer period with the collocated SCAQS measurements at Claremont. The transition flow reactor from EPRI's Operational Evaluation Network, EPA's version of the transition flow reactor, University of Denver's continuous nitric acid analyzer, ARB's dry deposition sampler, EPA's annular denuder, a turnable diode laser absorption spectrometer, a denuder difference method, and several other samplers will be operated simultaneously with the SCAQS sampler. Additional samples will be taken during non-intensive sampling periods to measure low as well as high pollution events. The data from this comparison will be used to evaluate the precision, accuracy, and validity of measurement methods used in SCAQS and in other studies.

3.8.6 Visibility Measurement Comparison

SCAQS also will provide an opportunity for a visibility measurement methods comparison. Several of the measurements cited with respect to relative humidity noted in Section 3.8.3 will provide visibility outputs and will be useful in determining the effects of different instrumental changes in humidity on visibility measurements. The B-site b_{abs} and nephelometer measurements are also available for comparison. In addition, long-path measurements of transmittance and path radiance will be made using a radiance difference technique, and contrast measurements will be made with teleradiometers. The information from this comparison will be used to address Objective 6, dealing with the validity and uncertainty of measurement methods. It will also allow the testing of visibility modules in air quality models.

3.8.7 Captive Air Experiments

While the testing of photochemical airshed simulation models will need all of the SCAQS measurements as a function of space and time, the testing of individual chemical mechanisms can be more easily addressed by more highly controlled experiments. Up to eight 450-liter transparent FEP-Teflon chambers will be filled in the morning and subjected to natural radiation until sundown on SCAQS intensive sampling days. Ambient air or prepared mixtures along with different initial concentrations of NO_x and ROG will be placed in the chambers, and the reaction products will be continuously monitored throughout the experiments. The experiments will be conducted at the downtown Los Angeles and the Claremont sites. The data from these experiments will be used to test different photochemical mechanisms for their potential incorporation into air quality models.

3.8.8 Fate of SOCAB Pollutants

The SCENES visibility study (Mueller et al., 1986) is concerned with the potential impacts from distant urban areas in the National Parks of the southwestern United States. Two studies will be conducted outside of the SOCAB to determine the chemical characteristics and the transport routes of air leaving the Basin. The Greater Los Angeles Distant Impact Study (GLADIS) will make continuous measurements of seven halocarbons, surface meteorology, and b_{scat} at Cajon Pass throughout the SCAOS period. GLADIS will also launch airsondes in the pass area. The SCENES summer intensive study will make intensive chemical measurements of halocarbons, fine particle chemistry, and particle precursors during outflow periods at Cajon Pass. A SOCAB chemical source signature of gaseous and particulate species will be measured to determine its chemical character and variability. Measurements will also be taken at distant receptors at Spirit Mountain, NV, and Hopi Point, AZ, to determine whether or not species in the SOCAB source signature can be detected. A continuous 15-station pibal network will take upper air measurements every six hours throughout the SCAQS summer period, and a primitive equations transport model will be applied to these pibal data and to SCAQS meteorological data to determine those trajectories which correspond and those which don't correspond to SOCAB contributions at the distant receptors. The SCAQS perflurocarbon detection network described in Section 3.8.1 will be extended to these receptors to verify the model predictions of impact or nonimpact from the SOCAB. This study will help complete a pollutant mass balance of atmospheric constituents in the SOCAB.

3.8.9 Mobile-Source Emissions Measurements

One of the most uncertain components of the emissions inventory is the mobile-source component. Field studies are planned in both a tunnel and a parking garage in order to improve the estimate of motor-vehicle emission factors. By making measurements in both tunnel and garage situations, these studies will estimate emission factors representative of tailpipe, evaporative, and wear-debris emissions under a variety of driving conditions, and with a realistic mix of vehicles. Chemical and physical measurements will be consistent with similar measurements being made during the SCAQS field studies. The vehicle emission factors estimated from this special study will be used to improve the existing estimates in emission inventories.