SCOS97-NARSTO
1997 SOUTHERN CALIFORNIA OZONE STUDY AND AEROSOL STUDY

VOLUME I: OPERATIONAL PROGRAM PLAN

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Volume I: Operational Program Plan

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ABSTRACT

The California Air Resources Board (ARB), San Diego County Air Pollution Control District (SDAPCD), South Coast Air Quality Management District (SCAQMD), Ventura County Air Pollution Control District (VCAPCD), U. S. Environmental Protection Agency (EPA) - Region IX, and the U. S. Navy are planning the 1997 Southern California Ozone Study (SCOS97). The goals of the study are to update and improve the existing aerometric and emission databases and model applications for representing urban-scale ozone episodes in southern California, and to quantify the contributions of ozone generated from emissions in one southern California air basin to federal and state ozone standard exceedances in neighboring air basins. These goals are to be met through a five-year process which includes analysis of existing data; execution of a large-scale field study to acquire a comprehensive database to support modeling and analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for southern California. SCOS97 is intended to provide another milestone in the understanding of relationships between emissions, transport, and ozone standard exceedances in southern California as well as to facilitate planning for further emission reductions needed to attain the NAAQS.

This field study plan summarizes existing information on emissions, summer ozone climatology, current air quality, and provides a conceptual model for the ozone episodes and transport scenarios of interest. It specifies a core measurement program along with optional elements to meet data requirements for data analysis and modeling. It also describes the required quality assurance, data validation, and data management needs. The field study plan is a working document, and this first draft represents the current status of the planning efforts for SCOS97 as of this date. Suggestions to improve the plan are welcome. Send comments to Mr. Bart Croes (916/323-1534) or Dr. Ash Lashgari (916/323-1506) of the ARB at the following address:

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1. INTRODUCTION

Southern California experiences the most severe smog in the United States. Extremely high concentrations of ozone and suspended particles result from the combination of emissions from the second largest urban area in the U.S. (after the northeast corridor), high mountains that contain air pollutants, and adverse meteorology which limit atmospheric dispersion. For example, prior to the implementation of emission reduction measures in the early 1950s, hourly averaged ozone concentrations approaching 0.70 ppm were reported in the South Coast Air Basin (SoCAB or Basin), and Stage III episodes (ozone exceeding 0.50 ppm) were relatively frequent events in the 1960s. As a result of three decades of progressively more stringent controls on emissions of reactive organic gases and oxides of nitrogen, the frequency and intensity of excessive ozone concentrations in the SoCAB have been significantly reduced (Davidson, 1993). Azusa, which is located in a main ozone-impacted receptor area of the Basin, recorded 221 days exceeding the National Ambient Air Quality Standard (NAAQS) of 0.12 ppm maximum hourly average in 1960, 190 days in 1970, 129 days in 1980 and 79 days in 1993 (SCAQMD, 1994). This progress has occurred despite a population increase of 84 percent between 1960 and 1990, and associated increases in commercial activities and vehicle miles traveled. Although air quality in the SoCAB has improved significantly, the state and national ozone standards continue to be exceeded frequently in this basin and in other air basins in southern California. Because the relatively easy and most cost effective emission controls have already been implemented in California, attainment of the ozone standards in southern California remains a long-term goal, and air pollution control agencies will face many difficult regulatory issues in the decade ahead.

Historically, the scientific and regulatory communities have learned a great deal about urban smog formation from air quality studies in southern California. The most comprehensive study in the SoCAB was the 1987 Southern California Air Quality Study (SCAQS) (Lawson, 1990). The SCAQS air quality, meteorological, and emission databases provided a rich source of information for understanding the ozone and suspended particle problems in the SoCAB. Similar studies were conducted in the San Diego area (Bigler-Engler and Brown, 1995; Hossain and Kaszuba, 1995), in the South Central Coast (Moore *et al.*, 1991), and in the San Joaquin Valley (Solomon and Silver, 1994). While much of the generally applicable and fundamental knowledge regarding emissions, air pollution meteorology, air pollution chemistry, and receptor concentrations of ozone and suspended particles has been derived from studies of the SoCAB, the complex meteorological and chemical processes taking place in the region under conditions in which high concentrations of ozone are formed above ground level and in which ozone is transported between air basins are still not completely understood.

1.1 Background and Issues

In November 1990, Congress enacted a series of amendments to the Clean Air Act (CAA) intended to intensify air pollution control efforts across the nation. One of the primary goals of the 1990 amendments was an overhaul of the planning provisions for those areas not currently meeting the National Ambient Air Quality Standard (NAAQS). The

NAAQS for ozone is exceeded when the daily maximum hourly average concentration exceeds 0.12 ppm more than once per year on average during a three-year period. The California State standard is more stringent: no hourly average ozone concentration is to exceed 0.09 ppm. The CAA identifies specific emission reduction goals, requires both a demonstration of reasonable further progress and attainment, and incorporates more stringent sanctions for failure to attain the ozone NAAQS or to meet interim milestones.

The 1990 CAA set a new classification structure for ozone nonattainment areas. These classifications are marginal, moderate, serious, severe, and extreme. Each nonattainment area is assigned a statutory deadline for achieving the national ozone standard. Serious areas must attain the NAAQS by the end of 1999, severe areas by 2005 or 2007 (depending on their peak ozone concentrations), and extreme areas by 2010. The San Diego area is classified as serious, the Ventura and Southeast Desert areas are classified as severe, and the SoCAB is the only area in the country that is classified as extreme. The CAA prescribes minimum control measures for each ozone nonattainment area with more stringent controls required for greater degrees of nonattainment.

Emission reduction plans for ozone precursors in serious, severe, and extreme nonattainment areas were due and submitted to the U.S. Environmental Protection Agency (EPA) on November 15, 1994, as a revision to the California State Implementation Plan (SIP). Each ozone plan contains a current emissions inventory, plans for enhanced monitoring of ozone and ozone precursors, and estimation of future ozone concentrations based on photochemical modeling. To ensure a minimum rate of progress, each plan shows a 15 percent reduction in emissions of reactive organic gases (ROG) between 1990 and 1996, an additional 9 percent reduction in ROG by 1999, and 3 percent reductions per year thereafter, quantified at three year intervals to the attainment date.

At the state level, pollutant transport is now a recognized cause of air quality degradation. The California Clean Air Act of 1988 requires the California Air Resources Board (ARB) to assess the relative contributions of upwind pollutants to violations of the state ozone standard in downwind areas. The California Health and Safety Code, Division 26, paragraph 39610(b) states "The state board shall, in cooperation with the districts, assess the relative contribution of upwind emissions to downwind ozone ambient pollutant levels to the extent permitted by available data, and shall establish mitigation requirements commensurate with the level of contribution" (California Air Pollution Control Laws, 1992 edition, p. 14). Previous studies in California have demonstrated pollutant transport between air basins on specific days, but these studies have not quantified the contribution of transported pollutants to ozone violations in downwind areas.

The emission, meteorological, and atmospheric chemistry models, used to develop SIPs for the nonattainment areas on a national level and to quantify inter-basin transport on a state level, have several shortcomings in their representation of the physical and chemical processes involved in ozone formation due to the lack of field measurements to evaluate and refine their capabilities (NRC, 1991). In addition, the field measurements used for input to these models and to evaluate their validity do not adequately represent current emission rates,

chemical composition, and air quality. The SCAQS was conducted almost nine years ago and the South Central Coast Air Basin (SCCAB) has not been extensively studied since the South Central Coast Cooperative Aerometric Monitoring Program (SCCCAMP) in 1984 and 1985. Since the SCAQS, there have been measurable changes in the air quality of the SoCAB based on analyses of the routinely available monitoring data (Fujita, 1992; Davidson, 1993). The 1997 Southern California Ozone Study (SCOS97) is intended to provide another milestone in the understanding of relationships between emissions, transport, and ozone standard exceedances, as well as to facilitate planning for further emission reductions needed to attain the NAAQS.

SCOS97 is being conducted under the Charter of the North American Research for Tropospheric Ozone (NARSTO). The NARSTO program is a public/private partnership, whose membership spans government, the utilities, industry, and academia throughout Mexico, the United States and Canada. Its primary mission is to coordinate and enhance policy-relevant scientific research and assessment of tropospheric ozone behavior and provide a cross-organization planning process for scientific investigations. SCOS97-NARSTO is the latest in series of large-scale field measurement programs addressing the urban ozone problem in North America.

Data collected in SCOS97 will be used to evaluate the ability of photochemical grid models to predict the change in ozone concentrations expected as a result of the change in emissions between 1987 and 1997. The feasibility of such a study was assessed by Stoeckenius *et al.* (1995). Ozone transport in southern California appears to be an important contributor to ozone exceedances, but these contributions have not been quantified. It was not previously possible to model the entirety of southern California owing to the limits of computational resources and the associated costs. More recently, computational power has increased while costs have declined, making regional modeling feasible. Another limitation has been the dearth of three-dimensional aerometric measurements to support regional modeling in the complex terrain of southern California. Recent developments in prognostic meteorological modeling combined with new measurement technologies (e.g., radar wind profilers, ozone lidars, NO_y analyzers) and recent enhancements in the aerometric network in southern California associated with the Photochemical Assessment Monitoring Stations (PAMS) have made it practical to perform modeling studies based on more cost-effective field programs than were previously conceived.

1.2 Goals and Technical Objectives of SCOS97-NARSTO

The goals of the study are to:

1. Update and improve the existing aerometric and emission databases and model applications for representing urban-scale ozone episodes in southern California, with a primary emphasis on high ozone concentrations in the South Coast Air Basin and secondary emphasis on high ozone concentrations in the San Diego Air Basin, the South Central Coast Air Basin, and the Southeast Desert Air Basin.

2. Quantify the contributions of ozone generated from emissions in one southern California air basin to federal and state ozone standard exceedances in neighboring air basins. Evaluate the interaction of transported ozone and ozone precursors, both at the surface and aloft, with emissions in neighboring receptor areas. Apply modeling and data analysis methods to design regional ozone attainment strategies.

These goals are to be met through a process which includes analysis of existing data; execution of a large-scale field study to acquire a comprehensive database to support modeling and analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for southern California.

Specific technical objectives of SCOS97 are as follows:

1. Obtain a documented data set of specified precision, accuracy, and validity that supports modeling and data analysis efforts.

2. Document the frequency, intensity, and character of high ozone concentrations and its VOC and NO_X precursors within and between neighboring southern California air basins, and determine how these have changed over the past decade.

3. Identify and describe transport pathways between neighboring air basins, and estimate the fluxes of ozone and precursors transported at ground level and aloft under meteorological conditions associated with high ozone concentrations.

4. Quantify the uncertainty of emissions rates, chemical compositions, locations, and timing of ozone precursors that are estimated by emission models.

5. Quantify the uncertainty of meteorological models in simulating transport and mixing of precursors and end-products within and between air basins.

6. Quantify the uncertainty of air quality models in simulating atmospheric transformation and deposition.

7. Provide the meteorological and air quality measurements needed to estimate, with stated uncertainty intervals, the contributions from background, regional mixing and transport, and local emitters to ozone concentrations that exceed standards in each of the air basins.

8. Provide the meteorological and air quality measurements needed to estimate the effects of different emission reduction strategies on ozone concentrations within and beyond each air basin, and identify those that cause the greatest reduction in population exposure for the least cost.

1.3 Objectives of SCOS97-NARSTO Field Study Plan

As an integrated study, SCOS97 will characterize prevailing ambient air quality, meteorology, and emissions in southern California. It will develop, test, and apply complex models that establish source-receptor relationships and quantify interbasin transport. This modeling will be performed for the entire region and on major sub-regions by the ARB, the South Coast Air Quality Management District, the SDAPCD, the VCAPCD and others. This SCOS97 field study plan addresses only the ambient measurements needed to support this work for the summer of 1997. The specific objectives of this plan are as follows:

1. Review previously acquired data sets and the published documents to develop a conceptual model of important meteorological and chemical processes associated with elevated ozone levels in southern California, and to refine it as new information becomes available.

2. Define criteria for meteorological and air quality measurements and to identify methods that can meet these criteria.

3. Specify meteorological and air quality field measurements in terms of locations, variables measured, spatial and temporal averaging intervals, precision and accuracy, and measurement period.

4. Outline procedures to collect, archive, and evaluate the quality of available meteorological and air quality data, as well as data acquired during the study period.

5. Propose and test methods to accurately forecast the occurrence of high ozone concentrations associated with different transport pathways for commencing intensive operating periods during 1997.

6. Outline data analysis and modeling activities and the uses of the acquired data by these activities.

7. Estimate costs of different program components and evaluate trade-offs among these components to attain budget constraints.

8. Specify levels-of-effort, necessary monetary expenditures, and responsibilities of participating agencies and contracted investigators.

9. Outline a management and communications structure among project participants.

10. Identify schedules, milestones, and deliverables required to bring the project to successful completion.

The field study plan is an evolving document, and first draft in June 1996 provided a starting point rather than an end-product. A final plan will be issued by March, 1997 to incorporate all of the current information to carry out the field study during the summer of

1997. The field study plan will be accompanied by two other plans for emission modeling and for meteorological and air quality modeling.

The emission plan will describe how to:

1. Develop a spatially and temporally (including day-specific inventories for weekdays and weekends) resolved inventory of emission estimates of ROG, NO_X, and CO from anthropogenic sources.

2. Improve and extend the existing SoCAB biogenic ROG emission estimates to the rest of southern California, and develop estimates of NO_X emission from fertilized soils and ROG emissions from geogenic sources.

3. Develop, evaluate, and apply methods to propagate ROG, NO_X, and CO emission inventory uncertainties.

4. Project the effects of future activity and alternative controls on emission estimates.

5. Acquire, archive, and manage activity data from which emission estimates can be developed.

6. Estimate costs, schedules, and responsibilities for emission modeling activities.

The modeling plan will describe procedures to:

1. Evaluate and select existing modeling codes and recent innovations in computation methods to determine the optimal software and hardware platforms for meteorological and chemical simulation.

2. Specify model domain boundaries, grid sizes, layers, and surface characteristics.

3. Identify performance measures and performance evaluation methods, and specify methods by which these will be applied.

4. Estimate costs, schedules, and responsibilities for meteorological and air quality modeling activities.

1.4 Management Structure

SCOS97-NARSTO will be a large undertaking involving many contractors, sponsoring organizations and governmental agencies. In a cooperative study such as this, no one person can have direct management authority over all phases of the study. Since direct fiscal responsibility will remain with the California Air Resources Board (ARB), South Coast Air Quality Management District (SCAQMD), San Diego Air Pollution Control District (SDAPCD), Ventura County Air Pollution Control District (VCAPCD), Mohave Desert Air

Quality Management District (MDAQMD), United States Navy, Coordinating Research Council (CRC), the management structure for SCOS97 reflects this consortium of sponsors.

The management structure will require at least the following elements.

- SCOS97 Technical Committee. Through consensus, this group sets the goals of the study and makes decisions regarding general study objectives, funding, and selection of contractors. The TC is made up of technical staff members from ARB (Research and Technical Support Divisions), SCAQMD, SDAPCD, VCAPCD, Santa Barbara APCD, MDAQMD, EPA-Region IX, and United States Navy. The Technical Committee will also include other sponsoring organizations. The TC directs the planning efforts and coordinates the technical activities of the contractors to ensure that the measurement, emission, modeling, and analysis activities are coordinated with each other and focused on the study objectives. It does most of the work of writing requests for proposals and evaluating proposals. It reviews the input of the planning, management, and technical contractors and makes recommendations to the management of their respective organizations regarding objectives, funding issues, and contractor selection. The members of this group work closely with the program management team and are involved in or approve most significant technical decisions. Individual members serve as liaison between the sponsors and the contractors and have day-to-day responsibility for such things as overseeing the contractors, approving invoices, and making contractual and management decisions. The membership of the TC is listed in Appendix C.

- Field Program Management Committee. The FPMC will provide the day-to-day technical management during the field study. The FPMC makes decisions regarding intensive operation periods, and contingency funding. This committee includes a single representative from the ARB Research Division (Bart Croes), ARB Technical Support Division (Don McNerny), SCAQMD (Henry Hogo), SDAPCD (Judy Lake - Chair), VCAPCD (Doug Tubbs), U.S. EPA (Carol Bohnenkamp), U.S. Navy (Jay Rosenthal).

- Forecast Team. The forecast team develops the Forecast Plan in conjunction with the field manager, reviews meteorological data, and provides consensus forecasts to the FPMC. The forecast team also documents the daily meteorological conditions during 1997. This team includes a single representative from the ARB (Steve Gouze), SCAQMD (Joe Cassmassi – Chair), SDAPCD (Virginia Bigler-Engler), VCAPCD (Kent Field), and U.S. Navy (Jay Rosenthal).

- Field Managers. The FMs coordinate the activities of the field contractors (in-kind personnel will be under the direction of their management/FPMC members). Jim Pederson (upper-air meteorology), Leon Dolislager (air quality), Dr. Ash Lashgari (surface meteorology, ozone and NOy) and Dr. Randy Pasek (VOC) of the Air Resources Board Research Division will be the FMs and the main contact points to

relay information on measurement readiness status during and between the intensive operational periods (IOPs).

- Quality Assurance Manager. The QA manager is responsible for developing the QA plan in conjunction with the field managers and field contractors. The QA manager manages the systems and performance audits and reports their results to the field manager and field contractors. The QA manager works with the data manager to develop quality assurance data screening protocols and manages the data quality assurance efforts. Dr. Eric Fujita of the Desert Research Institute will be the QA manager and will report to the SCOS97 Technical Committee.

- Data Manager. The data manager is responsible for developing the data management plan in conjunction with the field managers and field contractors. The data manager works with the field manager, measurement contractors, modelers, and analysts to develop standard data formats for use in the study. The data manager is responsible for obtaining project data and supplemental data, integrating the data into a common database, performing Level 1 screening of the data, providing the data to the QA, analysis, and modeling contractors, and documenting and maintaining the data archive. Richard Hackney of the Air Resources Board Technical Support Division will be the data manager.

1.5 Planning Process

In 1993, several air quality management districts in southern California proposed to sponsor the SCOS97 field study to address interbasin transport. In July 1994, the South Coast Air Quality Management District (SCAQMD) hosted an initial planning meeting. The meeting was attended by other districts (Mojave Desert, Santa Barbara County, San Diego, and Ventura County), EPA-Region IX, utilities (Pacific Gas & Electric and Southern California Gas Company), oil companies (Atlantic Richfield Company, Chevron, Texaco and Unocal), industrial research consortiums (Coordinating Research Council and Electric Power Research Institute), and representatives of academia. A technical committee and three working groups (meteorology, air quality, and emission inventory) were formed to define goals and technical objectives for the proposed study and to provide coordination among sponsoring organizations. Memberships of the working groups are listed in Appendix C. A conceptual plan was completed by the working groups and approved by the technical committee in November, 1995. This conceptual plan proposed the study goals and deliverables, the technical objectives, measurement requirements, data analysis activities, and modeling approaches.

The SCOS97 conceptual plan (ARB, 1995a) provided the basis for the June 1996 draft of the field study plan (Fujita et al., 1996). The draft field study plan matched the SCOS97 goals and objectives with the resources available to do the job, and specified the details of the field study plan that would allow the conceptual plan to be executed. The field study plan summarizes existing information on emissions, summer ozone climatology, and current air quality, and it provides a conceptual model for the ozone episodes and transport

scenarios of interest. It specifies a measurement program to meet data requirements for data analysis and modeling. It also describes the required quality assurance, data validation, and data management needs. This version of the field study and quality assurance plan reflects the final stages of the planning process for the SCOS97-NARSTO Field Study.

The overall design process is iterative and the final plan will incorporate the input from sponsors, other stakeholders, knowledgeable peer reviewers, and users of the data. The following are some of the planning considerations that have been found to be important in past studies (Blumenthal and Watson, 1991; Lawson et al., 1993) that guided the planning of SCOS97-NARSTO.

- Begin planning at least two years before the field program, and allow at least one year for incorporation of the results of pilot studies into the full program plan. Allow sufficient time for pre-field study activities (e.g., time required for the contracting process and lead time for the acquisition of expendables and for siting). Contracts should be in place for such activities as siting and QA long before the start of the field effort. There must be adequate time to develop plans or select sites, review the choices, and then modify them if necessary.

- Include all stakeholders and users of the data in the design and execution of the study. The uses of the data should be clearly defined during the planning stage, and the modelers and analysts who will use the data should be involved in the planning process. Changes in the study design should be evaluated in terms of their effects on the modeling and analysis tasks. To assist in the overall planning phase, form several working groups (Meteorology, Emissions, Air Quality, and Modeling) to establish sampling protocols, and identify data needs for subsequent data analysis and modeling. Document results of the planning process in writing.

- Design the planning process to accommodate parallel planning and mid-course corrections. An initial scoping plan is required by sponsors so they can estimate the funding that will be needed. This step involves identifying the source(s) of funds for the study and the general level of funding available. Once the general funding level is identified, it is often necessary to revise the objectives and the scope to fit within the funding constraints. The elements of the plan and the design of the elements subsequently evolve throughout the planning process. It is important to build the capability for mid-course corrections into the planning process. Develop strawman plans early, and allow for changes and tradeoffs later. Identify design questions requiring additional information. If necessary, and if sufficient time is available, design and perform small pilot studies to answer the design questions. Maintain continuity between planning and management. Once the study plans are completed, they must be implemented by the sponsors. Proposal requests must be written and contractors selected. During the process of selecting contractors and implementing the study plan, many decisions and tradeoffs must be made. During this process, it is important to maintain continuity of the planning team in the management and decision process. In this way, the decisions made to change one element of the study

will reflect an understanding of the study priorities and of how that change will affect other elements. Have a contingency plan for the field sampling program if meteorological conditions are not conducive for pollutant episode conditions.

- Before completing the plans, have the plans reviewed by a broad cross-section of interested and knowledgeable people. Modelers, analysts, potential measurement contractors, sponsors, and other knowledgeable scientists should be included in the review. One possible mechanism to accomplish the review is to convene a workshop. In addition, the costs of each component should be estimated and the plan reviewed in light of any funding limitations. Solicit evaluations by reviewers as to whether the plan will meet the objectives, whether the measurements are feasible and meet the needs of the modelers and analysts, whether the hardware and people resources are available in the required time frame, and whether the cost estimates are reasonable. Solicit suggestions for improvement. If changes are suggested which increase the cost, ask for suggestions to compensate for the changes to balance the budget. Assess the comments and recommendations in terms of the priorities and objectives, and revise the draft operational plan to reflect the changes due to budget and priority considerations as well as the input from the reviewers. After the resources and program objectives are reconciled, this information is compiled into the program (operational) plan.

- Integrate quality assurance (QA) into the planning process. The QA team should be chosen early and should be an integral part of the planning process. Allow enough funds to perform this task properly. Typically, about 5-10 percent of the total field and data processing budget is allocated to field QA, and additional QA resources are often provided directly by sponsoring agencies. Both quality control and quality assurance efforts for all program participants must be fully evaluated. Perform round-robin interlaboratory and intermethod comparisons before the field program begins. Build redundancy into all critical measurements. Use spectroscopic methods as "reference" methods where possible. In addition to lidar, there are several measurement methods for which accuracy and validity cannot be fully assessed through standard quality auditing procedures. These measurements include hydrocarbon speciation, carbonyl compounds, PAN, NO_y, and upper air meteorology. For these measurements, measurement comparisons are an acceptable means for estimating accuracy and validity. Section 8 describes the quality assurance issues related to these measurements and potential approaches for assessing data quality. The appropriate measurement comparisons and evaluations should be conducted well in advance of the SCOS97 field study, and coordinated through the quality assurance manager.

- Emphasize data archival as an integral part of the overall study. Data reporting conventions, site documentation, and units need to be established prior to delivery of data by the study participants. Funding and planning this activity up front (something that has not occurred in most studies) will greatly facilitate subsequent data analysis and modeling efforts. Recognize the need for extensive data management and "Level

2" data validation. The amount of effort required to get a database to a point where the validity of the numbers is understood is often greatly underestimated. Collecting data from many contractors into a single database is a tremendous task. To be reasonably confident in the data, temporal and spatial consistency checks (Level 2 validation) are useful. Aircraft and ground data and other collocated measurements should be compared. Screening tests should be performed to identify outliers and other inconsistencies (i.e., dew point higher than temperature, etc.). Analysts should quickly review the data to identify potential problems so that they can be resolved while the measurement personnel are still accessible.

- Provide sufficient funding for at least three types of data analysis: observation-based analyses; receptor modeling approaches; and airshed modeling. Provide for data to adequately evaluate the accuracy of emission inventory estimates and the performance of air quality models.

- Schedule symposia and workshops at appropriate intervals for presentation and discussion of data and results. Publish the results in peer-reviewed journals. Prepare a single volume that summarizes the study results. Allow several years for study results to be incorporated into policy. Five years elapsed between field measurements during the Southern California Air Quality Study (SCAQS) and formal presentation of data and modeling results. Scientific papers are still being published nearly 10 years after the field study. Shorter or legislatively mandated timelines must rely on interim results that are subject to revision.

1.6 SCOS97-NARSTO Schedule and Milestones

The schedule for SCOS97 is outlined in Table 1-1. The overall time scale shown is five years. To meet this schedule, however, will require careful planning, fast turn-around by the sponsors on requests for proposals and contracts, and much front-end work by the Technical Committee. In the early stages of the program, several tasks must be performed in parallel, and the technical committee and working groups must meet frequently and coordinate closely.

1.7 Guide to Field Study Plan

This introductory section has provided a background for the proposed study and has specified the goals and technical objectives. Section 2 presents a "conceptual model" of the ozone episodes and transport scenarios of interest which serves as the basis for the experimental design of SCOS97. Section 3 provides an overview of the SCOS97-NARSTO field study and the existing meteorological and air quality measurement networks and supplemental measurements during the field study. Section 4 through 7 provide the specifications for measurement of surface air quality and meteorology, aloft air quality, aloft meteorology, and volatile organic compounds, respectively. Sections 8 and 9 describe the quality assurance and data management activities of the study, respectively. Development of the SCOS97-NARSTO emissions inventory is described in Section 10. Section 11 describes

the data analysis and modeling tasks associated with the study. Section 12 provides an estimate of the costs for SCOS97 by program elements, and Section 13 includes a list of references cited in this document.

Table 1-1
Schedule of Major Milestones for the SCOS97

Due Date	Major Milestone
July 1994	Hold initial planning meeting for SCOS97.
January 1995	Feasibility study for a Southern California Air Quality Monitoring Study. Report prepared by Systems Application International for the Coordinating Research Council.
May-October 1995	Pilot studies (Barstow saturation monitoring, ozone aloft monitoring, and scanning lidar evalutions.
November 1995	Conceptual plan for SCOS97-NARSTO prepared by the Technical Committee and Working Groups.
June 1996	Draft SCOS97 Field Study Plan prepared by the Desert Research Institute with input from SCOS97-NARSTO TC and WGs.
August 1996	Preliminary regional meteorological modeling due.
October 1996	SCOS97 sponsors release requests for proposals.
December 1996 to March 1997	Contracts in place.
April 1997	Draft SCOS97 Quality Assurance Plan prepared by the Desert Research Institute with input from SCOS97-NARSTO TC, WGs, and measurement contractors.
June 1997	Final SCOS97-NARSTO Field Study and Quality Assurance Plan prepared by Desert Research Institute with input from SCOS97-NARSTO TC, WG, and measurement contrators.
June 15, 1997 to October 15, 1997	Conduct SCOS97-NARSTO field study.
June 1998	Complete assembly and validation of data archive.
1998	SCOS97-NARSTO symposium I - Review of field study and preliminary interpretation of data.
March 1999	Complete data analysis.
June 1999	Regional meteorological modeling evaluation and emission inventory due.
1999	SCOS97-NARSTO symposium II - Data Analysis
January 2000	Regional air quality model evaluation due.
June 2000	Regional control strategy assessment due.

2. BASIS FOR EXPERIMENTAL DESIGN

This section provides a summary of knowledge about emissions, transport, and transformation of air pollutants in southern California, and integrates this knowledge into a "conceptual model" of the phenomena that should be reproduced by the regulatory ozone models. This section also describes the data requirements for data analysis and modeling. Together they form the basis for the experimental design of the SCOS97-NARSTO field measurement program.

There are five air basins in the SCOS97 domain (shown in Figure 2-1): the San Joaquin Valley (southern part of Kern County only), South Central Coast (Ventura County, Santa Barbara County and southern portion of San Luis Obispo County), South Coast, San Diego and Southeast Desert Air Basins (abbreviated SJVAB, SCCAB, SoCAB, SDAB, and SEDAB, respectively). The study area includes about 53,000 square miles in the southern portion of the State, with a population of more than 18 million. Seven percent of the entire U.S. population, and more than half the population of California, lives in the South Coast Air Basin alone. This region of California is an area of complex terrain (see Figure 2-2) – bounded by the Pacific Ocean to the west; to the north by narrow coastal mountains and valleys, the San Joaquin Valley, and the Sierra Nevada Mountains; and to the south and east by the California state border. Although the air basin boundaries were established with topographical features in mind, winds can and do transport pollutants from one basin to another.

2.1 Emissions

Section 39607(b) of the California Health and Safety Code requires the California Air Resources Board (ARB) to inventory sources of air pollution within the 14 air basins of the state and to determine the kinds and quantities of pollutants that come from those sources. The pollutants inventoried are total organic gases (TOG), reactive organic gases (ROG), carbon monoxide (CO), oxides of nitrogen (NO_X), oxides of sulfur (SO_X), and particulate matter with an aerodynamic diameter of 10 micrometers or smaller (PM_{10}). TOG consist of hydrocarbons including methane, aldehydes, ketones, organic acids, alcohol, esters, ethers, and other compounds containing hydrogen and carbon in combination with one or more other elements. ROG include all organic gases except methane and a number of organic compounds such as low molecular weight halogenated compounds that have been identified by the U.S. Environmental Protection Agency (EPA) as essentially non-reactive. For ROG and PM_{10}, the emission estimates are calculated from TOG and PM, respectively, using reactive organic fractions and particle size fractions. Emission sources are categorized as on-road mobile sources, nonroad mobile sources, stationary point sources, stationary area sources, and biogenic sources.

Major inventory efforts were undertaken by the ARB for several base years: 1987, 1989, 1990, 1991, and 1993 (California Air Resources Board, 1990a, 1991a, 1993a, 1994). Because the emission reductions that are required to show "reasonable further progress" are referenced in the 1990 Federal Clean Air Act Amendments to a 1990 base year, additional efforts were made in compiling the emissions inventory for that year. Table 2-1 shows the

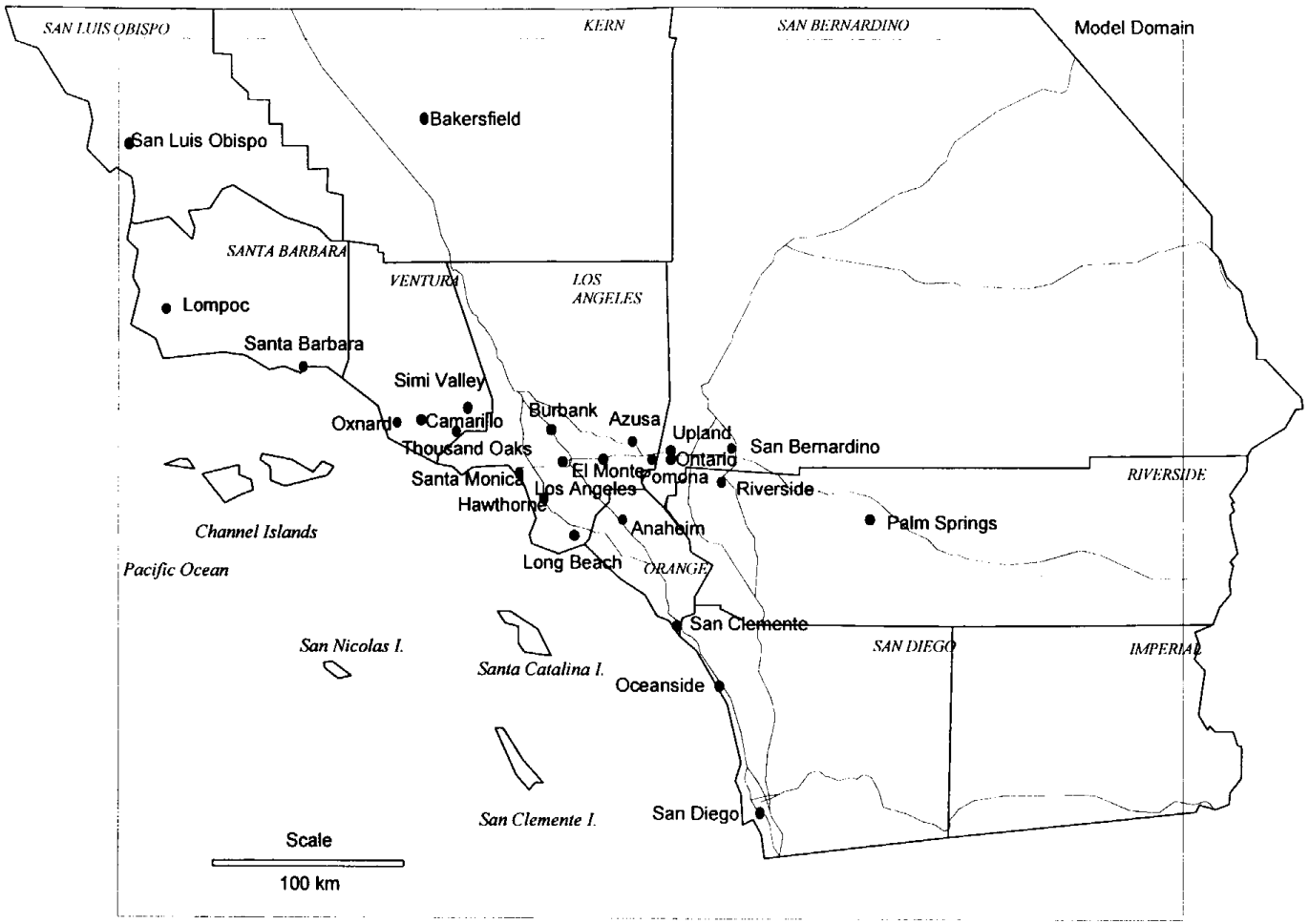


Figure 2-1. The SCOS97-NARSTO study area. Major cities, county boundaries, interstate highways, and the proposed modeling domain are shown.

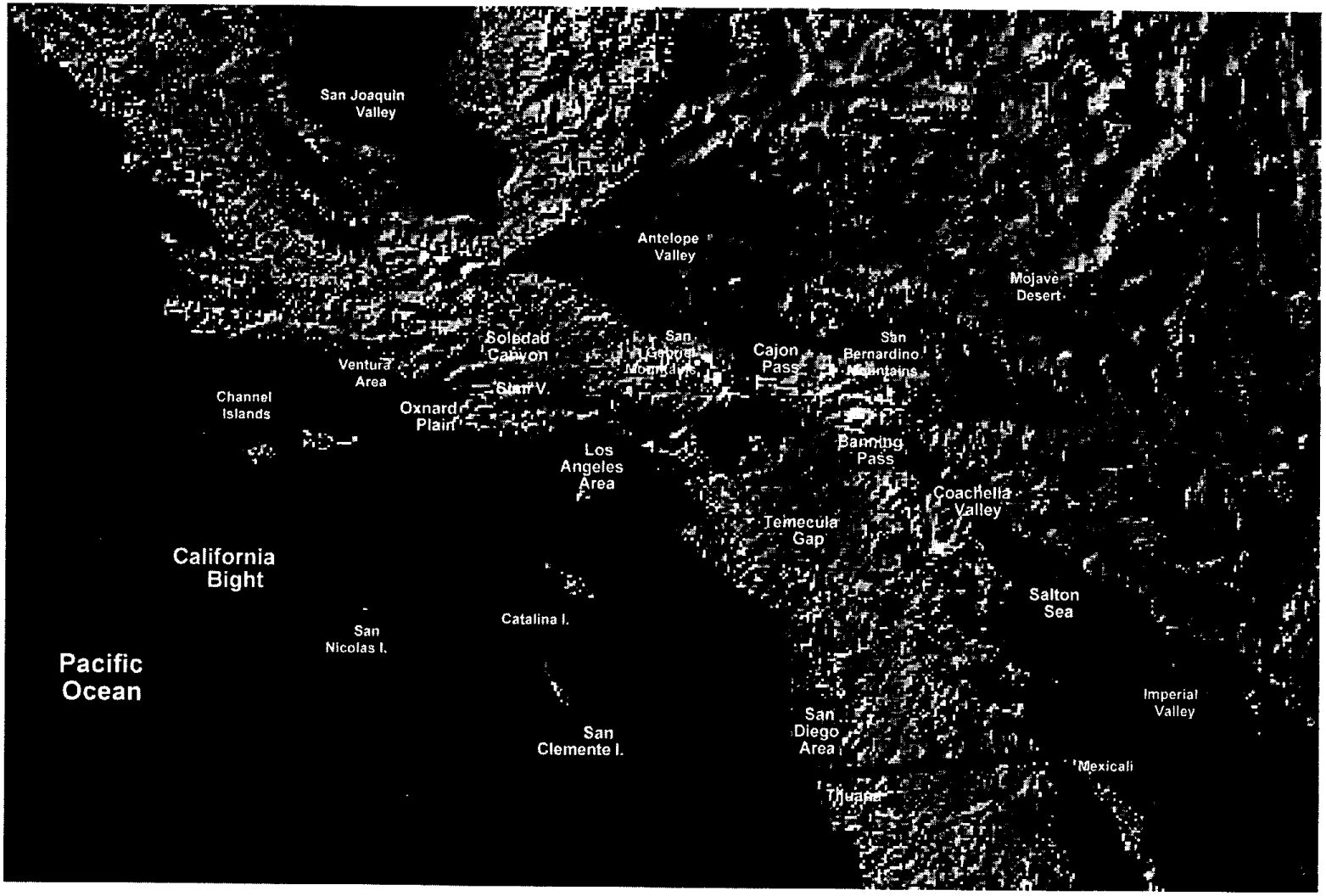


Figure 2-2. Topography of the SCOS97-NARSTO study area.

Table 2-1
Population, Area and Emissions by County in SCOS97 Study Domain
1990

County	Air Basin	Population	Area Sq. Mi.	Emissions, Tons/Day TOG	ROG	CO	NOx
Kern	San Joaquin	480,572	5,580	350	210	380	210
Santa Barbara	South Central Coast	373,844	2,740	280	72	220	45
Ventura	South Central Coast	676,271	1,860	99	72	340	64
Los Angeles	South Coast	8,736,520	2,770	1,300	920	4,000	790
Orange	South Coast	2,451,688	770	530	290	1,300	220
Riverside	South Coast	910,857	1,850	150	90	440	81
San Bernardino	South Coast	1,172,907	1,140	260	130	530	110
Imperial	Southeast Desert	112,748	4,240	34	30	140	38
Kern	Southeast Desert	79,990	2,570	25	18	69	47
Los Angeles	Southeast Desert	219,628	1,300	44	25	130	30
Riverside	Southeast Desert	321,018	5,330	120	54	190	60
San Bernardino	Southeast Desert	302,196	18,980	180	51	200	150
San Diego	San Diego	2,546,751	4,260	530	300	1,400	200
	Air Basin Subtotals						
	San Joaquin	480,572	5,580	350	210	380	210
	South Central Coast	1,050,115	4,600	379	144	560	108
	South Coast	13,271,972	6,530	2,240	1,430	6,270	1,200
	Southeast Desert	1,035,580	32,420	403	180	729	320
	San Diego	2,546,751	4,260	530	300	1,400	200
	TOTAL	18,384,990	53,390	3,902	2,264	9,339	2,038

total TOG, ROG, CO and NO_X emissions in 1990, by county, for the SCOS97 study area. Tables 2-2 and 2-3 show the 1990 daily average by air basins for ROG and NO_X emissions, respectively. Emissions from the study area in 1990 total 2259, 9339, and 2029 tons/day for reactive organic gases, carbon monoxide and nitrogen oxides, respectively (California Air Resources Board, 1993a), with 63 percent, 67 percent and 59 percent of those pollutants emitted within the SoCAB. Stationary sources and on-road mobile sources contribute equally to ROG emissions (45 and 46 percent, respectively) in the SoCAB, while mobile sources account for the majority of NO_X emissions (51% from on-road and 30% from nonroad). While these emission distributions also apply to total emissions for the entire study area, there are large regional differences in source contributions. Stationary sources account for the majority of ROG emissions in Kern County and the SCCAB, and for the majority of the NO_X emissions in Kern County.

Several other emissions that are not listed in Table 2-4 are important for understanding particulate and VOC concentrations in the SoCAB. Biogenic and geogenic emission rates are not included, and they can be significant. Biogenic ROG emissions in the SoCAB have been estimated to be 100 to 200 tons/day (Winer *et al.*, 1983; Horie *et al.*, 1990; Causley and Wilson, 1991), with substantial dependence on plant type, leaf biomass, wind speed, and temperature. Harley *et al.* (1993) used a value of 117 tons/day of biogenic ROG for ozone modeling of the August 27 to 29, 1987 SCAQS episode. This emission rate is comparable to those of many other source types in Table 2-2. Geogenic ROG emissions might be expected in areas where oil is extracted, but estimates of their magnitudes are not available.

These emission inventories provide a starting point for the updated 1997 emission inventory that will be required for the SCOS97 air quality modeling effort. Section 10 provides a summary of recent, current and planned projects that are related to development of the SCOS97 emission inventory, and an overview of emission inventory methodology and associated uncertainties.

2.2 Pollutant Transport and Summer Ozone Climatology

Given the primary emissions within the complex terrain of southern California, it is the climate of southern California that fosters generation of ozone, a secondary pollutant. High ozone concentrations most frequently occur during the "ozone season," spanning late spring, summer, and early fall when sunlight is most abundant. Meteorology is the dominant factor controlling the change in ozone air quality from one day to the next. Synoptic and mesoscale meteorological features govern the transport of emissions between sources and receptors, affecting the dilution and dispersion of pollutants during transport and the time available during which pollutants can react with one another to form ozone. These features are important to transport studies and modeling efforts owing to their influence on reactive components and ozone formation and deposition. This subsection provides a summary of meteorological features affecting southern California air quality, and provides a brief overview of the regulatory response to interbasin transport, i.e., the identification of "transport couples" and the characterization of the effect of transport on air quality in the

Table 2-2
1990 Daily Average ROG Emissions by Air Basins in SCOS97 Study Domain

Major Source Category	Air Basin					
	SJVAB (a)	SCCAB (b)	SoCAB	SEDAB	SDAB	Total
Fuel Combustion	11	2.5	15	4.6	2.5	36
Waste Burning	1.8	0.4	1.2	5.2	0.9	10
Solvent Use	14	32	420	29	76	571
Petroleum Processing, Storage & Transfer	120	33	96	3.6	8.2	260
Industrial Processing	1.1	0.6	41	2.5	2.9	48
Miscellaneous Processes	20	13	56	44	18	151
Miscellaneous	0	0	3.5	0	0	3.5
Stationary Sources	168	81	633	89	109	1,079
Light Duty Passenger	18	36	450	36	110	650
Light & Medium Duty Trucks	12	13	150	17	40	232
Heavy Duty Gas Trucks	1.8	2.2	30	5.4	6.8	46
Heavy Duty Diesel Trucks	3.7	2.1	21	9.1	3.8	40
Motorcycles	0.4	0.8	7.5	0.6	1.8	11
Diesel Urban Buses	0	0	1.6	0	0.3	1.9
On-Road Vehicles	36	54	660	68	163	981
Off-Road Vehicles	1.7	2.1	34	8.1	18	64
Trains	0.4	0.1	2.0	2.3		4.8
Ships		0.3	1.1		0.6	2.0
Aircraft - Government	0.4	0.4	7.6	5.4	2.1	16
Aircraft - Others	2.8	1.2	9.1	0.6	1.1	15
Mobile Equipment	1.8	3.2	56	3.2	2.5	67
Utility Equipment	0.9	1.9	22	1.8	4.3	31
Other Mobile	8	9	132	21	29	199
TOTAL	212	144	1,425	178	300	2,259

(a) Kern County only
(b) Santa Barbara and Ventura Counties

Table 2-3
1990 Daily Average NO_x Emissions by Air Basins in SCOS97 Study Domain

Major Source Category	Air Basin					
	SJVAB (a)	SCCAB (b)	SoCAB	SEDAB	SDAB	Total
Fuel Combustion	140	24	200	57	22	443
Waste Burning		0.2	2.0	0.2		2
Petroleum Processing, Storage & Transfer	0.8		4.8		0.1	6
Industrial Processing		0.1	5.8	56		62
Miscellaneous Processes	0.2	1	3.3	0.3	1.1	6
Miscellaneous			1.3			1
Stationary Sources	141	25	217	114	23	520
Light Duty Passenger	13	28	290	28	74	433
Light & Medium Duty Trucks	10	12	110	14	32	178
Heavy Duty Gas Trucks	4.0	4.7	56	17	12	94
Heavy Duty Diesel Trucks	27	15	140	72	25	279
Motorcycles	0.1	0.3	1.8	0.1	0.4	3
Diesel Urban Buses	0.2	0	10		1.8	12
On-Road Vehicles	54	60	608	131	145	998
Off-Road Vehicles	0.3	1.0	10	0.9	4.8	17
Trains	8.8	3.3	42	46	0.6	101
Ships		1.5	33		9.8	44
Aircraft - Government	0.1	0.5	3.3	3.8	1.7	9
Aircraft - Others	0.4	0.6	15	0.5	2.5	19
Mobile Equipment	12	16	250	25	17	320
Utility Equipment		0.1	0.8	0.1	0.2	1
Other Mobile	22	23	354	76	37	511
TOTAL	216	108	1,179	321	205	2,029

(a) Kern County only
(b) Santa Barbara and Ventura Counties

Table 2-4
South Coast Air Basin Airflow Types
Seasonal and Diurnal Percentages of Occurrence (1977-1981 Data)

Types	I	II	III	IV	V	VIa	VIb	VII
Time - PST	On-Shore South	Sea Breeze	Off-shore	Southerly	Downslope/ Transitional	Weak Santa Ana	Full Santa Ana (>20 kts)	Calm
Winter								
4 a.m.	3	3	25	3	17	10	7	29
10 a.m.	10	9	16	15	16	12	7	13
4 p.m.	24	51	4	11	4	4	2	0
10 p.m.	6	7	19	7	20	11	7	23
all times	11	18	16	9	14	9	6	16
Spring								
4 a.m.	10	8	19	6	26	4	3	24
10 a.m.	43	29	3	12	5	2	1	2
4 p.m.	31	61	2	4	1	1	1	*
10 p.m.	23	26	9	4	23	3	1	10
all times	27	31	8	6	14	3	2	9
Summer								
4 a.m.	10	5	4	4	34	1	1	37
10 a.m.	51	41	1	6	1	*	*	0
4 p.m.	26	73	0	1	0	0	0	0
10 p.m.	34	39	2	2	18	1	*	5
all times	30	40	2	3	13	1	*	11
Fall								
4 a.m.	7	10	16	2	26	7	4	25
10 a.m.	33	29	5	6	10	6	4	7
4 p.m.	20	67	4	2	2	1	1	4
10 p.m.	16	19	13	2	27	5	3	15
all times	19	31	10	3	16	5	3	13
Yearly								
4 a.m.	8	7	16	4	26	6	4	29
10 a.m.	34	27	6	10	8	5	3	6
4 p.m.	25	63	3	5	2	2	1	1
10 p.m.	20	23	11	4	22	5	3	14
all times	22	30	9	6	14	4	3	12

* < 0.5 percent

receptor air basin. Specific transport studies are discussed in greater detail with the introduction of a conceptual model of ozone episodes and transport scenarios of interest in Section 2.6.

Southern California is in the semi-permanent high pressure zone of the eastern Pacific. During summer, average temperatures are ~25 °C, with maximum daily readings often exceeding 35 °C. Precipitation events are rare. Frequent and persistent temperature inversions are caused by subsidence of descending air which warms when it is compressed over cool, moist marine air. These inversions often occur during periods of maximum solar radiation which create daytime mixed layers of ~1,000 m thickness, though the top of this layer can be lower during extreme ozone episodes (Blumenthal *et al.*, 1978). Relative humidity depends on the origin of the air mass, proximity to the coast, altitude, and the time of day, and can exceed 50 percent during daytime throughout the SoCAB with the intrusion of a deep marine layer. Relative humidity is higher near the coast than farther inland (Smith *et al.*, 1984).

Several experiments and data analysis studies examined the relationship of meteorology to air pollutant transport pathways, diffusion, vertical mixing, and chemical transformation in the SoCAB (e.g., Edinger, 1959, 1973; Edinger and Helvey, 1961; Pack and Angell, 1963; Kauper and Hopper, 1965; Schuck *et al.*, 1966; Estoque, 1968; Lea, 1968; Stephens, 1968, 1969; Miller and Ahrens, 1970; Edinger *et al.*, 1972; Rosenthal, 1972; Shettle, 1972; Smith *et al.*, 1972, 1976, 1984; Drivas and Shair, 1974; Angell *et al.*, 1975, 1976; Kauper and Niemann, 1975, 1977; Husar *et al.*, 1977; Keith and Selik, 1977; Blumenthal *et al.*, 1978; McRae *et al.*, 1981; Witz and Moore, 1981; Farber *et al.*, 1982a, 1982b; McElroy *et al.*, 1982; Reible *et al.*, 1982; Sackinger *et al.*, 1982; Schultz and Warner, 1982; Shair *et al.*, 1982; Witz *et al.*, 1982; Smith and Shair, 1983; Cass and Shair, 1984; Smith and Edinger, 1984; Zeldin *et al.*, 1989; Douglas *et al.*, 1991; Bigler-Engler and Brown, 1995; Lea *et al.*, 1995). These experiments and others reveal several general features.

Smith *et al.* (1972), Keith and Selik (1977), and Hayes *et al.* (1984) describe wind flow patterns in the SoCAB. During summer, the sea-land breeze is strong during the day with a weak land-sea breeze at night. Owing to the high summer temperatures and extensive urbanization in the SoCAB, the land surface temperature does not usually fall below the water temperature at night, and nocturnal and morning winds are less vigorous than daytime winds. The land surface cools sufficiently to create surface inversions with depths as shallow as ~50 m. Surface heating usually erodes the surface and marine layers within a few hours after sunrise each day. Summertime flow patterns are from the west and south during the morning, switching to predominantly westerly winds by the afternoon. The land/sea breeze circulation moves air back and forth between the SoCAB and the Pacific Ocean, as well as along the coast to other air basins. Cass and Shair (1984) estimated that up to 50 percent of the sulfate measured at Lennox was due to emissions which had been transported to sea on the previous day. When wind speeds are low, air tends to slosh back and forth within the SoCAB.

In addition to these general features, there are many smaller features that affect the movement of pollutants within the SoCAB. Heating of the San Gabriel and San Bernardino Mountains during the daytime engenders upslope flows that can transport pollutants from the

surface into the upper parts of, and sometimes above, the mixed layer. When the slopes cool after sunset, the denser air flows back into the SoCAB with pollutants entrained in it. Convergence zones occur where terrain and pressure gradients direct wind flow in opposite directions, resulting in an upwelling of air. Smith *et al.* (1984) have identified 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. Rosenthal (1972) and Mass and Albright (1989) identified a Catalina Eddy, a counterclockwise mesoscale circulation within the Southern California Bight, as a mechanism for transporting air pollution. This eddy circulation transports pollutants from the SoCAB to Ventura, especially after the SoCAB ozone levels drop due to wind ventilation caused by an approaching low-pressure trough from the northwest. However, any southeast wind in southern California is initially capable of transporting polluted air consisting of ozone precursors and particulate matter from the SoCAB.

Blumenthal *et al.* (1978) describe the meteorology for a July 24 to 26, 1973, ozone case study during which the maximum hourly ozone average reached 630 ppb. During this episode, a strong high pressure ridge near the coast induced a cap of warm air over the SoCAB that limited the mixing depth for dispersing emissions. Nighttime surface inversions were strong and stable with little air movement until late morning. Ozone above the surface layer was not ventilated, and remained through the following day. The afternoon sea breeze was weak. On the second day, the surface layer increased in depth and entrained the ozone aloft with the ozone generated from fresh emissions. When the high pressure system weakened, the mixing depth increased and more vigorous on-shore winds ventilated the SoCAB.

General meteorological conditions and trajectories during the 1987 SCAQS episodes have been examined by Douglas *et al.* (1991). Flows during the summertime were westerly, and residence times were often less than 12 hours. The backward trajectories from Claremont and Riverside on August 27 and 28, 1987 show an upper level recirculation in the middle of the SoCAB that probably led to the build-up of ozone and precursors during this episode. Trajectories during SCAQS episodes were consistent with stagnation conditions desired for selecting episodes, and they provide confidence that the SCAQS forecasting methods can be successfully adapted to SCOS97 to evaluate high ozone episodes in the SoCAB. Summer episodes showed west to east transport with potential for pollutant carryover aloft. Forecasting methods for transport from the SoCAB to other air basins, or between other southern California basins, are more problematic and additional work will be needed to improve forecasting procedures.

Green *et al.* (1992a) classified wind field patterns in the SoCAB, San Joaquin Valley, and Mojave Desert during 1984 and 1985 to evaluate visibility reduction in the desert. This analysis evaluated transport between the SoCAB and the Mojave and Arizona deserts. Winds were found to be directly related to the pressure field, which, in summer, resulted from a consistent mesoscale component added to a varying synoptic-scale component. Three main summer patterns were found, all of which had some transport into the SEDAB from the SoCAB. The first, and predominant, pattern indicated typical summer conditions with the wind field driven by the ocean/interior temperature difference and terrain features. The second pattern typically occurred in early summer (May-early June), and had stronger flow

into the desert due to synoptic-scale pressure gradients (upper level low pressure over the west coast, surface low over the Intermountain region). This type was also less stable due to cold air aloft. The third pattern showed weaker flow into the desert (and flow from the SEDAB to the SoCAB for a few hours per day) due to higher pressure to the northeast.

The predominant surface wind climatologies for California have been compiled for ARB by Hayes *et al.* (1984) based on 1977-1981 wind data. Figure 2-3 (after Hayes *et al.*, 1994) shows seven types of wind flow patterns for the SoCAB and the surrounding air basins. Not shown is an eighth possible condition of essentially calm winds. Table 2-4 gives the frequency of occurrence, expressed as a percentage, of each of these eight wind-pattern types for four times daily during each season. It should be noted that for certain times of day, particularly during the summer, southeast winds may be the predominant wind near and within the inversion (Lea *et al*, 1995; Fisk, 1996a, 1996b).

During summer (June-August) and fall (September-November), the Calm (Type VII), Offshore (Type III), and Downslope/Transitional (Type V) patterns dominate the early morning hours, allowing pollutants to accumulate in SoCAB industrial and business areas. Pollutants then move inland with the Sea Breeze (Type II) in the afternoon hours. However, a period of southeast flow towards Ventura County can occur as the land breeze veers to a daytime sea breeze. While this diurnal sequence is most common during the ozone season, other combinations of wind patterns occur that drive interbasin transport. For example, off-shore surface transport from the SoCAB to San Diego may occur with the Offshore winds (Type III), the Downslope/Transitional winds (Type V), and/or the Weak Santa Ana winds (Type VIa).

2.2.1 Transport Couples

The California Clean Air Act of 1988 required the Air Resources Board (ARB) to identify districts in which emissions and end-products transported from upwind areas outside the districts cause or contribute to exceedances of the state ozone standard within the district. The topography and wind climatology of California produce combinations of adjacent air basins, called "transport couples," where the upwind-downwind transport and emissions sources must be considered by regulators. This coupling effect has been clearly demonstrated, although not quantified, in southern California on a number of occasions through the use of tracer releases (e.g., Reible *et al.*, 1982; Smith and Shair, 1983) and other studies (e.g., Bigler-Engler and Brown, 1995; Lea *et al.*, 1995). The most significant transport couples have been identified (California Air Resources Board, 1990b, 1993) consistent with California wind flow patterns (Hayes *et al.*, 1984).

The impact of pollutant transport on the ozone air quality in a downwind basin is a function of the precursor emissions in the upwind basin, the losses of pollutants by deposition and reaction along the transport path, the formation of ozone along the transport path, the meteorological situation which transports and mixes the pollutants, and the local precursor emissions in the downwind basin. The geography of the region often influences the potential transport between air basins and the transport path. Since precursors are lost via reaction and deposition, the time of transport will have a significant influence on the amount of transported precursors still existing at the receptor site.

Given the difficult numerical problem of turbulence and diffusion in complex terrain, and given only limited resources for collection of meteorological and air quality data, *qualitative* characterizations of transport contributions to downwind exceedances have been defined in lieu of a more desirable but currently unattainable *quantitative* apportionment of upwind and downwind source contributions. These qualitative estimates are described as:

- *Overwhelming.* An ozone exceedance in the downwind area occurred with little or no emissions contribution from the downwind area. Transport alone caused the exceedance. An overwhelming transport day is also commonly called a "Transport Day."

- *Significant.* Emissions in the upwind air basin plus emissions in the recipient air basin contributed to the recipient's ozone exceedance. Both transported and local emissions are necessary to cause the exceedance. A significant transport day is also commonly called a "Shared Day."

- *Inconsequential.* Upwind emissions did not contribute to the exceedance in the recipient air basin. Local contribution alone caused the exceedance. An inconsequential transport day is also commonly called a "Local Day."

For this study, the most important transport couples previously identified by ARB are:

- SoCAB to the South Central Coast Air Basin (SCCAB, including Ventura and Santa Barbara).

- SoCAB to the Mojave Desert Air Basin (MDAB, the western and northern portions of the former Southeast Desert Air Basin, SEDAB).

- SoCAB to the San Diego Air Basin (SDAB).

- SCCAB to the SoCAB.

The reverse transport couples, i.e., SCCAB to SoCAB, MDAB (or SEDAB) to SoCAB, and SDAB to SoCAB, occur only occasionally, if at all, and they seldom result in high ozone concentrations in the SoCAB. Other transport couples influence air quality in several of the air basins surrounding the SoCAB, for example, transport from the San Joaquin Valley to the SEDAB and from Mexico to San Diego. While these transport couples are not directly studied in SCOS97, the study will include them indirectly via boundary measurements at the upwind edges of the modeling domain.

2.3 Transformation and Deposition

The role of VOCs in the formation of tropospheric ozone (O_3) has been well established (Seinfeld, 1986). The only significant chemical reaction producing ozone in the atmosphere is the reaction of atomic and molecular oxygen. While molecular oxygen (O_2) is abundant in the atmosphere, free oxygen (O) atoms are not. At lower altitudes, where only UV-radiation with wavelengths greater than 280 nm is present, the only significant oxygen

atom production is from photodissociation of nitrogen dioxide (NO_2) into nitric oxide (NO) and atomic oxygen. NO reacts rapidly with ozone to regenerate NO_2. The first and third reactions occur rapidly, establishing a steady-state equilibrium ozone concentration that depends on the ratio of NO_2 to NO which in turn depends on the intensity of UV-radiation driving the photodissociation. One O_3 molecule is required to regenerate NO_2 from NO, so these reactions are insufficient, by themselves, to create excessive ozone levels. When reactive organic gases are present, however, their oxidation produces hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2) which react with NO to form NO_2 without destruction of ozone, thereby allowing ozone to accumulate.

Other tropospherically important reactions involve oxides of nitrogen (NO_X, sum of NO and NO_2). The recombination reactions of OH with NO to form nitrous acid (HONO) and HO_2 and NO_2 to form pernitric acid ($HOONO_2$) do not affect the fate of NO_X because of the rapid photodissociation of HONO to OH radical and NO and the thermal decomposition of $HOONO_2$ back to reactants. HONO is also formed at night from the heterogeneous hydrolysis of NO_2, and is also directly emitted from combustion sources. The rapid photolysis of HONO in the early morning can lead to a rapid increase in the number of OH radicals and to rapid initiation of photochemical activity.

The reaction of OH with NO_2 to form nitric acid (HNO_3) is the major gas-phase sink for NO_2 in the troposphere. Reaction of HNO_3 with ammonia (NH_3) yields particulate ammonium nitrate (NH_4NO_3) and with sodium chloride (NaCl) to form sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl). While $NaNO_3$ is associated with coarse particles (2 to 10 μm) and is stable, NH_4NO_3 is associated primarily with fine particles (less than 2 μm) and is in equilibrium with NH_3 and HNO_3 at typical summertime ambient temperatures in southern California.

Ozone also reacts with NO_2 to form nitrate (NO_3) radicals, and the NO_3 radical and NO_2 form an equilibrium with nitrogen pentoxide (N_2O_5). Because NO_3 radicals rapidly photolyze and react rapidly with NO, concentrations of the NO_3 radical, and N_2O_5 remain low during daytime but can increase during evening and nighttime hours in the absence of NO.

For the majority of VOCs emitted from anthropogenic and natural sources, reaction with the hydroxyl radical is the major cause of chemical change, and atmospheric lifetimes can be estimated from typical and maximum reaction rates for different organic compounds when the hydroxyl radical is present at urban concentrations. Typical lifetimes of some VOCs due to reaction with the hydroxyl radical are given in Table 2-5. This table shows that all the acetylene, most of the alkanes, benzene, and toluene have lifetimes which exceed the typical summer residence time of air masses during SCAQS (~12 hours according to SCAQS trajectories by Douglas *et al.*, 1991). Most of the other species in Table 2-5 will retain their relative abundances to other species when emissions are fresh (i.e., sampled within a few hours after release) but will have substantially changed in proportion to the other species after the air mass containing them has aged for a few hours. The degradation reactions for all classes of VOCs, in addition to the conversion of NO to NO_2 and the formation of ozone, lead to the formation of carbonyl compounds (aldehydes, ketones, hydroxycarbonyls, and

Table 2-5
Typical Lifetimes of Some VOCs Due to Reaction with OH Radical

Compound	10E12 x k cm3/mol-sec @ 298 deg. K	Lifetimes Daytime 12-hour mean low		Daytime 12-hour mean high		Midday Peak	
OH/cm3		5.0E+05		5.0E+06		1.0E+07	
Alkanes							
Methane	0.00836	15.2	years	1.5	years		
Ethane	0.268	173	days	17.3	days		
Propane	1.15	40	days	4.0	days		
n-Butane	2.54	18	days	1.8	days		
2-Methylpropane (i-Butane)	2.34	20	days	2.0	days		
n-Pentane	3.94	12	days	1.2	days		
2-Methylbutane (i-Pentane)	3.90	12	days	1.2	days		
n-Hexane	5.61	8.3	days	9.9	hours	5.0	hours
2-Methylpentane	5.6	8.3	days	9.9	hours	5.0	hours
3-Methylpentane	5.7	8.1	days	9.7	hours	4.9	hours
2,4-Dimethylpentane	5.1	9.1	days	10.9	hours	5.4	hours
Heptane	7.2	6.5	days	7.8	hours	3.9	hours
Methylcyclohexane	10.4	4.5	days	5.3	hours	2.7	hours
Alkenes							
Ethylene	8.5	5.4	days	6.5	hours	3.3	hours
Propene	26.3	1.8	days	2.1	hours	1.1	hours
Butene	31.4	1.5	days	1.8	hours	0.9	hours
cis-2-Butene	56.1	9.9	hours	1.0	hours	0.5	hours
trans-2-Butene	63.7	8.7	hours	0.9	hours	0.4	hours
3-Methyl-1-Butene	31.8	1.5	days	1.7	hours	0.9	hours
Cyclohexene	67.4	8.2	hours	0.8	hours	0.4	hours
Isoprene	101.0	5.5	hours	0.6	hours	0.3	hours
Alkynes							
Acetylene	0.9	51.4	days	5.1	days		
Aromatics							
Benzene	1.2	37.6	days	3.8	days		
Toluene	6.0	7.8	days	9.3	hours	4.7	hours
m-Xylene	23.6	2.0	days	2.4	hours	1.2	hours
p-Xylene	14.3	3.2	days	3.9	hours	1.9	hours
o-Xylene	13.7	3.4	days	4.1	hours	2.0	hours
Ethylbenzene	7.1	6.5	days	7.8	hours	3.9	hours
1,2,4-Trimethylbenzene	32.5	1.4	days	1.7	hours	0.9	hours

Lifetimes are for summer conditions. Lifetimes in winter are about 3-4 times longer.
Rate constants from Atkinson (1989)

dicarbonyls), organic acids, organic nitrates (including peroxylacyl nitrates, the simplest member of which is peroxyacetyl nitrate [PAN]). PAN thermally decomposes back to its reactants, NO_2 and acetylperoxy radical. Thus, like HONO, PAN can serve as a nighttime reservoir for NO_X and means of transport of NO_X to downwind areas. Recent measurements have indicated that carbonyl compounds that are produced from hydrocarbon oxidation can be important reactive VOCs themselves, and thus important sources of peroxy radicals responsible for ozone production (Martin *et al.*, 1991). Both the absolute concentrations of the carbonyl compounds, and the ratio of the product to the parent hydrocarbon can provide useful information regarding the extent of hydrocarbon oxidation chemistry occurring in a particular air mass.

The reactive nitrogen compounds (NO_y), NO, NO_2, NO_3, N_2O_5, $CH_3COO_2NO_2$ (PAN), HNO_3, HONO, and other organic nitrogen-containing species are coupled by a complex sequence of reactions in the atmosphere which generate ozone, other oxidants, organic and inorganic acids, and various hydrocarbon oxidation products. Because the amount of NO_y in a given air mass is dependent only on the sources and sinks of its component species and not on interconversion chemistry, NO_y is a conserved quantity. Thus, NO_y is a measure of the amount of nitrogen containing "pollution", independent of the air mass's age. It is NO_y rather than NO_X that is of primary interest in establishing the nitrogen budget across a transport flux plane. In addition, our understanding of the reaction pathways which involve nitrogen species can be aided by the measurement of the total abundance of atmospheric reactive compounds.

Much of the difficulty in addressing the ozone problem is related to ozone's complex photochemistry. The rate of O_3 production is a non-linear function of the mixture of VOC and NO_X in the atmosphere. Depending upon the relative concentration of VOC and NO_X and the specific mix of VOC present, the rate of O_3 formation can be most sensitive to changes in VOC alone or to changes in NO_X alone or to simultaneous changes in both VOC and NO_X. Understanding the response of ozone levels to specific changes in VOC or NO_X emissions is the fundamental prerequisite to developing a cost-effective ozone abatement strategy, and is the principal goal of SCOS97-NARSTO.

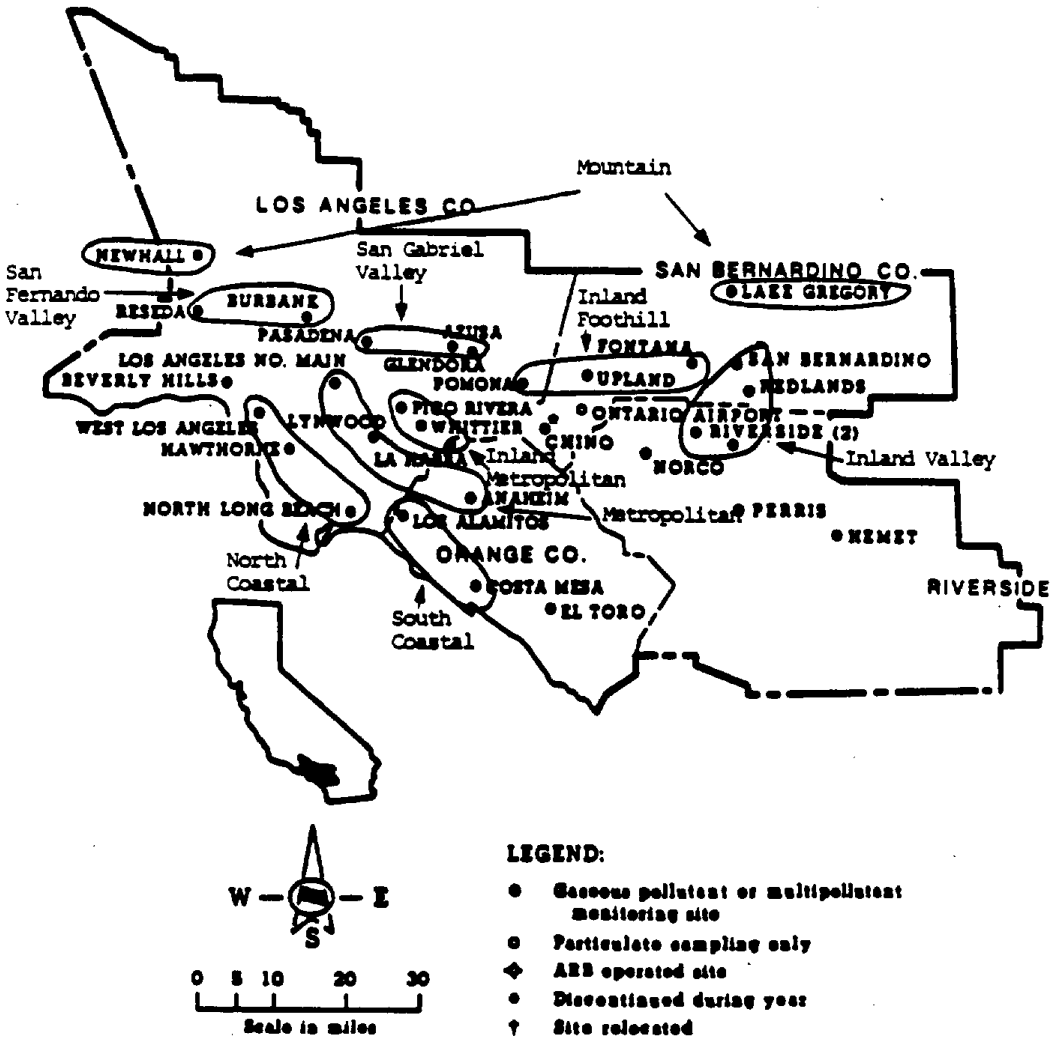
2.4 Spatial and Temporal Ozone Patterns

In a modeling study, Ireson and Hogo (1983) generated expected contours of peak ozone concentrations in the SEDAB. Smith and Shair (1983) have provided contour plots from ozone measurements on transport days during the tracer study of summer 1981 showing the spatial distribution of ozone in the SoCAB and the SEDAB. Figure 2-4 (from Stoeckenius *et al.*, 1992) shows functional grouping of sites within the SoCAB that exhibit similar ozone time series. Stoeckenius *et al.* (1992) describe the similarities between the sites in each of the following nine functional groups:

1. North Coast (West LA, Hawthorne, N. Long Beach)

2. South Coast (Los Alamitos, Costa Mesa)

Figure 2-4 Sites within SoCAB that exhibit similar ozone time series



3. Metropolitan (Los Angeles, Lynwood, Anaheim)

4. San Fernando Valley (Burbank, Reseda)

5. San Gabriel Valley (Pasadena, Azusa, Glendora)

6. Inland Metropolitan (Pico Rivera, Whittier, La Habra)

7. Inland Foothill (Pomona, Upland, Fontana)

8. Inland Valley (San Bernardino, Redlands, Riverside)

9. Mountain (Newhall, Lake Gregory)

During the most typical summer conditions (corresponding to Scenario #3 introduced in Section 2.5), the maximum ozone concentrations experienced in the SoCAB are in the San Gabriel Valley group. A "Southern Route" pattern (Section 2.5, Scenario #1) produces the greatest ozone along the North and South Coast as well as in the Metropolitan and Inland Metropolitan functional groups. The Eddy Pattern (Section 2.5, Scenario #4) tends to produce higher relative ozone concentrations in the San Fernando Valley and at both the Mountain sites.

Table 2-6 lists the number of state, federal, and first stage health advisory exceedances for the 1990-93 ozone seasons that have occurred at each monitoring station in the Mojave Desert, South Central Coast (Ventura and Santa Barbara), and San Diego Air Basins and for selected SoCAB monitoring stations (one from each functional group after Stoeckenius *et al.*, 1991). The temporal pattern of exceedances in the Mojave Desert closely follows that of the SoCAB, while a relationship with the other three areas — Ventura, Santa Barbara, and San Diego — is less clear. Downtown San Diego (sites SD 123 & 138) exhibit a bimodal distribution with the majority of exceedances occurring in the fall. The elevated Alpine site, on the other hand, more closely follows the SoCAB distribution and has the worst ozone air quality in San Diego.

2.5 Conceptual Model of Ozone Episodes and Transport Scenarios of Interest

As part of the SCOS97 effort, the Meteorological Working Group has formed five scenarios of ozone episodes which include suspected accompanying interbasin transport. Figure 2-5 shows the suspected transport pathways for the following five types of ozone episodes and transport scenarios, listed in order, as prioritized by the Meteorological Working Group:

1. SoCAB Ozone Maximum. SoCAB pollutants remain trapped within SoCAB. There may be "local" exceedance days for other basins. This condition may be accompanied by a "coast hugger," a near-coast flow of SoCAB pollutants toward the southeast.

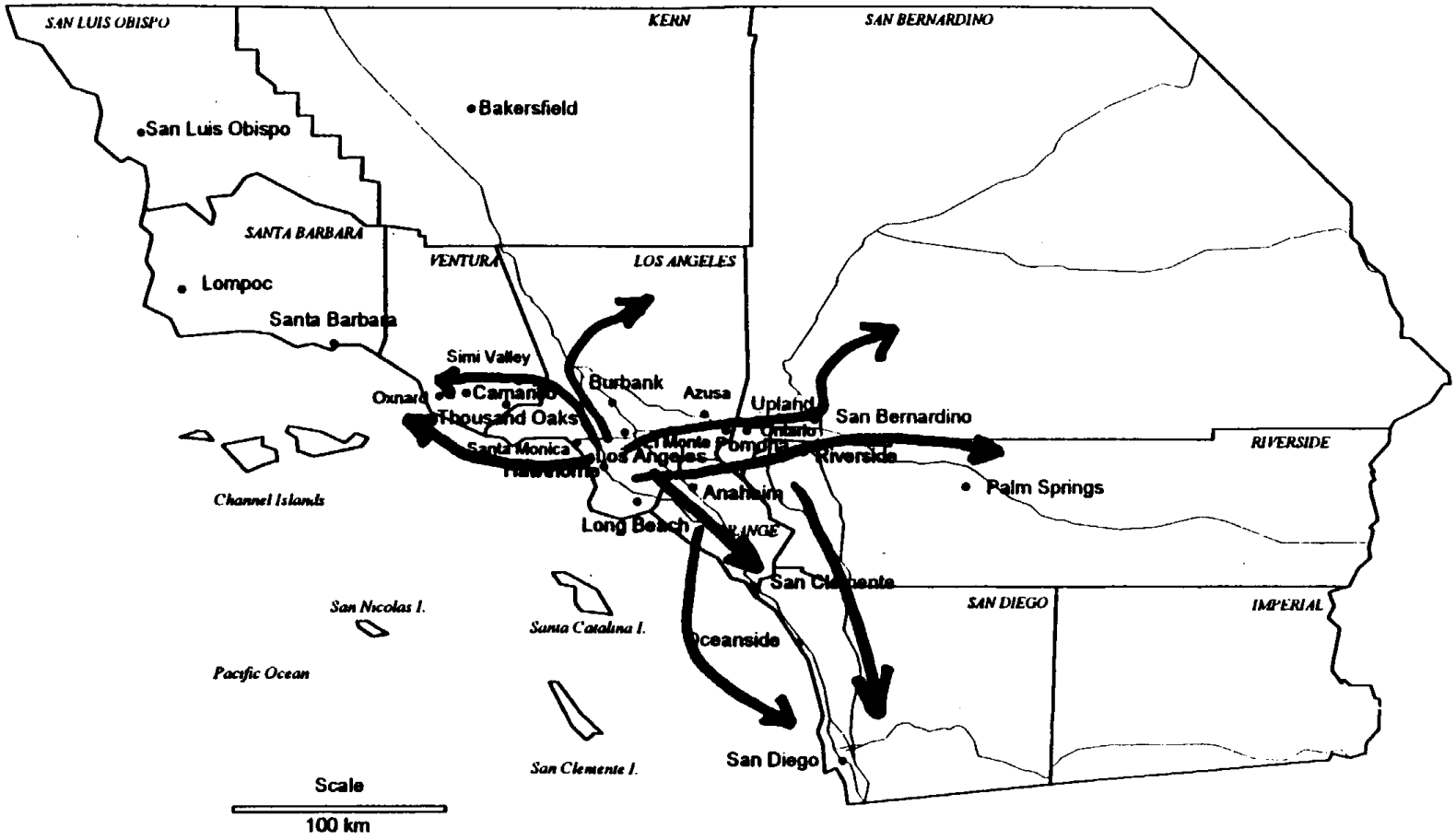
Table 2-6
Southern California Ozone Standard Exceedances for June-October 1990-93

APCD or AQMD	June			July			Aug			Sept			Oct		
	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage
South Coast															
Hawthorne	2/120	0	0	1/124	0	0	4/121	0	0	8/120	0	0	7/124	0	0
Los Alamitos	13/120	3/120	1/120	6/124	2/124	1/124	17/124	2/124	0	29/119	10/119	5/119	21/123	5/123	3/123
Los Angeles	30/120	11/120	3/120	39/123	15/123	4/123	38/124	14/124	5/124	50/114	21/114	9/114	30/121	12/121	3/124
Burbank	56/118	21/118	12/118	65/124	34/124	19/124	74/123	36/123	20/123	61/116	30/116	13/116	43/122	19/122	6/122
Azusa	71/119	47/119	35/119	95/124	59/124	40/124	101/124	72/124	50/124	93/119	71/119	45/119	49/123	34/123	23/123
Pico Rivera	38/118	18/118	10/118	53/120	24/120	17/120	70/123	33/123	20/123	78/120	47/120	33/120	45/124	26/124	14/124
Pomona	56/120	29/120	23/120	78/124	43/124	29/124	83/124	47/124	37/124	79/119	47/119	29/119	39/124	27/124	17/124
San Bernardino	68/120	38/120	31/120	91/124	59/124	38/124	95/124	57/124	47/124	90/120	55/120	41/120	42/122	27/122	20/122
Lake Gregory	93/120	69/120	49/120	117/123	94/123	72/123	115/124	92/124	69/124	94/120	59/120	39/120	36/122	12/122	4/122
Ventura															
Piru	12/	1/118	0	16/124	0	0	24/124	1/124	0	18/120	3/120	1/120	19/124	1/124	0
Ojai	19/120	1/120	0	10/119	1/119	0	26/124	0	0	16/120	2/120	1/120	20/124	3/124	0
Simi Valley	27/120	5/120	1/120	54/124	8/124	1/124	70/124	16/124	3/124	47/120	16/120	6/120	32/124	8/124	0
Ventura	4/111	0	0	0/124	0	0	2/124	1/124	0	6/120	0	0	5/123	0	0
Thousand Oaks	13/120	1/120	1/120	2/122	0	0	13/122	1/122	0	23/120	3/120	0	18/124	0	0
El Rio	5/119	0	0	2/119	0	0	6/124	0	0	5/120	0	0	9/124	0	0
Santa Barbara															
Carpenteria	4/120	0	0	4/114	1/114	0	3/124	0	0	4/117	0	0	3/124	0	0
Santa Ynez	1/119	0	0	2/124	0	0	0	0	0	1/119	0	0	4/124	0	0
Loma Poc	0	0	0	1/110	0	0	0	0	0	0	0	0	1/123	0	0
Santa Maria	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Goleta	1/119	0	0	3/124	0	0	1/121	0	0	3/120	0	0	3/121	0	0
El Capitan	1/120	0	0	2/124	0	0	0	0	0	1/118	0	0	2/124	0	0
SB 388	1/118	0	0	5/124	1/124	0	0	0	0	0	0	0	3/123	0	0
SB 401	1/120	0	0	1/124	0	0	0	0	0	1/120	0	0	1/124	0	0

Table 2-6 (continued)
Southern California Ozone Standard Exceedances for June-October 1990-93

APCD or AQMD	June			July			Aug			Sept			Oct		
	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage
Mojave Desert															
29 palms	45/120	1/120	0	34/124	3/124	0	20/94	0	0	May-89	0	0	Mar-93	0	0
Victorville	64/119	13/119	4/119	76/123	22/123	10/123	56/122	12/122	4/122	24/120	2/120	0	6/118	0	0
Trona	7/107	0	0	Apr-78	0	0	3/100	0	0	Feb-97	0	0	0	0	0
Phelan	81/119	46/119	25/119	106/124	69/124	38/124	96/124	47/124	23/124	54/120	19/120	6/120	15/119	5/119	0
Hesperia	85/120	45/120	18/120	102/122	47/122	26/122	95/109	46/109	21/109	65/117	21/117	9/117	17/124	2/124	1/124
Barstow	25/112	0	0	36/121	4/121	0	22/99	0	0	Jul-88	0	0	1/123	0	0
San Diego															
Oceanside	4/120	0	0	0	0	0	1/123	0	0	11/119	5/119	3/119	16/122	5/122	2/122
Escondido	9/120	2/120	1/120	5/124	0	0	10/124	1/124	0	20/120	4/120	2/120	22/124	7/124	4/124
SD 123	9/120	4/120	1/120	2/122	0	0	3/111	1/111	0	20/111	5/111	2/111	21/121	9/121	5/121
SD 138	6/120	0	0	1/124	0	0	1/124	0	0	10/120	1/120	0	18/124	7/124	4/124
Delmar	5/118	1/118	0	0	0	0	2/124	1/124	0	14/120	4/120	2/120	26/123	9/123	2/123
Chula Vista	4/120	1/120	1/120	1/124	0	0	1/124	0	0	16/119	3/119	1/119	18/124	5/124	1/124
El Cajon	18/120	3/120	3/120	10/124	1/124	0	16/124	0	0	21/120	3/120	0	30/124	4/124	0
Alpine	48/120	11/120	3/120	58/124	5/124	1/124	63/124	14/124	2/124	58/120	11/120	3/120	46/124	10/124	2/124
El Centro	14/120	1/120	0	3/122	0	0	0	0	0	3/120	1/120	1/120	5/124	0	0

Figure 2-5 Possible transport corridors for transport couples of interest



2. Upper-level transport to San Diego Air Basin. Ozone in a layer 300-500 m MSL above the marine layer or above the nocturnal inversion jets southeast toward San Diego. The centerline and width of this pathway are uncertain, and may range from the Interstate 15 route (east) to an off-shore route (west).

3. Secondary SoCAB Maximum. An on-shore breeze causes inland transport, with likely transport into the Mojave Desert. This situation may also correspond to local exceedances for Ventura, Santa Barbara, and San Diego Counties.

4. Coastal Day with Eddy. This is an extended SoCAB episode that ends with a southeast wind offshore, over the basin, and even sometimes in the desert. It is possibly an extension of Scenario #1 or #2. The ozone peaks are often seen at Newhall or Simi Valley on these days.

5. Off-shore surface transport direct to the San Diego Air Basin. This event is characterized by a mild Santa Ana wind condition followed by the on-shore flow. It occurs with greatest frequency later in the ozone season (September-October).

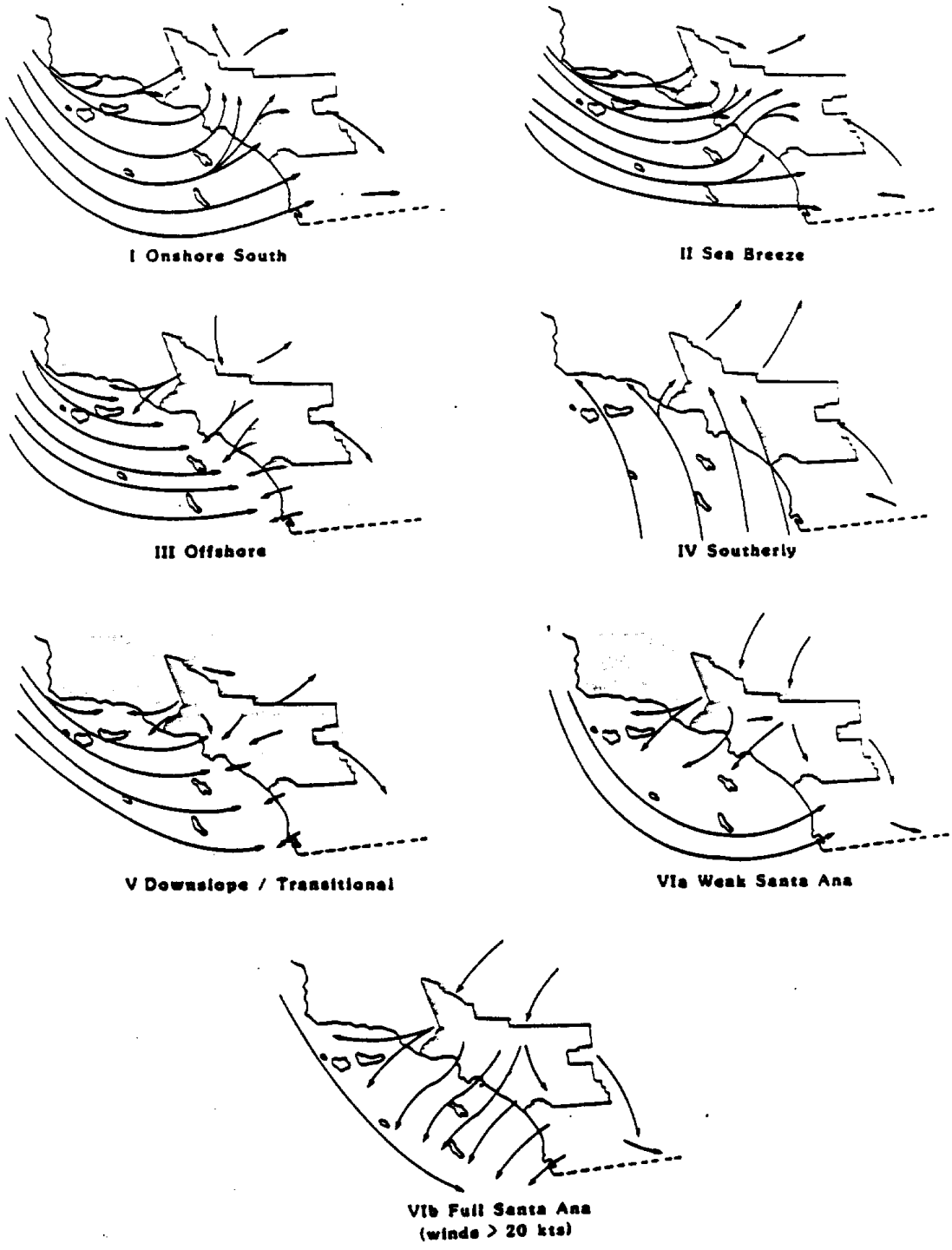
These five scenarios comprise the core of a conceptual model. In practice, there may be overlap between the scenarios. For example, also related to the Santa Ana winds discussed in Scenario #5 are subsequent periods of southeast flow which cause transport to the South Central Coast Air Basin as discussed in Scenario #4. Mild Santa Ana winds may be associated with simultaneous transport from southern portions of SoCAB to SDAB and from northern portions of the SoCAB to the SCCAB. (See wind-pattern type VIa in Figure 2-3.) The sampling network should be designed to accommodate potential overlap. Each scenario and relevant past studies are discussed in the following five subsections.

2.5.1 SoCAB Ozone Maximum

Stoeckenius *et al.* (1992) have studied days when SoCAB pollutants remain trapped within the SoCAB. Pollutants may move back and forth in a weak land/sea breeze. This situation is characterized by "sloshing" of pollutants back and forth. This phenomena is sometimes called "recirculation," though recirculation better describes a simultaneous return flow aloft. This scenario may also lead to a "coast hugger" or "Southern Route Day" because of the near-coast flow of pollutants toward the southeast.

These days are characterized by high 850-mb temperatures, weak offshore surface pressure gradients (higher pressure to the north or northeast) and an upper level ridge inland from the Pacific Coast. Weak off-shore flow during night and morning hours and on-shore flow in the afternoon, combined with low mixing depths gives low dispersion and high concentrations near the coast and in nearby valleys. A period of southeast flow between the night-time land-sea breeze and the daytime sea-land breeze may cause transport to Ventura County and beyond. (See wind-pattern type V in Figure 2-3.) Subsidence aloft, enhanced by downslope flow over the mountains, causes warm temperatures aloft and results in low mixing heights throughout the Los Angeles Basin. Afternoon mixing heights may be only 500-700 feet at inland locations. This pattern can be forecast using prognostic maps from the

Figure 2-3 South Coast Air Flow Pattern Types



National Meteorological Center (NMC) models, such as the NGM and ETA models. Weak upper air gradients, with an upper high inland of the Pacific Coast, and surface pressure slightly higher to the northeast of the SoCAB predicted by the models should result in these conditions.

2.5.2 Upper-Level Transport to San Diego Air Basin

Under this scenario, it is hypothesized that transport from the South Coast Air Basin (SoCAB) occurs in the layer just above the marine layer and then may be mixed to the surface during the late morning or early afternoon due to diurnal heating in inland portions of the San Diego Air Basin (SDAB). In the Los Angeles to San Diego Three-Dimensional Ozone Transport Study, Kauper and Niemann (1977) noted that on many days during which trajectories based upon surface winds would indicate ozone from San Diego area sources, ozone and wind data aloft suggested that sources in the SoCAB may have been responsible for high ozone levels in the SDAB. Kauper and Niemann speculated that under typical summertime conditions, northwesterly flow (i.e., flow from the northwest) aloft would transport elevated ozone layers from SoCAB toward the SDAB. They also suggested that surface heating would mix ozone to the ground, but questioned whether the high surface concentrations measured at some locations could result only from ozone layers aloft mixing to the surface. They suggested that mixing layers aloft to the surface would dilute the ozone to lower levels than those measured at the surface sites.

The San Diego Air Quality Study (SDAQS) was conducted during the summer of 1989 (Bigler-Engler and Brown, 1995; Hossain and Kaszuba, 1995). The objective of the SDAQS was to provide a high quality database for air quality simulation modeling and development of control strategies. Analysis of data from one study episode shows that ozone and its precursors from the SoCAB were transported overnight and in the early morning and that these pollutants fumigated to the surface in the San Diego Air Basin at multiple sites. The data from the study indicate that these transported pollutants can play a key role in ozone episodes in the SDAB.

Bigler-Engler and Brown (1995) report on a case of high ozone concentrations at Alpine (42 km east of downtown San Diego) during the SDAQS that initially appeared, based on surface winds, to be due to San Diego area (local) emissions. During this September 26, 1989 case, transport within the lowest few hundred meters above the surface was from the coast to inland; this seemed to imply high concentrations at Alpine due to transport from San Diego. However, ozone levels in San Diego remained low, and ozone at Alpine increased dramatically in the hour from 10 am to 11 am. This rapid increase during late morning, coinciding with deepening of the mixed layer due to solar insolation, suggested that fumigation from aloft was primarily responsible for the high concentrations (0.17 ppm) observed at Alpine. Direct advection into elevated terrain may also play a role. Vertical wind profiles showed transport from the northwest over night on September 25-26 and into mid-morning on September 26. This implicated the South Coast Air Basin as the predominant source of the high ozone recorded at Alpine, according to Bigler-Engler and Brown (1995).

The meteorological conditions that may lead to ozone transport aloft from the SoCAB to the SDAB may be hypothesized. If the synoptic scale flow leads to light north-northwesterly transport above the marine layer, then ozone layers that have been lifted aloft in the SoCAB may then be transported toward the SDAB, where they may be mixed to the surface in inland SDAB sites during midday due to solar insolation-caused deepening of the mixed layer. Direct advection of SoCAB air into elevated terrain in the SDAB may also contribute to high ozone at Alpine. The mechanisms for formation of ozone layers aloft in the SoCAB (slope flows, undercutting by the sea-breeze, upward motion in convergence zones, and transport into the inversion layer by convective elements) are described by Smith and Edinger (1984) and McElroy and Smith (1993). Thus, under periods of light north-northwesterly flow aloft, such as with a 500-mb ridge over or off the west coast and higher surface pressure to the north or northwest, elevated layers may be transported aloft overnight from the SoCAB and mixed to the surface at inland locations the following day in the SDAB.

2.5.3 Secondary SoCAB Ozone Maximum

This scenario occurs with an on-shore breeze causing inland transport and represents the typical summer day. The SoCAB is ventilated when air exits to the Mojave Desert and the Coachella Valley (Green *et al.*, 1992a, b). With weak synoptic gradients, the mesoscale effects of the seabreeze and the thermal low over the desert dominate the transport. This scenario often causes violation of the ozone standard at inland areas of the SoCAB and may be associated with locally caused violations in Ventura, Santa Barbara, and San Diego Counties. Due to the transport into the Mojave Desert during the late afternoon and evening, this scenario may also be expected to cause violations at Victorville and Palmdale. Green *et al.* (1992b) found that transport of visibility reducing pollutants into the Mojave Desert from the SoCAB was greatest for typical summer days.

This scenario is especially important for the SoCAB/SEDAB transport couple. Several studies have shown that high ozone levels in the SEDAB result primarily from transport of ozone and precursors from the SoCAB (e.g., Shettle, 1972; Smith *et al.*, 1972, 1976, 1984; Drivas and Shair, 1974; Angell *et al.*, 1976; Reible *et al.*, 1982; Shair *et al.*, 1982; Smith and Shair, 1983; Cass and Shair; 1984; Smith and Edinger, 1984; Raudy, 1990; Tilden *et al.*, 1991; Roberts *et al.*, 1992; California Air Resources Board, 1990b, 1993; Keislar *et al.*, 1994; Keislar and Schorran, 1995). The time of maximum ozone concentrations is progressively later at sites located at increasing distances from the coast (Smith *et al.*, 1983), which is consistent with the timing of transport from the SoCAB to the SEDAB. Smith *et al.* found that high morning ozone levels in the desert were usually associated with transport during the previous afternoon and night. Increases from the morning minimum to daily maximum averaged 30-40 ppb regardless of absolute concentration, suggesting that carryover of pollutants contributed to high baseline levels, but did not provide additional reactive material.

Using tracer releases, pollutants have been shown to travel from the SoCAB into the SEDAB through Cajon, San Gorgonio (Banning), and Soledad passes (Drivas and Shair, 1974; Angell *et al.*, 1976; Reible *et al.*, 1982; Smith and Shair, 1983). Smith and Shair (1983) also found evidence of transport aloft from the San Fernando Valley into eastern

Ventura County under certain circumstances. Perfluorocarbons, methylchloroform, and hydrocarbons were also measured in canisters on ARB and Project MOHAVE aircraft. The halocarbon methylchloroform is primarily emitted within the SoCAB (Bastable *et al.*, 1990) and has been used to identify the influence of SoCAB air on downwind sites in California, Nevada, and Arizona (Rogers *et al.*, 1987; Miller *et al.*, 1990; Schorran *et al.*, 1990; White *et al.*, 1990; Pryor and Hoffer, 1992; Keislar *et al.*, 1994).

During summer 1992, several radar wind profilers were used in the SEDAB and in the eastern SoCAB. The NOAA Environmental Technology Laboratory, operators of the 1992 southern California radar wind profiler (RWP) network, drew the following conclusions (NOAA, 1994) about SoCAB-to-SEDAB transport:

- Daytime winds in the lowest 500 to 1000 meters AGL showed nearly continuous transport from the SoCAB to the SEDAB at Cajon and Banning passes.

- While synoptic scale weather patterns had little effect on winds in the SoCAB and SEDAB, they affected mixing depths, which were in turn related to 500-mb heights and ozone concentrations at San Bernardino.

- When mixing heights at San Bernardino rose above the height of Cajon Pass, and good transport occurred through the pass, ozone violations were likely at Hesperia.

- During high ozone days at Barstow, CA, in the interior of the Mojave Desert, flow was directly from Cajon Pass; on low ozone days, flow from Cajon Pass was transported south of Barstow, and flow from Tehachapi Pass (from the San Joaquin Valley) remained north of Barstow.

During the summer months, ozone concentrations in Barstow regularly exceed the 0.09 ppm California standard. While the majority of these exceedance days can be directly attributed to transport from the SoCAB, the cause of some exceedances is less straightforward (Roberts *et al.*, 1992). Analyses performed by California Air Resources Board (1990b, 1993) directly support inconsequential transport and the existence of two locally generated Barstow ozone exceedances (i.e., generated from emission sources within the SEDAB only). Based on this analysis, the ARB proposed rule-making for stationary sources within the MDAB.

However, controversy surrounded the ARB conclusion. The Mojave Desert Air Pollution Transport Committee (MDAPTC) was established by the ARB in December 1993 to bring together the regulating, regulated, and scientific communities to evaluate the existing evidence from past studies and to present conclusions and recommendations to the Board. The MDAPTC found no clear indication of local ozone formation. However, the MDAPTC did not reach consensus on which of the studies provided the most valid evidence that emissions from within the desert did not cause or contribute to exceedances of the state ozone standard in the desert. This lack of consensus was due, in part, to the fact that most past studies focused on transport episodes and not on the local contribution. No one study was deemed conclusive of the existence or not of locally caused exceedances of the state

standard, and the conclusions of those few studies which address the issue of local generation are conflicting (MDAPTC, 1996). Thus, the MDAPTC recommended further studies which include:

- The 1995 Mojave Desert Transport Study conducted by ARB. Measurements taken during May-October 1995 included enhanced surface monitoring in suspected transport corridors, mountain top monitoring for ozone aloft, two radar wind profilers. During August, the NOAA ozone lidar with 2D scanning mode capability was deployed with a radar wind profiler and aircraft measurements were taken. Data validation is underway, with reports expected by the end of 1996.

- The Barstow Halocarbon Study was designed to provide a complementary characterization of the SoCAB influence on Barstow ozone by using halocarbon tracers of opportunity (methylchloroform and perchloroethylene) to detect the presence or absence of SoCAB (and possibly SJVAB) air in Barstow. The study period was August 1994 through October 1995, which included the time period for the 1995 Mojave Desert Transport Study.

This scenario should be easy to forecast. It occurs frequently and is associated with a thermal low over the lower Colorado River Valley and a surface high pressure over the eastern Pacific Ocean. The main exceptions to this pattern are conditions of offshore pressure gradients (Santa Ana winds), which are most likely late in the ozone season, and synoptic scale low pressure over the Great Basin, which occurs typically in late spring. Weak Santa Ana conditions lead to high ozone near the coast and prevent substantial transport into the Mojave Desert, whereas the Great Basin low results in good dispersion due to enhanced vertical mixing and relatively strong winds (Green *et al.*, 1992b).

2.5.4 Coastal Day with Eddy

Typically a few times each summer, the usual westerly to northwesterly low-level winds near the Pacific Coast in southern California become south to southeast and are accompanied by an increased depth of the marine layer and an increase in low-level stratus. These conditions are typically associated with a cyclonic eddy, named the "Catalina Eddy," centered over the Southern California Bight. Because of the change in wind, mixing depths, and cloud cover, ozone concentration fields during eddy events may be expected to differ substantially from typical summer patterns. During the mature phase of the eddy, the increased marine layer depth (up to 3000 m) and lack of sunshine required for ozone formation would tend to result in relatively low ozone levels. However, at the beginning of an eddy event, as the southeasterly coastal winds begin, and before full development of the eddy, air with high ozone concentrations may be transported to the northwest. This scenario has been considered in a review of air pollution transport mechanisms affecting Ventura County (Lea *et al.*, 1995). It should be noted that even on days with no obvious eddy circulation, there is often a shear zone and region of cyclonic curvature to the wind flow offshore. Also, a tendency for southeast flow in late morning is typically observed for at least a few hours. Thus, transport toward the South Central Coast may occur even without a discernible, closed eddy circulation (Rosenthal, 1972).

Wakimoto (1987) presents a case study of a Catalina Eddy (August 8-10, 1984) that occurred during Project BASIN, which included enhanced surface and upper air monitoring. Ozone concentrations at nine locations are presented for the period. On August 8, prior to the eddy, high ozone concentrations (up to 0.31 ppm at Glendora) occurred at Glendora, Newhall, and Banning. Ozone at these sites decreased substantially during the eddy. However, ozone to the northeast of Los Angeles at Simi Valley, Thousand Oaks, and Goleta (near Santa Barbara) increased as eddy winds transported pollutants into these areas. Interestingly, at El Rio, just inland from Ventura, ozone levels did not increase; presumably due to inland penetration of the sea-land breeze resulting in less transport of ozone and its precursors. Wakimoto speculated that the high ozone concentrations at Goleta were due to transport above the sea-breeze front and mixing to the ground. Different mixing processes in the coastal zone could explain why increased ozone was observed at Goleta, but not at El Rio. A limitation of the Wakimoto analysis is that it is applied to only one case of a Catalina Eddy, which may or may not represent typical ozone patterns associated with the Catalina Eddy.

Mass and Albright (1989) produced averaged fields of wind, pressure, and other variables for 50 Catalina Eddy events in the 15-year period 1968-1982. Their criteria for a Catalina Eddy included a southerly surface wind component at San Diego of 1.5 m/s or more for 18 hours, and with at least 4 of those hours having a southerly component of 4 m/s or greater. The months used were May-September. Mass and Albright give a hypothesis for the mechanisms causing the Catalina Eddy and describe what features to look for using output from operational weather forecasting products from the National Meteorological Center. Unfortunately, Mass and Albright did not present averaged ozone concentration fields to correspond to their averaged pressure and wind fields.

According to Mass and Albright, during the eddy events, a 500-mb trough enters the Pacific Northwest from the eastern Pacific Ocean and broadens and deepens to the south along the coast. At 850 mb, the trough over the southwestern United States deepens and the Pacific High builds, causing an increase in the east-west pressure gradient. At the surface, the thermal low expands northwestward into the Central Valley of California. The increased pressure gradients cause strong northerly winds over the San Rafael Mountains north of Santa Barbara. These winds initiate the formation of a lee trough over the ocean south of Santa Barbara. Higher pressure to the south causes an ageostrophic flow from south to north near the coast. Because nearly geostrophic northerly winds are occurring further offshore, cyclonic vorticity is generated, thus forming the Catalina Eddy.

Mass and Albright found that the Catalina Eddy is often preceded by high pressure at the surface and aloft over the Great Basin or Rocky Mountains. This may be expected to give weak Santa Ana conditions with the potential for buildup of ozone in the SoCAB, which may then be transported as a "blob" toward the South Central Coast Air Basin during the early stages of the Catalina Eddy that follows.

Mass and Albright state that the above described 500-mb, 850-mb, and surface pressure patterns leading to Catalina Eddies are well forecasted a day in advance by the Nested Grid Model (NGM). Presumably, the ETA model, which is slated to replace the NGM will also do a reasonable job at predicting conditions leading to the formation of the

Catalina Eddy. The high-resolution Navy Operational Regional Atmospheric Predictions System (NORAPS) and other follow-on forecast models developed by the Naval Research Laboratory may also be available for SCOS97. The NORAPS model has shown good potential for forecasting Catalina Eddy circulation.

Transport aloft from the SoCAB toward the SCCAB may occur frequently in summer without a noted eddy circulation. Lea *et al.* (1995) point out that in the late spring to early autumn, the predominant wind directions at 1000-3000 feet MSL during the night and morning hours are from the southeast over near coastal locations of the SoCAB and SCCAB (Point Mugu, Laguna Peak, El Monte, Los Angeles Airport, and Santa Monica). Ozone and precursors injected into the elevated inversion layer during the previous day thus may be frequently transported toward the northwest into the South Central Coast Air Basin. If a mechanism exists to transport this ozone to the surface, such as diurnal heating, then high surface concentrations could result in the SCCAB. This would appear to be most likely at inland locations that experience significant heating prior to arrival of the seabreeze front.

2.5.5 Off-Shore Surface Transport Direct to San Diego Air Basin

This transport scenario considers offshore transport from the SoCAB to the San Diego Air Basin at low levels. During weak Santa Ana conditions, light flow from the north to northeast in the Los Angeles area transports ozone and precursors offshore. As pressure gradients weaken and become onshore during the daytime, the polluted layer may then be transported onshore in the San Diego Air Basin (SDAB). Surface pressure gradients within the SoCAB undergo a diurnal pattern. During late afternoon, pressure gradients between coastal areas and inland areas reach a relative maximum. Under weak Santa Ana conditions, offshore flow occurs from evening through mid-morning. During mid-afternoon, in spite of offshore synoptic scale gradients, weak onshore seabreeze flows may occur. This may cause very high ozone concentrations in the SoCAB. If offshore gradients intensify slightly, pollutants may be transported offshore toward San Diego. They can then be brought onshore with the seabreeze in San Diego when coast to inland gradients in the SDAB become favorable for onshore flow. It may be that only slight variations in the synoptic pressure gradients lead to significant changes in the mesoscale transport and distribution of ozone, complicating the forecasting and modeling of ozone concentrations. Under these conditions, high ozone concentrations may occur anywhere within the SDAB (Bigler-Engler and Brown, 1995a).

Kauper and Niemann (1977), Bigler-Engler and Brown (1995b) and others have shown the SoCAB to be the main source of high ozone concentrations in the SDAB associated with weak Santa Ana conditions. Also, during weak Santa Ana winds or immediately following them, there is often a period of southeast flow causing transport in the opposite direction, towards the South Central Coast.

2.6 Requirements for Data Analysis and Modeling

The data required for this study are primarily driven by the need to drive and evaluate the performance of modeling systems. In evaluating the model performance, the primary concern is replicating the physical and chemical processes associated with actual ozone

episodes. This necessitates the collection of suitable emissions, meteorological, and air quality data that pertain to these episodes. This section describes the data requirements of meteorological and air quality models.

2.6.1 Meteorological Modeling

The specification of the meteorological fields which drive the transport and dispersion of atmospheric pollutants is the critical component in mesoscale air quality modeling. The primary objective is to obtain wind fields over the model grid and determine mechanical and convective mixing depths. The simplest way is to use field measurements and interpolate the values over the entire domain. However, field measurements are generally spatially and temporarily sparse, and can be especially inadequate in areas with complex terrain and land-sea interactions such as southern California. Another way is to use diagnostic and prognostic meteorological models to estimate meteorological fields from existing data and then to adjust these fields through parameterizations of physical processes. Transport and dispersion of atmospheric pollutants is governed by the dynamics and thermodynamics of the atmospheric boundary layer (ABL). The main difficulties in dispersion estimates arise with topographic complexity and increasing atmospheric stability. Turbulence in the ABL is created by wind shear and destroyed by buoyancy and dissipation. Since these effects are nearly balanced in the stable ABL, turbulence intensities are usually low and intermittent. In some cases of stagnant stable conditions the horizontal diffusion of the plume can be of the same magnitude or larger than the actual transport. Moreover, turbulent velocities are frequently affected by gravity waves and the stable ABL undergoes non-stationary evolution. Additional dispersion due to wave phenomena also needs to be resolved. During stable conditions the ABL flow usually decouples from the synoptic winds and its flows are dominated by the local circulations. In some cases a low-level jet can develop at the top of the surface stable layer and the fate of pollutants at various elevated layers can be completely different over a very small vertical separation. In contrast, during stable and stagnant conditions the winds close to the surface are weak and sometimes below the detection limit of usual instrumentation. Radiation and advection can also cause fog and cloud formation and significantly change the rate of chemical reactions for some species and deposition processes. The depth of the stable ABL is of the order of 100 m, and radiation processes, as well as local effects such as urban effects, vegetation, soil properties, and small-scale topographic features, can significantly influence ABL characteristics. Plume meandering is frequently observed during stable conditions in topographically complex terrain, and use of data from limited measurement sites can yield erroneous conclusions. All these effects significantly modify transport and dispersion as well as removal of pollutants. Consequently, an extensive measurement network is necessary in order to capture the spatial and temporal structure of the ABL in a mesoscale domain. The success in any type of dispersion calculation will be limited to appropriate capture and input of atmospheric parameters.

One of the diagnostic models recommended for this study is CALMET. Wind fields in CALMET are calculated in a user specified number of vertical levels by taking into account the influence of terrain on the atmospheric flow and applying an inverse weighting scheme. The initial terrain-adjusted domain mean horizontal components of the wind at each grid point are modified to obtain the final interpolated wind components. CALMET can

calculate a spatially variable initial guess field using objective analysis of the measurements. Moreover, CALMET allows use of gridded wind fields created by a prognostic atmospheric model, such as the Penn State University Meteorological Model (MM4, MM5), as "initial guess" fields or as substitutes for observations. CALMET has detailed algorithms for the depth of the convective layer as a function of the potential temperature lapse rate in the layer above the mixing depth, the time step, and the temperature discontinuity at the top of the mixed layer. The daytime mechanical mixing depth is determined from the Coriolis parameter, the friction velocity and the Brunt-Vaisala frequency in the stable layer above the mixed layer. The nighttime depth of mechanical mixing is determined from the friction velocity. CALMET uses an upwind-positioned averaging scheme to smooth out the mixing depths through use of determined weighting factors. Since CALMET has detailed algorithms for wind fields and mixing depth, and furthermore allows initialization with the output from the prognostic atmospheric model, it is an optimum tool for obtaining the initial meteorological fields necessary for estimation of transport, dispersion, and chemical transformation of atmospheric pollutants.

Based on the complexity of terrain in southern California, the MM5 model developed by Penn State University and the National Center for Atmospheric Research (NCAR) represents an appropriate tool for resolving dynamics and thermodynamics if used on the scale of 1-2 km horizontal resolution with nesting capabilities. It should include a nonhydrostatic option and full parameterization of physical processes including turbulent transfer. MM5 uses an advanced four-dimensional data assimilation scheme connected to either measurements or synoptic fields. However, uncertainty exists as to the extent to which MM5 can be used to infer turbulence properties in complex terrain. One of the main components in the study is a characterization of the origin and fate of atmospheric pollutants in the SoCAB. The main difficulties are due to complex terrain and a number of significant sources within the basin and its surroundings. The results from wind field modeling will be used as an input for dispersion and chemical modeling of relevant pollutants also for the entire intensive study period. Atmospheric modeling should treat formation and evolution of fog and clouds which are essential determinants for liquid-phase chemistry. The detailed information of the three-dimensional plume structure from different sources for the worst case scenarios (highest ground concentrations at the monitoring of interest) will be obtained by wind field, dispersion, and chemical modeling.

The final task is reconciliation of all source apportionment approaches and evaluation of uncertainties, model assumptions, and differences compared to measurements. The main objectives of this task are:

- Simulate atmospheric processes using MM5 in both fully predictive and data assimilation modes. Since a number of airborne and remote sensing upper-air measurements will be available, it is desirable to place emphasis on the data assimilation mode for the entire field program period. The fully prognostic mode may be desirable for understanding basic characteristics of specific weather episodes with high pollutant concentrations.

- Determine flow patterns in southern California with acceptable horizontal and vertical resolution, using physical parameterization of the main atmospheric processes (radiation, moisture, clouds, and fog).

- Provide detailed information on the vertical wind and temperature structure of the atmospheric boundary layer during the case studies. Determine elevated layers with specific stability and dynamics. The vertical structure is essential for estimates of transport and dispersion of atmospheric pollutants, as well as for determination of the amount of decoupling of local flows from the air aloft.

- Determine properties of land-sea breezes, urban circulations, local flows (slope and drainage), and diurnal variation of thermal stability and shear.

- Determine spatial characteristics of mixing depth for both convective and stable conditions.

- Estimate properties of turbulence transfer and associated vertical fluxes in the boundary layer.

- Conduct sensitivity tests of the input parameters (topographic resolution, model grid, synoptic fields vs. radiosonde network, range and variation of sea/surface temperature, urban effects/roughness, sinks and sources of heat).

- Quantify differences between the predicted and observed wind fields and stability parameters for specific case studies.

The *advantages* in using a prognostic modeling approach are:

- High resolution in horizontal and vertical directions.

- Topography with resolution of 30 seconds embedded within the model structure.

- Detailed prognostic fields of meteorological parameters (wind, temperature, humidity, turbulence, radiation, clouds).

- Physically-based estimate of mixing depth in both convective and stable cases, with full spatial and temporal variability.

- Detailed structure of the small-scale local flows that cannot be resolved through simplified parameterization.

- Detailed vertical structure of meteorological parameters and stability, which is especially important near sources and receptors and along the transport path.

The *disadvantages* in using a prognostic modeling approach are:

- The models are fairly complex and expensive to run. Usually they are limited to certain case studies.

- The models have assumptions in simplification of basic differential equations and numerical techniques and in the parameterizations of physical processes.

- Integration with dispersion models is usually one of the critical problems.

Nevertheless, atmospheric models are useful tools in understanding the structure and evolution of boundary layer dynamics and providing meteorological fields as input for dispersion models.

2.6.2 Air Quality Modeling

After numerous air quality modeling efforts over the last two decades, the ARB has provided technical guidance for photochemical modeling (DaMassa *et al.*, 1992). This guidance includes methods for assessing the performance of a model and criteria for accepting a model.

In the application of a model, parameters such as the size of the modeling domain, the number of vertical levels, and the horizontal grid resolution must be chosen to provide adequate characterization of the physical setting and the major atmospheric features without incurring excessive computer run times. Selection of episodes is also important for providing physical insight into the reasons behind the observed pollutant species concentrations and spatial patterns for those episodes.

In the evaluation of the model, the quality of the input aerometric data and the emission inventory must also be considered. DaMassa *et al.* (1992) provide guidance in classifying these input databases.

2.6.3 Contribution of Transported Pollutants to Ozone Violations in Downwind Areas

Although past transport studies have documented pollutant transport on specific days, they have not always quantified the contribution of transported pollutants to ozone violations in the downwind area. Quantitative estimates of the contribution of transported pollutants to ozone violations in the downwind area can be accomplished by photochemical grid modeling and by advanced data analysis techniques such as "flux planes" measured by aircraft which traverse a vertical plane perpendicular to a suspected transport corridor at different elevations.

In principle, well-performing grid models have the ability to quantify transport contributions. However, many of the interbasin transport problems involve complex flow patterns with strong terrain influences which are difficult and expensive to model. Upper-air meteorological and air quality data in critical transport locations is generally required in order to properly evaluate and use grid models for quantifying transport contributions. In combination with modeling, data analyses can improve the evaluation of modeling results and provide additional quantification of transport contributions.

In order to quantify pollutant transport and to provide data for modeling and data analyses, surface and aloft measurements are needed at locations where transport can occur and at the times when transport is occurring. These monitoring locations include in and near

mountain passes, along coastlines, offshore, and at various locations in the downwind air basin. For example, when pollutants are transported from the SoCAB to the SCCAB via the overwater route, measurements are needed along the western shore of the SoCAB as pollutants leave the SoCAB, offshore along the westerly transport route, and along the Ventura and/or Santa Barbara shoreline as the pollutants return onshore in the SCCAB.

Previous studies (e.g., Roberts *et al.*, 1992) have used aircraft measurements to calculate transport across flux planes. Vertical planes, intersecting the profiler sites downwind of and perpendicular to the mountainous SoCAB exits, can be defined and will provide estimates of transport through these passes using surface and aircraft measurements of pollutant concentrations and surface and wind profiler data for volume flux estimations. In addition, flux planes can be used to investigate over-the-mountain transport because Smith and Shair (1983), among others, have shown this to be a possible transport route under certain meteorological conditions. Flux planes for SCOS97 are further discussed in Section 11.6

2.7 SCAQS Scientific Findings Relevant to SCOS97

The 1987 Southern California Air Quality Study (SCAQS) was the largest single air pollution study conducted in southern California, with more than $14 million contributed by 10 government, industry, and trade association sponsors. It has served as a prototype for subsequent large-scale field studies in the United States. This section presents a summary of key scientific findings and the operational and organizational lessons learned from SCAQS.

The SCAQS field program plan and field program have been described by Blumenthal *et al.* (1987), Lawson (1990), and Lawson *et al.* (1995). Prior to the 1987 field study, technical support studies were carried out in Los Angeles in the summers of 1985 and 1986 to evaluate methods for sampling important intermediate and product species to be measured in the 1987 field study.

The 1985 Nitrogen Species Methods Comparison Study (NSMCS) evaluated measurement methods for nitric acid, ammonia, nitrous acid, and particulate nitrate, all important participants in the nitrogen air pollution cycle in Southern California. More than 20 research groups participated in the study, and the results have been published in Atmospheric Environment (Lawson, 1988).

The 1986 Carbonaceous Species Methods Comparison Study (CSMCS) was conducted to evaluate analytical and sampling methods for gas- and particle-phase carbonaceous pollutants, including formaldehyde and hydrogen peroxide. Thirty research groups took part in the study, and the results have been published in Aerosol Science and Technology (Lawson and Hering 1990). The results from the NSMCS and CSMCS were used to design and develop the SCAQS aerosol and gas sampler (Fitz *et al.*, 1989). The data analysis and modeling results, as of mid-1992, have been published in the proceedings of the SCAQS Data Analysis Conference (Fujita, 1995). The NSMCS, CSMCS, and SCAQS have resulted in more than 300 peer-reviewed publications.

The SCAQS field study consisted of 11 intensive study days during five separate episodes in the summer of 1987 and six intensive study days during three separate episodes in the fall of 1987. The summer study was designed to collect data during high ozone periods. The summer study included upper air measurements at six rawinsonde and two airsonde sites, in addition to aircraft measurements. The fall study consisted of six "B" sites and one "A" site and was designed to study air quality during stagnation conditions conducive to buildup of NO_2 and PM_{10}. The "B" sites were established along two separate pollutant transport routes across the SoCAB. Each of these sites contained the specially designed SCAQS aerosol and gas sampler (Fitz *et al.*, 1989; Chow *et al.*, 1993). Two of the "B" sites were heavily instrumented with numerous research projects — the upwind Long Beach site and the downwind Claremont site — these were also called "A" sites. There were 36 "C" sites, which consisted of the routine monitoring sites operated by the SCAQMD and other groups. The fall study also had aircraft measurements, one airsonde, and five rawinsonde sites.

2.7.1 Emissions

- Nonmethane organic gas (NMOG, or nonmethane hydrocarbons plus oxygenated compounds) composition and NMOG to NO_X ratios were similar throughout the SoCAB. This suggests a common source of emissions (presumably motor vehicles), and continuous injection of fresh emissions. However, the total NMOG concentrations had significant spatial, day-to-day, and seasonal variations due to meteorological factors and the non-uniformity of emission rates.

- The 1987 SCAQS Van Nuys Tunnel study suggested that nonmethane hydrocarbon (NMHC) and CO emissions may be underestimated by about a factor of 2 in EMFAC7E, the California Air Resources Board's motor vehicle emission factor model, version 7E (July 1991). Model estimates of NO_X emissions appeared to be in reasonable agreement with the tunnel measurements. These conclusions are consistent with those of other studies throughout the country.

- Measurements in 1987 of ambient NMOG to NO_X ratios were 2 to 2.5 times higher than estimates from EMFAC7E. Ambient CO to NO_X ratios were $\approx$1.5 times higher than emission ratios (Fujita *et al.*, 1992). (The agreement between ambient and emission NMOG to NO_X ratios has improved since 1987 because ambient NMHC, and presumably NMOG, concentrations have declined faster than the emission model predicts, and the model has been modified to include previously uninventoried sources of NMOG and CO.)

- There is more unburned gasoline in the atmosphere than estimated by the emission inventory. It is not clear whether tailpipe exhaust, evaporative emissions, or fuel spillage is the source of these uninventoried emissions (Harley *et al.*, 1992; Fujita *et al.*, 1994). Since NMOG compositions in other cities in California and the U.S. are similar to the SoCAB, these conclusions may apply to the rest of the country (Fujita *et al.*, 1995).

- The accuracy of the non-motor vehicle component of the emission inventory could not be evaluated because of the proximity of most monitoring stations to roadways and the lack of marker species to provide unique source signatures.

- Airshed model predictions were in better agreement with ozone measurements when the official on-road motor vehicle ROG emissions were increased by substantial margins. ARB (Wagner and Wheeler, 1995) and SCAQMD (Chico *et al.*, 1995) increased total on-road motor vehicle emissions by a factor of 2.5, and Carnegie Mellon/California Institute Technology (Harley *et al.*, 1993) increased hot exhaust emissions by a factor of 3.

- The relative composition of the NMOG inventory is biased toward overestimation of alkenes and underestimation of aromatic hydrocarbons and higher ($>C_2$) carbonyl compounds. The reactivities of the emission inventory composition profiles are about 10 and 30 percent higher than the ambient composition profiles in summer and winter, respectively.

2.7.2 Factors Controlling Ozone Accumulation

- Nitrous acid (HONO), directly emitted and presumably formed by nighttime reactions involving NO_X, water, and aerosols, is potentially the single largest source of hydroxyl radicals that initiate the ozone photochemistry in the early part of the day.

- There appears to be a large amount of carbonyl species formation in the urban atmosphere from photo-oxidation of hydrocarbons. The secondary photochemical contributions to C_1 to C_4 carbonyl compounds are probably larger than the primary source contributions, although the peak concentration events are dominated by primary source contributions. Sources of C_{4+} carbonyl compounds could not be identified. Some evidence indicates landfills, and perhaps microbial decomposition of industrial, household, and agricultural waste products, as primary sources of C_{4+} carbonyl compounds.

- Overall, biogenic hydrocarbons play a small role in ozone formation in the urban area of the SoCAB. On average, isoprene contributed 0.2 percent of the NMOG carbon, and 0.7 percent of the NMOG reactivity (using the maximum incremental reactivity scale of Carter *et al.*, 1994) in the summer. However, because isoprene reacts rapidly, and because the measurement system did not measure the intermediate products of isoprene reactions, the ambient measurements underestimate its relative contribution.

- Although the hydrocarbon measurement system was set up to detect monoterpenes, none were found.

2.7.3 Performance of Urban-Scale Models

- The airshed models used to model the SCAQS episodes appear to underpredict NO_X oxidation products, leading to concerns about their ability to quantify the effectiveness of NO_X controls.

- High concentrations of ozone and other pollutants were often found aloft in layers covering much of the SoCAB near the top of the daytime mixed layer. Model predictions of ozone aloft for one of the case studies were about 0.05 to over 0.10 ppm less than the measured concentrations. In the surface layer, depending on the model application and location in the modeling domain, predicted ozone concentrations were significantly lower or higher than observations.

- Because current airshed modeling efforts may be missing an important upper air recirculation feature, uncertainties in the modeling results must be determined and potentially reduced. Models should not use a terrain-following coordinate system, as the observed pollutant and temperature structure aloft appears to be more horizontal in nature. Clean boundary conditions should be used above the mixed layer, typically above 1,500 to 2,000 meters.

2.7.4 Management of Ozone Accumulation

- Under the combined NMOG and NO_X control program in the SoCAB, peak ozone concentrations have declined by 20 percent and exposure to unhealthful concentrations has declined by 50 percent since the early 1980s; at the same time, concentrations of NMOG have declined by about 40 percent and concentrations of both NO_X and CO have declined by about 20 percent.

- Consensus exists that NMOG and CO emissions from motor vehicles are significantly underestimated, but there is no agreement on the cause.

- Further refinement of models applied in the SoCAB is needed, as the current treatment of recirculation, and possible underestimation of ROG emission rates may underestimate the benefits of NO_X control strategies.

- Modeling studies for a range of ozone episodes and base emission inventories determined that the maximum incremental reactivity (MIR) scale is a valid approach for reactivity scaling of NMOG emissions (National Research Council, 1991).

2.7.5 Potential Nationwide Research Needs Arising from SCAQS

- Top-down comparisons of ambient measurements with the emission inventories have demonstrated a need for more accurate methods of assessing the contribution and importance of various pollution source types on air quality in urban areas.

- Conditions aloft have a significant influence on surface air quality; boundary conditions also have a significant influence on modeling results. Development of reliable and cost-effective methods for measuring meteorological conditions and pollutant concentrations (aloft and in "clean" air) is needed to support modeling applications.

- Smog formation is sensitive to small concentrations of critical pollutants such as hydroxyl and hydroperoxy radicals, nitrous acid, etc. Development of reliable methods for measuring these critical compounds is needed to support modeling applications.

- The performance of photochemical models is somewhat dependent on their formulation. Improvements are needed in the meteorological and chemical formulations to improve model accuracy, precision, and validity.

3. MEASUREMENT APPROACH

Field monitoring includes continuous measurements over several months and intensive studies that are performed on a forecast basis during selected periods when episodes are most likely to occur. The continuous measurements are made in order to assess the representativeness of the intensive study days, to provide information on the meteorology and air quality conditions on days leading up to the episodes, and to assess the meteorological regimes and transport patterns which lead to ozone episodes. The intensive study components are designed to provide a detailed aerometric database which, along with the emission estimates and continuous monitoring data, can be used to improve our understanding of the causes of pollutant episodes in the study region and to provide data for input to the models and for model evaluation. This section describes the existing routine air quality and meteorological monitoring network in southern California, and the options for continuous and intensive air quality and meteorological measurements (surface and aloft) to be made during SCOS97.

3.1 Surface Meteorology

The types of surface meteorological measurements needed for this study include measurements of wind speed, wind direction, and temperature. Measurements of humidity, pressure, visibility, solar radiation, and ultraviolet radiation are also available at some sites. Within the study area (modeling domain), these measurements are provided by several existing networks of sites operated by several organizations including:

- Surface Airways Observations sites from the National Weather Service (NWS), operating in conjunction with the Federal Aviation Administration
- California Irrigation Management Information System sites from the California Department of Agriculture
- Remote Automated Weather Station sites from the Bureau of Land Management, California Department of Forestry, National Park Service, and U.S. Forest Service
- APCD/AQMD Aerometric Monitoring Station sites from the South Coast AQMD, the Mojave Desert AQMD, San Diego AQMD, Ventura County APCD, Santa Barbara APCD, Kern County APCD, San Joaquin Valley Unified Control District, Imperial County APCD, and California Air Resources Board
- County flood control districts in Los Angeles (LAFCD), Ventura County (VCFCD), and Santa Barbara County (SBCFCD)
- Off-shore buoys sites operated by the Mineral Management Service
- Military installations
- Private companies

- Public organizations such as universities

Appendix B provides a list of the surface meteorology sites in the study domain. A comprehensive discussion of the accuracy and methodology of surface measurements is provided in the SJVAQS/AUSPEX Meteorological Field Measurement Program report (Thuillier, 1994).

These surface sites use instruments deployed about 1.5–10 meters above the ground to measure surface hourly wind speed and wind direction, temperature, humidity, and pressure. Temperature is obtained by thermistor or platinum resistance elements and has a nominal accuracy of 1 °C or better. Typical sampling rates are from once per second to once per minute, with hourly averages reported. At some surface airways sites which do not utilize the newer Automated Surface Observing System (ASOS) equipment, temperature measurements are taken for a few minutes near the hour.

Wind speed and direction are usually obtained by cup or propeller anemometers and wind vanes. Response times are on the order of a second and threshold values for an accurate response are about 0.5 meters per second (~1 mph).

Humidity measurements are taken by hygroscopic films or solutions exposed to ambient air. These sensors have a known electrical resistance that is a function of relative humidity. Reported values of relative humidity are usually ±5 percent, with better accuracy in the mid range but lower accuracy at either extreme.

Surface sites are generally inexpensive, and can be easily outfitted for unattended operation. Thus, many sites can be deployed. However, they do not cover aloft conditions unless deployed on elevated sites like mountain tops thought to be representative of flow aloft.

Other surface sites could be used to conduct tracer tests and to deploy sonic anemometers for better boundary-layer turbulence characterization. Tracers can be released in a few selected upwind surface sites and collected by short-term (1-12 hour) samples at many surface sites downwind. Tracers specifically tag polluted air from upwind air basins, and multiple tracer releases can help determine the relative contributions of upwind pollutants to downwind ozone. The surface samplers can operate routinely with little operator attention. However, tracer material is expensive, and large quantities of tracer are required if long transport distances are to be studied. Also, several days may be needed to disperse the tracer before another test can be conducted.

Sonic anemometers deployed at surface sites would provide estimates of turbulent fluxes for the modeling effort. The variations in sound propagation over a short (30 cm) path are typically sampled at 10 Hz, providing an estimate of turbulent fluctuations over that path. One-dimensional sonic anemometers measure vertical turbulent flux, while three-dimensional sonic anemometers include turbulent fluxes in the two horizontal dimensions. These data provide boundary layer characterization, representative of the type of terrain over which the measurement is taken. Urban effects could be better incorporated in the mesoscale

model. The measurement could provide better dispersion estimates for models run in the data assimilation mode, and provide real-world measurements against which model estimates of turbulent flux are compared.

3.2 Upper-Air Meteorology

The types of upper-air meteorological measurements needed include wind speed, wind direction, temperature, and mixing height. Measurements of humidity are also useful where they are available at some sites. A comprehensive discussion of the accuracy and methodology of upper air measurements is provided in the SJVAQS/AUSPEX Meteorological Field Measurement Program report (Thuillier, 1994).

3.2.1 Existing Measurements

Upper air data routinely available in the study region consist of radiosonde data from the National Weather Service (NWS) site at San Diego, military bases (Vandenberg AFB, NAWC [Pt. Mugu, San Nicolas Island], Edwards AFB, China Lake NAWS, and Fort Irwin), and the Mexican Weather Service site at Hermosillo. The NWS Oakland site and the Desert Rock site in Nevada (100 km NW of Las Vegas) are outside the proposed modeling domain but will be of interest. The NWS and NAWC sites release at the standard 0000 Z (0400 PST) and 1200 Z (1600 PST) times, while the schedules for the other sites may vary depending on military mission requirements.

Radar wind profiler data are currently available from five sites at Simi Valley, LAX, San Diego (Pt. Loma), Ontario Airport, and Vandenburg AFB. A sixth site should be in operation for this 1997 study at a north San Diego County site near Escondido. These data averaging times are typically hourly.

Satellite observing systems can provide some wind and temperature data for the troposphere. These may be useful in initializing mesoscale meteorological models. Also, wind data are available from the WSR-88D Doppler weather radars operated by the National Weather Service at seven sites covering parts of the model domain.

3.2.2 Radiosondes

Radiosondes provide in situ measurements of pressure, temperature, and humidity from the ground to more than 4,500 m AGL using a manually released balloon. A radio transmitting instrument package is carried aloft by a freely ascending helium balloon. The balloon is tracked optically or electronically to provide its position relative to the release site such that estimates of the wind speed and direction can be derived. Radiosondes provide wind data that are averaged over short vertical distances and are thus nearly instantaneous measurements at a particular location. Although the radiosonde directly measures temperature and humidity during the short balloon flight, it is only a "snapshot" at each level of the atmosphere. The labor and expendable costs are significant, and prohibit performing soundings more frequently than once every 12 hours. As the radiosonde rises, it is

transported downwind, so measurements are not made above a fixed location, as within a wind profiler, for example.

3.2.3 Radar Wind Profilers

Radar wind profilers (RWPs) provide continuous remote measurements of wind speed and direction to altitudes of ~3 km AGL. The profilers emit short pulses of generally 915 MHz electromagnetic radiation which scatter off inhomogeneities in the index of refraction of an air mass. By emitting energy directionally in three orthogonal components, the received scattered radiation provides estimates of wind speed and direction. Because of the finite length of the emitted pulse train, vertical resolution is limited to approximately 100 m. Echoes received during the detector downtime cannot be processed and this raises the threshold height to approximately 100 m above ground level. The typical five-degree beam width also limits the resolution of wind direction in a height dependent manner. There are general trade-offs between maximum range and vertical resolution and between averaging time and accuracy.

Radar wind profiler data are generally reported as 15-minute up to hourly averaged data and are representative of a three-dimensional cell. Because wind vectors may vary significantly over the course of an hour, the near-instantaneous radiosonde measurements may not compare well with radar wind profiler measurements on a case-by-case basis. However, if radiosondes and wind profilers are deployed in areas with similar winds, the statistical distribution of winds may be expected to be reasonably similar. The RWP is highly sensitive to stray electromagnetic signals and stationary or solid objects in the beam paths or their side lobes. Thus, it should be sited away from large objects such as buildings and trees and away from frequent overflights by aircraft.

3.2.4 Acoustic Sounders (Sodars)

The sodar uses an observational process that is similar to the RWP except that the sodar uses pulses of acoustic instead of electromagnetic energy. The sodar then detects returned acoustic energy scattered from turbulent density fluctuation (instead of index of refraction fluctuations). It provides hourly averaged wind speed and direction up to a 500-600 m maximum range with a threshold height of approximately 50-60 m. The sodar can operate routinely with little or no on-site care, but compared to radiosondes it does not measure humidity, and the equipment is expensive. The sodar is highly sensitive to extraneous sources of sound. Thus, it should be sited away from substantial and continuous noise sources such as heavily traveled roads. The sodar acoustic emissions are audible and may disturb nearby residents, which can be a siting disadvantage compared with the RWP. With the lower vertical range, sodars should be deployed in areas of lower expected mixing heights, such as in marine layers.

3.2.5 Tethered Balloons

Tethered balloons employ an instrument package, called a tethersonde, which provides in situ measurements of wind speed and direction, temperature, dew point, and

pressure. The package is deployed on a blimp-shaped helium balloon that is tied by light cord to a mechanical winch system. The altitude range is usually limited to less than 1 km; wind speeds over 10 meters per second may cause loss of the balloon. The tethersonde transmits the information back to a ground station, with values taken every few seconds corresponding to one value every 2-3 meters apart for average ascent and descent speeds. The accuracy of the measurements compares to that of any surface station, since the sonde package is akin to a miniature surface station carried aloft by the balloon. Advantages of the tethersonde include much better vertical resolution with no threshold height compared to the RWP or sodar. Once the system is set up and manned, soundings can be taken through the surface layer as often as every 15 minutes. However, disadvantages of the tethersonde include site setup/breakdown time, the need for continual manning during operations, and the difficulty in obtaining FAA permits to operate within 8 km of any airport. In a populated area like the SoCAB, FAA permits would significantly impact the scope of operations.

3.2.6 Radio-Acoustic Sounding Systems (RASS)

Temperature aloft up to 500-700 m can be characterized using a RASS. The RASS essentially uses collocated radio wave and acoustic sources such that radio waves are scattered off the acoustic wavefronts. The propagation velocity of the acoustic wave fronts is then measured, which can be related to the (virtual) temperature of the air. This effort could install one radar profiler with RASS at critical locations along major transport paths, such as mountain passes or the coastal shoreline, for example, near Cajon and Banning Passes and along the downwind shorelines in San Diego and Santa Barbara. There is considerably less accuracy in the RASS temperature profiles compared to the those obtainable from tethersonde measurements, particularly in areas of complex terrain where radar side lobes may present a problem. However, the RASS temperature data may be compared to QA radiosonde or tethersonde temperature data because the virtual temperature can also be calculated from the sonde measurements of ambient temperature, dew point or relative humidity, and pressure. A favorable comparison under representative conditions would increase confidence in the RASS data at these sites.

3.3 Surface Air Quality

In the SCOS97 study region, the Ventura County Air Pollution Control District (VCAPCD), South Coast Air Quality Management District (SCAQMD), Mohave Desert Air Quality Management District (MDAQMD), and San Diego Air Pollution Control District (SDAPCD) are charged with the responsibility for determining compliance with state and federal air quality standards, proposing plans to attain those standards when they are exceeded, and for implementing those plans. To these ends, the four agencies operate a network of sampling sites which measure ambient pollutant levels. Three types of surface air quality monitoring stations are operated by the air pollution control districts. The National Air Monitoring Stations (NAMS) were established to ensure a long term national network for urban area-oriented ambient monitoring and to provide a systematic, consistent database for air quality comparisons and trend analysis. The State and Local Air Monitoring Stations (SLAMS) allow state and local governments to develop networks tailored to their immediate

monitoring needs. Special purpose monitors (SPM) fulfill very specific or short-term monitoring goals. SPMs are typically used as source-oriented monitors rather than monitors which reflect the overall urban air quality. Data from all three types are submitted by state and local agencies to EPA's Aerometric Information Retrieval System (AIRS), which serves as the national repository for air quality, meteorological and emissions data.

Under Title I, Section 182, of the 1990 Amendments to the Federal Clean Air Act, the EPA proposed a rule to revise the current ambient air quality surveillance regulations. The rule requires implementing a national network of enhanced ambient air monitoring stations (Federal Register, 1993). States with areas classified as serious, severe, or extreme for ozone nonattainment are required to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan (SIP). In California, PAMS are required in Ventura County, and the South Coast, Southeast Desert and San Diego air basins. Each station measures speciated hydrocarbons and carbonyl compounds, ozone, oxides of nitrogen, and surface meteorological data. Additionally, each area must monitor upper air meteorology at one representative site. The program is being phased in over a five-year schedule, beginning in 1994, at a rate of at least one station per area per year. Intended applications for the PAMS database include ozone and precursor trends, emission inventory reconciliation and verification, population exposure analyses, photochemical modeling support, and control strategy evaluation.

3.3.1 Routine Air Quality Monitoring Stations

There are 100 active monitoring stations in southern California. Table 3-1 contains a list of the monitoring sites and the air quality parameters measured at each site. Of the active sites, 96 measure ozone and 81 measure NO_X. Carbon monoxide and total hydrocarbons are measured at 46 and 42 sites, respectively. Data from these sites will be routinely acquired and archived by the Districts and integrated into the SCOS97 database after the 1997 measurement program. The following is a brief description of the measurement methods that are commonly used at routine air quality monitoring stations.

Ozone

Ozone is continuously measured either by ultraviolet absorption photometry or by gas- phase ethylene-ozone chemiluminescence. In the ultraviolet analyzer, a mercury vapor lamp is used to produce ultraviolet radiation at 254 nm which is absorbed by the ozone in the air sample. The ozone signal is determined by the difference between ambient air containing ozone and ambient air with the ozone removed or scrubbed. The ultraviolet analyzer is calibrated by comparison with an ozone photometer which is certified as a transfer standard. The transfer standard is certified against absolute ozone photometers located at the California Air Resources Board test and laboratory facilities. The minimum detectable level of UV monitors is about 2-5 ppbv. Accuracies and precisions are on the order of 10-15 percent or 2-5 ppbv, whichever is larger. Interferences with the UV measurement method include any gas or fine particle that absorbs or scatters light at 254 nm. Gaseous inorganic compounds normally found in the atmosphere, including NO_2 and SO_2, do not interfere, and particles are

Table 3-1
Air Quality Monitoring Sites in Southern California

Site ID	Air Basin	County	Data Source	Site Name	Variables Measured						
					O3	NO	NOx	CO	THC	CH4	NMHC
ARVN	SJVAB	Kern	CARB	ARVIN-20401 BEAR MTN BLVD	x	x	x				
BKGS	SJVAB	Kern	SJVUCD	BAKERSFIELD-1138 GOLDEN STATE	x	x	x	x	x	x	x
BLFC	SJVAB	Kern	CARB	BAKERSFIELD-5558 CALIFORNIA ST	x	x	x	x	x	x	x
EDSN	SJVAB	Kern	CARB	EDISON-JOHNSON FARM	x	x	x				x
OLDL	SJVAB	Kern	CARB	OILDALE-3311 MANOR ST	x	x	x		x	x	x
ARGR	SCCAB	San Luis Obispo	XONTEC	ARROYO GRANDE-RALCOA WAY					x	x	x
ATAS	SCCAB	San Luis Obispo	SLOCO	ATASCADERO-6005 LEWIS AVE	x	x	x				
GCTY	SCCAB	San Luis Obispo	SLOCO	GROVER CITY-9 LE SAGE DR	x	x	x				
MOBY	SCCAB	San Luis Obispo	SLOCO	MORRO BAY-MORRO BAY BL & KERNR	x						
NIPO	SCCAB	San Luis Obispo	UNOCAL	NIPOMO-1300 GUADALUPE RD	x						
NPSW	SCCAB	San Luis Obispo	SLOCO	NIPOMO-148 S WILSON ST	x	x	x				
PSRB	SCCAB	San Luis Obispo	CARB	PASO ROBLES-235 SANTA FE AVE	x						
SLPL	SCCAB	San Luis Obispo	EMC	SAN LUIS OBISOP-7020 LEWIS		x	x		x		
SLOM	SCCAB	San Luis Obispo	CARB	SAN LUIS OBISPO-1160 MARSH ST	x	x	x	x	x		
CPGB	SCCAB	Santa Barbara	CHVRON	CARPINTERIA-GOBERNADOR RD	x	x	x				
ECSP	SCCAB	Santa Barbara	SBAPCD	EL CAPITAN STATE PARK	x	x	x		x		
GAVE	SCCAB	Santa Barbara	CHVRON	GAVIOTA EAST-N OF CHEVRON PLAN	x	x	x		x		
GAVW	SCCAB	Santa Barbara	CHVRON	GAVIOTA WEST-NW OF CHEVRON PLA	x	x	x		x		
GTCA	SCCAB	Santa Barbara	TEXACO	GAVIOTA-GTC A .5 MI SW OF PLT	x	x	x				
GTCC	SCCAB	Santa Barbara	TEXACO	GAVIOTA-GTC C 1 MI E OF PLANT	x	x	x		x		
GLWF	SCCAB	Santa Barbara	SBAPCD	GOLETA-380 W FAIRVIEW AVE	x	x	x	x			
LPSH	SCCAB	Santa Barbara	SBAPCD	LOMPOC-128 S 'H' ST	x	x	x	x			
LPHS	SCCAB	Santa Barbara	UNOCAL	LOMPOC-HS&P FACILITY 500 M SW	x	x	x		x		
LOSP	SCCAB	Santa Barbara	UNOCAL	LOS PADRES NF-PARADISE RD	x	x	x				
GTCB	SCCAB	Santa Barbara	TEXACO	NOJOQUI PASS-GTC B HWY 101	x	x	x				
PTAR	SCCAB	Santa Barbara	UNOCAL	POINT ARGUELLO-NE OF SLC	x	x	x		x		
PTCL	SCCAB	Santa Barbara	CHVRON	POINT CONCEPTION LIGHTHOUSE	x	x	x				
SBWC	SCCAB	Santa Barbara	CARB	SANTA BARBARA-3 W. CARRILLO ST	x	x	x	x			
SMSB	SCCAB	Santa Barbara	CARB	SANTA MARIA-500 S BROADWAY	x	x	x				
SMBB	SCCAB	Santa Barbara	UNOCAL	SANTA MARIA-BATTLES BETTERAVIA	x	x	x		x		
SYAP	SCCAB	Santa Barbara	SBAPCD	SANTA YNEZ-AIRPORT RD	x						
UCSB	SCCAB	Santa Barbara	EXXON	UCSB WEST CAMPUS-ARCO TANK, IS	x	x	x		x		

Table 3-1
Air Quality Monitoring Sites in Southern California

Site ID	Air Basin	County	Data Source	Site Name	Variables Measured						
					O3	NO	NOx	CO	THC	CH4	NMHC
VBPP	SCCAB	Santa Barbara	VBGAFB	VANDENBERG AFB-STS POWER PLANT	x	x	x	x	x		
ELRO	SCCAB	Ventura	VCAPCD	EL RIO-RIO MESA SCHOOL	x	x	x	x	x	x	x
EMMA	SCCAB	Ventura	VCAPCD	EMMA WOOD STATE BEACH	x	x	x				
THOS	SCCAB	Ventura	CARB	OAK VIEW-5500 CASITAS PASS RD	x	x	x		x		
	SCCAB	Ventura	VCAPCD	OJAI - OJAI AVENUE	x	x	x				
OJAI	SCCAB	Ventura	VCAPCD	OJAI-1768 MARICOPA HIWY	x	x	x				
PRTG	SCCAB	Ventura	VCAPCD	PIRU-2SW, 2815 TELEGRAPH RD	x						
SVAL	SCCAB	Ventura	VCAPCD	SIMI VALLEY-5400 COCHRAN ST	x	x	x	x	x	x	x
TOMP	SCCAB	Ventura	VCAPCD	THOUSAND OAKS-9 2323 MOORPARK	x	x	x				
AZSA	SoCAB	Los Angeles	SCAQMD	AZUSA-803 N LOREN AVE	x	x	x	x	x	x	x
BRBK	SoCAB	Los Angeles	SCAQMD	BURBANK-228 W PALM AVE	x	x	x	x	x		x
GLDR	SoCAB	Los Angeles	SCAQMD	GLENDORA-840 LAUREL	x	x	x				
HAWH	SoCAB	Los Angeles	SCAQMD	HAWTHORNE-5234 W. 120TH ST	x	x	x	x			
NLGB	SoCAB	Los Angeles	SCAQMD	LONG BEACH-3648 N LONG BEACH	x	x	x	x	x	x	x
LANM	SoCAB	Los Angeles	SCAQMD	LOS ANGELES-1630 N MAIN ST	x	x	x	x	x	x	x
LYNW	SoCAB	Los Angeles	SCAQMD	LYNWOOD-11220 LONG BEACH BLVD	x	x	x	x	x	x	
PDSW	SoCAB	Los Angeles	SCAQMD	PASADENA-752 S. WILSON AVE	x	x	x	x			
PICO	SoCAB	Los Angeles	SCAQMD	PICO RIVERA-3713 SAN GABRIEL	x	x	x	x	x		x
POMA	SoCAB	Los Angeles	SCAQMD	POMONA-924 N. GAREY AVE	x	x	x	x	x		x
RSDA	SoCAB	Los Angeles	SCAQMD	RESEDA-18330 GAULT ST	x	x	x	x	x		
	SoCAB	Los Angeles	SCAQMD	SAN DIMAS-GLADSTONE (open by 1/96)	x	x	x				
CLAR	SoCAB	Los Angeles	SCAQMD	SANTA CLARITA-SAN FERNANDO RD	x	x	x	x			
VALA	SoCAB	Los Angeles	SCAQMD	W LOS ANGELES-VA HOSPITAL	x	x	x	x	x	x	
ANAH	SoCAB	Orange	SCAQMD	ANAHIEM-1610 S HARBOR BLVD	x	x	x	x	x		
CMMV	SoCAB	Orange	SCAQMD	COSTA MESA-2850 MESA VERDE DR	x	x	x	x			
ELTR	SoCAB	Orange	SCAQMD	EL TORO-23022 EL TORO RD	x	x	x	x	x		
LHAB	SoCAB	Orange	SCAQMD	LA HABRA-621 W. LAMBERT	x	x	x	x	x		
HEMT	SoCAB	Riverside	SCAQMD	HEMET-880 STATE ST	x						
LELS	SoCAB	Riverside	SCAQMD	LAKE ELSINORE-506 W FLINT ST	x	x	x				
	SoCAB	Riverside	SCAQMD	MIRA LOMA-BELLEGRAVE AVE (by 1/96)	x						
PERR	SoCAB	Riverside	SCAQMD	PERRIS-237 .5 N "D" ST	x						
RIVM	SoCAB	Riverside	SCAQMD	RIVERSIDE-7002 MAGNOLIA AVE		x	x	x	x		

Table 3-1
Air Quality Monitoring Sites in Southern California

Site ID	Air Basin	County	Data Source	Site Name	Variables Measured						
					O3	NO	NOx	CO	THC	CH4	NMHC
RUBI	SoCAB	Riverside	SCAQMD	RUBIDOUX-5888 MISSION BLVD	x	x	x	x	x	x	
TCCC	SoCAB	Riverside	SCAQMD	TEMECULA-COUNTY CENTER	x	x	x	x			
UCDC	SoCAB	Riverside	RIVER	UC RIVERSIDE-4919 CANYON CREST	x						
LGRE	SoCAB	San Bernardino	SCAQMD	CRESTLINE-LAKE GREGORY-LAKE DR	x						
FONT	SoCAB	San Bernardino	SCAQMD	FONTANA-14360 ARROW BLVD	x	x	x				
	SoCAB	San Bernardino	SCAQMD	LAKE ARROWHEAD (Open by 1/96)	x	x	x				
RDLD	SoCAB	San Bernardino	SCAQMD	REDLANDS-DEARBORN	x						
SANB	SoCAB	San Bernardino	SCAQMD	SAN BERNARDINO-24302 4TH ST	x	x	x	x			
UL	SoCAB	San Bernardino	SCAQMD	UPLAND	x	x	x				
CLXC	SEDAB	Imperial	ICAPCD	CALEXICO-900 GRANT ST	x	x	x				
CALE	SEDAB	Imperial	CARB	CALEXICO-CALEXICO HS ETHEL ST	x	x	x	x			x
EC9S	SEDAB	Imperial	ICAPCD	EL CENTRO-150 9TH ST	x						
WEST	SEDAB	Imperial	ICAPCD	WESTMORLAND-202 W FIRST ST	x						
MOJP	SEDAB	Kern	CARB	MOJAVE-923 POOLE ST	x	x	x				
LANC	SEDAB	Los Angeles	SCAQMD	LANCASTER-315 W. PONDERA ST	x	x	x	x			x
BANN	SEDAB	Riverside	SCAQMD	BANNING-135 N ALLESANDRO	x				x		x
INDO	SEDAB	Riverside	SCAQMD	INDIO-46-990 JACKSON ST	x						
PALM	SEDAB	Riverside	SCAQMD	PALM SPRINGS-FS 590 RACQUET CL	x	x	x	x	x		x
BARS	SEDAB	San Bernardino	MDAQMD	BARSTOW-401 MOUNTAIN VIEW	x	x	x	x			
HESP	SEDAB	San Bernardino	MDAQMD	HESPERIA-17288 OLIVE ST	x	x	x	x			
JOSH	SEDAB	San Bernardino	NPS	JOSHUA TREE NATIONAL MONUMENT	x						
PHEL	SEDAB	San Bernardino	MDAQMD	PHELAN-BEEKLEY & PHELAN RDS	x	x	x	x			
TRNA	SEDAB	San Bernardino	MDAQMD	TRONA-83732 TRONA ROAD	x	x	x				
29PM	SEDAB	San Bernardino	MDAQMD	TWENTYNINE PALMS-6136 ADOBE DR	x	x	x	x			
VICT	SEDAB	San Bernardino	MDAQMD	VICTORVILLE-14029 AMARGOSA RD	x	x	x	x			
ALPN	SDAB	San Diego	SDAQMD	ALPINE-2300 VICTORIA DR	x	x	x		x	x	
CHVT	SDAB	San Diego	SDAQMD	CHULA VISTA-80 E "J" ST	x	x	x	x	x		x
DMMC	SDAB	San Diego	SDAQMD	DEL MAR-MIRACOSTA COLLEGE	x						
ECAJ	SDAB	San Diego	SDAQMD	EL CAJON-1155 REDWOOD AVE	x	x	x	x	x	x	x
ESCO	SDAB	San Diego	SDAQMD	ESCONDIDO-600 E. VALLEY PKWY	x	x	x	x	x		x
OCEA	SDAB	San Diego	SDAQMD	OCEANSIDE-1701 MISSION AVE	x	x	x	x	x		
OTAY	SDAB	San Diego	SDAQMD	OTAY-1100 PASEO INTERNATIONAL	x	x	x	x			

Table 3-1
Air Quality Monitoring Sites in Southern California

Site ID	Air Basin	County	Data Source	Site Name	Variables Measured						
					O3	NO	NOx	CO	THC	CH4	NMHC
SDUN	SDAB	San Diego	SDAQMD	SAN DIEGO-1133 UNION ST				x			
SD12	SDAB	San Diego	SDAQMD	SAN DIEGO-330A 12TH AVE	x	x	x	x	x	x	x
SDOV	SDAB	San Diego	SDAQMD	SAN DIEGO-5555 OVERLAND AVE	x	x	x	x	x	x	x

largely removed by a pre- filter. The most likely interferent is gaseous hydrocarbon compounds that are strong absorbers at 254 nm and are either partially or completely absorbed onto the scrubber. Examples are aromatic compounds, such as benzene and substituted benzenes. Interferences from hydrocarbons can account for a positive bias in the UV measurement for ozone of up to 40 ppb based on the concentration of the interferences occurring during peak ozone periods (Leston and Ollison, 1992). Kleindienst *et al.* (1993) observed about a 3 percent interference with ozone measurements under hydrocarbon loadings typical of ambient smoggy conditions. Water vapor may also interfere with the UV method when water vapor concentrations are high and variable. These interferences appear to be due to the condensation of water vapor on imperfect absorption cell windows.

The ozone/ethylene chemiluminescence method (ECL) is a Federal Reference Method for measuring ozone in ambient air (EPA, 1971). The ECL method is based on the reaction of ozone with ethylene, which produces formaldehyde in an electrically excited state and, on transition to the ground state, emits light in the visible range. This reaction is rapid and specific to ozone and takes place in a chamber coupled to a sensitive photomultiplier tube. Under controlled conditions, the signal produced by the ozone-ethylene reaction is proportional to the ozone concentration in the reaction chamber and with proper calibration it is proportional to ambient ozone concentrations. The chemiluminescence analyzer is calibrated in the same manner as the ultraviolet analyzers. The minimum detection level of commercial ECL monitors is about 2-5 ppbv. Accuracies and precisions are on the order of 10-15 percent or 2-5 ppbv, whichever is larger. The only major interference for measuring ozone by the ECL method is water vapor. The positive interference ranges from 3-12 percent. However, this interference can be adjusted for by calibrating the ECL monitors at humidities expected during peak ozone periods. In practice, this is rarely done.

The Luminox® ozone analyzer (LOZ-3) or ozone/eosin-Y chemiluminescence (EYC) method developed by Unisearch Associates, Inc., is a relatively new method for measuring ozone. The EYC method continuously measures ozone based on the reaction of eosin-Y in solution with ozone. Ambient air is drawn across a fabric wick that is continuously flushed with a specially formulated solution containing eosin-Y (proprietary information, Unisearch Associates, Inc.). A red sensitive photomultiplier tube measures the chemiluminescence at the liquid/air interface. The reaction is rapid and very specific to ozone. The minimum detectable level of the EYC monitor is about 0.1 ppb, with a precision of about 0.8 to 2.0 ppb at ozone concentrations of 100 and 400 ppb, respectively. The response time of the EYC analyzer (2-3 s for 95% response to a 400-ppb sample) is much faster than the response time of the ECL or the UV analyzers (0.5 minute or more). The fast response time and low limits of detection make this unit well suited for measurement aboard aircraft. Species that are normally found in the atmosphere (NO, NO_2, H_2O_2, NH_3 and H_2CO) do not interfere with the measurement of ozone by the EYC method.

Nitrogen Oxides

Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with

ozone. In this method an ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal which is proportional to the NO concentration. To measure NO_X concentrations, the sum of NO and NO_2 (nitrogen dioxide), the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using $FeSO_4$, adding to the NO already present in the sample, then into the reaction chamber for measurement as described above. The NO_2 concentration is derived by subtracting the NO concentration measurement from the NO_X concentration measurements. The reduction of NO_2 to NO by these methods is not specific and a number of other nitrogen-containing species are reduced to NO that can interfere with the measurement of NO_2 (e.g., HNO_3, PAN, N_2O_5, HONO, and NO_3). Therefore the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group. If the group is not well defined, it is referred commonly as NO_X, since the species included in the group depend on factors such as inlet and line losses and environmental factors. Standard sensitivity instruments have detection limits of about 3-5 ppb and are most suitable for air quality monitoring in heavily polluted areas such as major urban centers. Thermo Environmental Instruments, Inc. (TEI) Model 14 and Monitor Labs 8440 and 8840 are examples of this type of instrument. These and similar instruments from Columbia Scientific and Bendix have been used widely by federal, state, and local agencies for routine monitoring of NO and NO_2 (actually NO_X minus NO plus other interfering nitrogen oxides). High-sensitivity OCM instrument and methods for specific measurements of oxidized nitrogen species are discussed in Section 3.4.1.

3.3.2 Photochemical Assessment Monitoring Stations (PAMS) Program

Design criteria for the PAMS network are based on selection of an array of site locations relative to ozone precursor source areas and predominant wind directions associated with high ozone events. Specific monitoring objectives are to characterize precursor emission sources within the area, transport of ozone and its precursors into and out of the area, and the photochemical processes related to ozone nonattainment, as well as developing an initial urban toxic pollutant database. A maximum of five PAMS sites are required in affected nonattainment areas, depending on the population of the Metropolitan Statistical Area/Consolidated Metropolitan Statistical Area (MSA/CMSA) or nonattainment area, whichever is larger. Specific monitoring objectives associated with each of these sites result in four distinct site types.

Type 1 sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and to identify those areas which are subjected to overwhelming transport. Type 1 sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions during the ozone season. Typically, Type 1 sites will be located near the edge of the photochemical grid model domain in the predominant upwind direction from the city limits or fringe of the urbanized area.

Type 2 sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions are expected. These sites also are suited for the monitoring of urban air toxic pollutants. Type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district. Additionally, a second Type 2 site may be required depending on the size of the area, and will be placed in the second-most predominant morning wind direction.

Type 3 sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Typically, Type 3 sites will be located 10 to 30 miles downwind from the fringe of the urban area.

Type 4 sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and identify those areas which are potentially contributing to overwhelming transport in other areas. Type 4 sites are located in the predominant afternoon downwind direction, as determined for the Type 3 site, from the local area of maximum precursor emissions during the ozone season. Typically, Type 4 sites are located near the downwind edge of the photochemical grid model domain.

The current status of the implementation of PAMS by local air pollution control districts in southern California is outlined in Table 3-2. PAMS precursor monitoring is conducted annually in California during the peak ozone season (July, August and September) according to the schedule shown in Table 3-2. Thirteen PAMS sites will be operational by 1997 (three in Ventura County; five in the South Coast Air Basin, one in the Southeast Desert Air Basin, and four in the San Diego Air Basin). The table includes minimum network requirements that are specified in the EPA rule and the alternative network specifications submitted to EPA by ARB on behalf of the affected districts in the state. The California Alternative Plan was deemed by EPA to satisfy the PAMS monitoring objectives and has been approved for use by districts in California.

EPA methods TO-14 and TO-11 are specified by the EPA for sampling and analysis of speciated hydrocarbons and carbonyl compounds, respectively (EPA, 1991). Table 3-3 contains the minimum list of targeted hydrocarbon species. For carbonyl compounds, state and local agencies are currently required to report only formaldehyde, acetaldehyde and acetone. The districts may be able to quantify and report several C_3 to C_7 carbonyl compounds that appear in the HPLC chromatograms. The EPA rule requires eight 3-hour hydrocarbon samples (midnight-3 am, 3-6 am, 6-9 am, 9-noon, noon-3 pm, 3-6 pm, 6-9 pm, and 9-midnight PDT) every day at Type 2 sites and every third day at all other PAMS sites. Sampling for carbonyl compounds is required at Type 2 sites only. In addition, one 24-hour sample is required every sixth day year-round at Type 2 sites and during the summer monitoring period at all other sites. Under the California Alternative Plan, four 3-hour samples (3-6 am, 6-9 am, 1-4 pm, and 5-8 pm, PDT) are collected every third day during the monitoring period at all PAMS sites for speciated hydrocarbons and at Type 2 sites only for carbonyl compounds. In addition to the regularly scheduled measurements, samples are collected on a forecast basis during up to five high-ozone episodes of at least two consecutive

Table 3-2
PAMS Sites in Southern California

	Type of Site	Year Deployed	VOC Method	Carbonyl Method	Frequency of VOC Measurements		Frequency of Carbonyl Measurements	
					EPA Rule	CA Alternative Plan	EPA Rule	CA Alternative Plan
Ventura County								
El Rio	2	1994	Canister/GC-FID	DNPH/HPLC	B	E, F	D	E
Simi Valley	3	1995	Canister/GC-FID		A or C	E, F		
Ventura - Emma Wood Sta	1	1996	Canister/GC-FID		A or C	E, F		
South Coast Air Basin								
Pico Rivera	2	1994	Auto-GC	DNPH/HPLC	B	E, F	D	E
Upland	4	1994	Canister/GC-FID		A or C	E, F		
Azusa	3	1995	Canister/GC-FID		A or C	E, F		
Hawthorne	1	1996	Canister/GC-FID		A or C	E, F		
Burbank	2	1997	Auto-GC	DNPH/HPLC	B	E, F	D	E
Southeast Desert Air Basin								
Upland	1	1994	Canister/GC-FID		A or C	E, F		
Banning	2	1995	Canister/GC-FID	DNPH/HPLC	A or C	E, F	D	E
Burbank	1	1997	Canister/GC-FID		A or C	E, F		
Lancaster	2	1998	Canister/GC-FID	DNPH/HPLC	A or C	E, F	D	E
San Diego Air Basin								
El Cajon	2	1994	Canister/GC-FID	DNPH/HPLC	B	E, F	D	E
Alpine	3	1995	Canister/GC-FID		A or C	E, F		
Camp - Del Mar	1	1996	Canister/GC-FID		A or C	E, F		
San Diego - Overland	2	1994	Canister/GC-FID	DNPH/HPLC	B	E, F	D	E

Type 1 - Upwind background.
Type 2 - Maximum precursor emissions (typically located immediately downwind of the central business district).
Type 3 - Maximum ozone concentration.
Type 4 - Extreme downwind transported ozone area that may contribute to overwhelming transport in other areas.
A. Eight 3-hour samples (starting at midnight, PDT) every third day and one additional 24-hour sampler every sixth day during monitoring period (July-September).
B. Eight 3-hour samples (starting at midnight, PDT) every day during the monitoring period (July-Sept and one additional 24-hour sample every sixth day year-round.
C. Eight 3-hour samples on the 5 peak ozone days plus each previous day, eight 3-hour samples every sixth day, and one additional 24-hour sample every sixth day during monitoring period.
D. Eight 3-hour samples (starting at midnight, PDT) every day during the monitoring period (July-September).
E. Four 3-hour samples (3-6am, 6-9am, 1-4pm, 5-8pm, PDT) every third day during monitoring period (probably July-September), and four samples (6-9am, 9-noon, 1-4pm, 5-8pm, PDT) per day
F. Continuous NMHC analyzer (e.g., Bendix 8202 or automated Preconcentration Direct injection Flame Ionization Detection gas chromatography, PDFID).

Table 3-3.
Target Ozone Precursors for PAMS

1	Ethylene	29	2-Methylhexane
2	Acetylene	30	2,3-Dimethylpentane
3	Ethane	31	3-Methylhexane
4	Propene	32	2,2,4-Trimethylpentane
5	Propane	33	n-Heptane
6	Isobutane	34	Methylcyclohexane
7	1-Butene	35	2,3,4-Trimethylpentane
8	n-Butane	36	Toluene
9	trans-2-Butene	37	2-Methylheptane
10	cis-2-Butene	38	3-Methylheptane
11	Isopentane	39	n-Octane
12	1-Pentene	40	Ethylbenzene
13	n-Pentane	41	m&p-Xylene
14	Isoprene	42	Styrene
15	trans-2-Pentene	43	o-Xylene
16	cis-2-Pentene	44	n-Nonane
17	2,2-Dimethylbutane	45	Isopropylbenzene
18	Cyclopentene	46	n-Propylbenzene
19	Cyclopentane	47	1-ethyl 3-methylbenzene
20	2,3-Dimethylbutane	48	1-ethyl 4-methylbenzene
21	2-Methylpentane	49	1,3,5-Trimethylbenzene
22	3-Methylpentane	50	1-ethyl 2-methylbenzene
23	2-Methyl-1-Pentene	51	1,2,4-Trimethylbenzene
24	n-Hexane	52	n-decane
25	Methylcyclopentane	53	1,2,3-Trimethylbenzene
26	2,4-Dimethylpentane	54	m-diethylbenzene
27	Benzene	55	p-diethylbenzene
28	Cyclohexane	56	n-undecane
			Total NMOC

days. Episodic measurements consist of four samples per day (6-9 am, 9-noon, 1-4 pm and 5-8 pm, PDT) for speciated hydrocarbons at all PAMS sites and for carbonyl compounds at Type 2 sites. The VCAPCD and SDAPCD operate their PAMS sites according to the alternative plan, while SCAQMD operates theirs according to the EPA Rule. SCAQMD's 3-hour sampling schedule (on PST year round) begins one hour later than sampling times used by VCAPCD and SDAPCD (on PDT for PAMS). The PAMS 3-hour VOC sampling schedule should be consistent throughout the SCOS97 study area.

Total nonmethane hydrocarbon (NMHC) concentrations are monitored at some PAMS sites by automated-Preconcentration Direct Injection Flame Ionization Detection (PDFID) (e.g., Xontech 850). Total NMHC is measured by passing the air sample through a chromatographic column to separate methane from other hydrocarbons and analyzing the bulk hydrocarbon sample by FID. In the FID, sample air is burned in a hydrogen flame creating a quantity of ions from the hydrogen molecules in the air sample. The ions conduct a small electrical current which is measured by an electrometer, which in turn produces an electronic signal proportional to the number of ions collected. Thus, the total hydrocarbon data are reported as parts per billion carbon (ppbC).

Surface meteorological measurements consist of temperature, wind direction and speed, and solar radiation at all sites, and upper air measurements will consist of at least one radar wind profiler with RASS in each of the four nonattainment areas. The PAMS upper air meteorological measurements will be supplemented by existing scheduled radiosonde releases at military installations at San Nicolas Island, Pt. Mugu, Vandenburg AFB, Edwards AFB, Miramar NAS and China Lake NAS.

3.4 Supplemental Air Quality Measurements

Supplemental air quality measurements are needed during Intensive Operational Periods (IOPs) in order to examine the three-dimensional distribution of ozone in the study area and to quantify some of the important species, other than those routinely monitored, which participate in ozone photochemistry.

3.4.1 Ozone Aloft — Lidar Measurements

In the more than 30 years since the invention of the laser, the evolution of lidar (light detection and ranging) technology has led to great advances in atmospheric remote sensing (Measures, 1984). A particular form of lidar, the Differential Absorption Lidar (DIAL) has made it possible to measure the concentration distributions of many tropospheric trace gases and pollutants (Rothe *et al.*, 1974a; Measures, 1984; Grant *et al.*, 1992).

A basic lidar system consists of a transmitter and a receiver located next to each other. The transmitter, typically a pulsed laser, sends a short pulse of collimated light into the atmosphere. A small part of this light pulse is scattered back into the receiver by atmospheric particles and gas molecules. Light scattered at a distance r will arrive at the receiver after a

round trip time t = 2r/c, where c is the speed of light. The lidar return signal S as a function of distance r is described by the lidar equation (Measures, 1984).

$$S(r,\lambda) = A(r,\lambda)C(\lambda)\frac{\beta(r,\lambda)}{r^2}\exp\left[-2\int_0^r \sigma(x,\lambda)dx\right] \quad ,$$

where A is the overlap integral between the transmitted laser beam and the field of view of the telescope, C is the system constant, ß is the backscattering coefficient, σ is the volume extinction coefficient, and λ is the wavelength of the laser. While the overlap integral A can be determined from measurements in a homogeneous atmosphere, the system constant C is generally unknown and for each measured signal S(r,λ) there are two atmospheric parameters ß(r,λ) and σ(r,λ) one would like to determine. The lidar equation is therefore under-determined and cannot be solved without additional assumptions or data. To obtain at least semi-quantitative information about the range-resolved atmospheric extinction, one generally assumes an empirical relationship between the backscattering coefficient ß(r,λ) and the extinction coefficient σ(r,λ) (Gibson, 1994), together with an estimate of a boundary condition for the extinction coefficient within the measurement range (Fernald *et al.*, 1972; Klett, 1981). The mathematical technique used for this semi-quantitative analysis is based on Hitschfeld's work for the analysis of radar data (Hitschfeld and Bordan, 1954) and is often referred to as Klett inversion (Klett, 1981).

Differential **a**bsorption **li**dar (DIAL) is a multi-wavelength lidar that uses the wavelength-dependent absorption of atmospheric constituents to measure their range resolved concentration (Measures, 1984). For this purpose, the extinction coefficient σ at a distance r and wavelength λ_i may be written as

$$\sigma(r,\lambda_i) = \sigma_i(r) + \alpha_i\, n(r) \quad ,$$

where σ_i is the extinction coefficient due to scattering at λ_i, α_i denotes the absorption coefficient at λ_i, and n is the concentration of the absorbing gas. If the lidar equation is applied at two different wavelengths λ_i and λ_j with substantially different absorption coefficients, the concentration n at range r can be calculated from the ratio of the lidar signals at the two wavelengths as

$$n(r) = \frac{1}{2\Delta\alpha_{ij}}\frac{d}{dr}\left[\ln\frac{S_j(r)}{S_i(r)}\right] - \frac{\Delta\sigma_{ij}(r)}{\Delta\alpha_{ij}} + \frac{1}{2\Delta\alpha_{ij}}\frac{d}{dr}\left[\ln\frac{\beta_i(r)}{\beta_j(r)}\right] + \frac{1}{2\Delta\alpha_{ij}}\frac{d}{dr}\left[\ln\frac{A_i(r)}{A_j(r)}\right],$$

where $\alpha_{i,j}=\alpha_i-\alpha_j$ and $\sigma_{i,j}=\sigma_i-\sigma_j$. The laser line (wavelength) with the larger (smaller) absorption coefficient is referred to as "on-line" ("off-line"). The first term in this equation is the main term, while the others are correction terms; the second term and the third term, respectively, are corrections for differential aerosol extinction $[E_{i,j}]$ and backscatter $[B_{i,j}]$ between the two wavelengths, whereas the fourth term is a correction for the incomplete overlap $[O_{i,j}]$. The extinction correction vanishes ($[E_{i,j}]=0$) if the extinction due to scattering is identical for λ_i and λ_j, the backscatter correction vanishes ($[B_{i,j}]=0$) if the ratio of the backscattering coefficients for λ_i and λ_j is independent of distance, and the overlap correction

vanishes ($[O_{i,j}]=0$) if the ratio of the overlap integrals for λ_i and λ_j is independent of distance. In contrast to extinction and backscattering corrections, the overlap correction is a pure system parameter, independent of atmospheric conditions, requiring only an initial system calibration.

Several criteria pollutants (i.e., ozone (O_3) (Molina and Molina, 1986), sulfur dioxide (SO_2) (Manatt and Lane, 1993), and nitrogen dioxide (NO_2) (Davidson *et al.*, 1988)) have absorption features in the middle ultraviolet (shown in Figure 3-1) where an absence of disturbing interference from other atmospheric gases, large backscattering cross-sections for both particles and gases, low solar background, and the commercial availability of both tunable and fixed frequency lasers as radiation sources make the development of appropriate active remote sensors feasible.

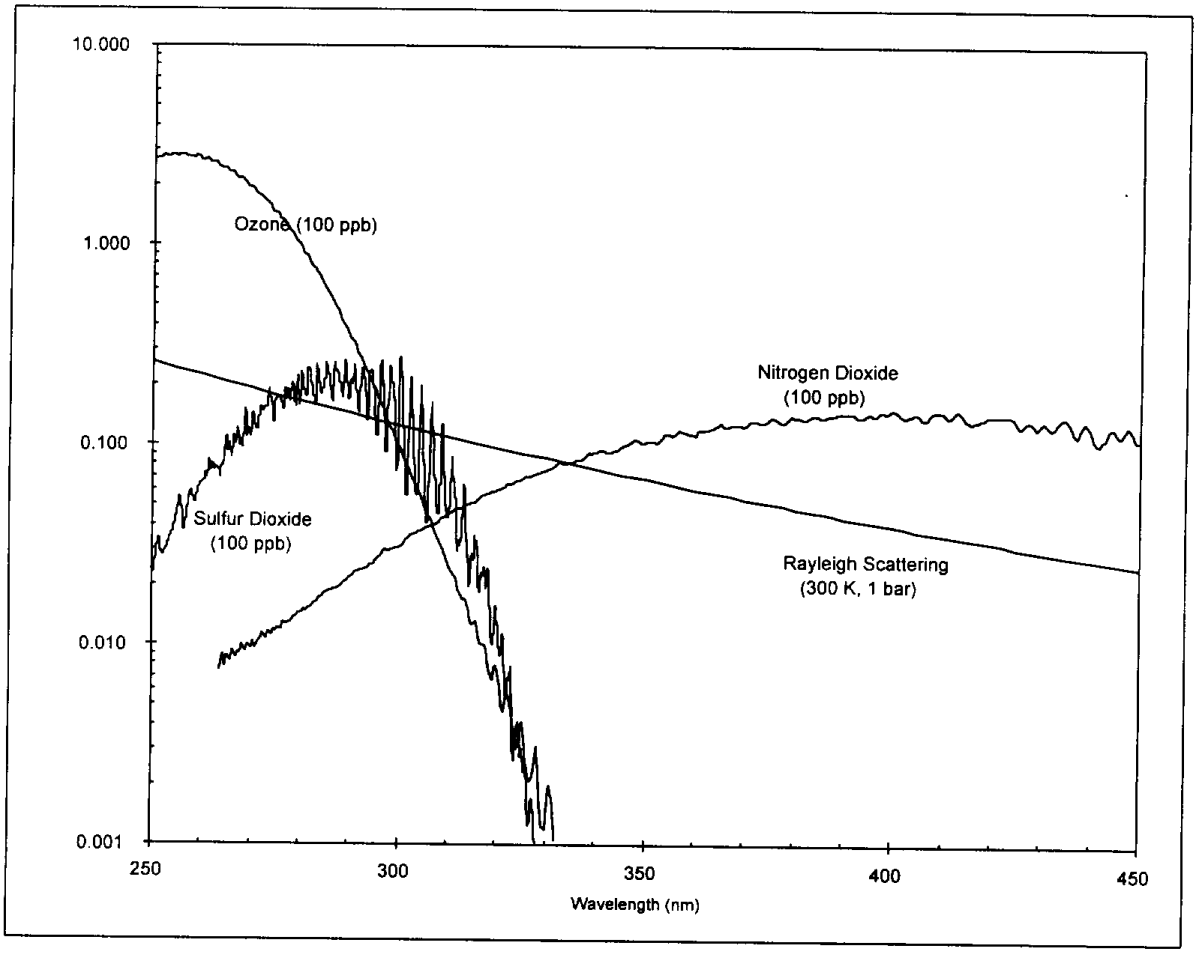
In particular, SO_2 and NO_2 have enough fine structure in their spectra so that their concentration can be measured with DIAL utilizing two closely ($\approx$ 1 nm) spaced wavelengths (Rothe *et al.*, 1974b; Browell, 1982; Galle *et al.*, 1988). In this case differential extinction and backscattering corrections are negligible and the systematic errors of the DIAL measurement become independent of aerosol loading. However, to utilize the spectral fine structure efficiently, tunable lasers have to be used.

In contrast, the O_3 absorption spectrum is quite smooth, necessitating a wider spacing between the two wavelengths, on the order of 20 nm. Therefore, differential extinction and backscattering corrections become important. While the extinction correction is generally negative (i.e., the measured concentration is too high without correction) and on the order of a few ppb, the backscattering correction can become much larger in regions with large gradients of aerosol concentration. For small aerosol loading the backscattering is dominated by Rayleigh scattering with its λ^{-4} wavelength dependence, while for large aerosol loading particle scattering with its approximately λ^{-1} wavelength dependence contributes most of the backscattering. Therefore, a rapid change with distance r from polluted to clear air, as encompassed for example in inversion layers, requires a positive backscattering correction, while the opposite change requires a negative correction. In the case of thin aerosol layers this can lead to a dispersion shape of the required correction or of the uncorrected, measured ozone concentration.

To calculate the backscattering correction one needs range resolved data for the aerosol backscatter coefficient at both DIAL wavelength. Generally, one can guess the wavelength dependence of the backscattering coefficient (Charlson, 1972) and may try to obtain the backscattering coefficient at the "off" wavelength from a lidar inversion (Klett, 1981). However, even this task is quite difficult in the near ultraviolet, especially in the lower troposphere (Kovalev and Moosmüller, 1994).

Ozone DIAL measurements can also be influenced by the simultaneous optical absorption by SO_2 and to a far lesser degree by NO_2. Generally this effect becomes only problematic in power plant plumes and can be minimized by proper selection of laser wavelengths (Moosmüller *et al.*, 1994).

Figure 3-1. Ultraviolet Absorption Spectra of Ozone, Sulfur Dioxide, and Nitrogen Dioxide.



While DIAL systems have been used for the remote measurement of atmospheric pollutants for more than two decades (Rothe *et al.,* 1974a), their hardware, use, and data analysis procedures have not become routine. They still require close attention, skilled personnel and considerable resources. Of particular importance are well designed, implemented, and tested hardware and data analysis algorithms. Especially the interdependence between hardware and data analysis algorithms has to be stressed. Generally, their performance evolves, and hopefully improves, together in an iterative fashion. The successful use of these systems is highly dependent on skilled, experienced, and dedicated operators and developers, which are often identical.

It should be noted that range, precision, spatial, and temporal resolution of DIAL measurements are closely related and fair comparisons between different systems can only be made if all of these parameters are given. Lower and upper range limits are of different importance for zenith looking ground based systems and nadir looking airborne systems. For ground based systems the lower range limit is of particular importance as it is identical to the height above ground at which measurements start for a zenith looking operation. For airborne systems, the flight altitude can generally be chosen so that the upper range limit approximates the height above ground.

The precision of the DIAL measurements is generally best around the distance from the system where complete overlap between laser beams and field of view of the telescope is obtained. With increasing distance from the system the signal level and consequently the signal-to-noise ratio and precision of the DIAL measurement deteriorate. For ground based systems this trend is frequently reduced by decreasing the range resolution with increasing distance. This is a sensible approach, as the scale of atmospheric structure generally increases with increasing altitude. However, for airborne, downlooking lidar systems the opposite is true — the finer scale atmospheric structure is generally encountered towards the far end of their measurement range, close to the ground where the measurement precision is the lowest. In addition, these systems are moving, with a typical averaging time of 15 s corresponding to about 1 km of horizontal movement. If atmospheric structure smaller than the distance covered in the averaging time (e.g., 1 km) is encountered, the data averaging becomes rather problematic. Both these problems can make measurements close to the ground difficult for airborne, downlooking lidar systems.

Aerosol extinction and backscattering corrections have not been implemented in the routine data analysis for any of the following systems. Its inclusion would be a worthy goal for the analysis of SCOS97 data.

Transportable Ground Based Systems

The ground based systems described in this section are transportable in the sense that they are installed in containers/trailers which can be moved around. Shutting such a system down, getting it ready for transport, and starting it up at a new location requires about one to two days, if no unforeseen problems are encountered.

Los Alamos National Laboratory (LANL)

General sources of information: Personal communication with Dr. Bill Cottingame 1995 & 1996 and unpublished system descriptions

The Lidar/Environmental Applications (L/EA) team at LANL has recently acquired a mobile, tunable UV-DIAL system. It has been used to measure nitrogen dioxide and sulfur dioxide at power plants, etc., several times before it was acquired by LANL. It has not been used for field measurements since then.

This system is based on two solid state, tunable Ti:sapphire lasers pumped by two frequency doubled Nd:YAG lasers. These lasers operate at 10 Hz pulse repetition rate and are used alternating as input into a four-pass Ti:sapphire amplifier operating at 20 Hz pulse repetition rate. The fundamental wavelength range and pulse energy are specified to be 710 to 910 nm and 100 mJ/pulse, respectively. In practical operation the output energy is generally around 50–60 mJ/pulse and the lasers have been used between 875 and 890 nm. Frequency doubled and tripled output energies for this wavelength range have been around 25 mJ/pulse and 5–8 mJ/pulse, respectively. The frequency doubled wavelength range (355–455 nm; specs) is well suited for the DIAL measurement of NO_2, while the frequency tripled wavelength range (237–303 nm; specs) is well suited for the DIAL measurement of SO_2 and O_3. Previous operation between 875 and 890 nm includes the ideal wavelengths for NO_2 measurement (freq. doubled) and SO_2 measurements (freq. tripled). For the measurement of ozone the system will be operated frequency tripled but at a shorter wavelength than for SO_2 detection. Some of the output optics will need to be modified for operation below 290 nm as needed for ozone measurements.

The receiver section utilizes an 11" diameter, vertically mounted telescope and a single PMT detector preceded by an interference filter. For NO_2 or SO_2 measurements this arrangement is fully satisfactory as sequential laser pulses at closely spaced ($\approx$ 1 nm) wavelengths are used. In this case both wavelengths are well within the spectral width of the interference filter. For ozone measurements the on- and off-wavelengths are about 20 nm apart and the interference filter will have to be replaced by a double notch or edge interference filter. Another option is the use of two PMTs with their own filters. The PMT signals are digitized by a 12 bit A/D converter for further digital processing.

The measurement range for this system is estimated to be between 250 m and perhaps 1 km. The commercial scanning system is mounted on the roof of the lidar van and provides coverage of the full hemisphere.

National Oceanic and Atmospheric Administration (NOAA)

General sources of information: (Zhao et al., 1994) and personal communication with Dr. Mike Hardesty and Dr. Yan Zhao 1995 & 1996.

The Atmospheric Lidar Division of NOAA's Environmental Technology Laboratory in Boulder has developed a transportable ozone and aerosol lidar specifically for the

measurement of ozone in the boundary layer and the lower free troposphere. This lidar has been employed in several field experiments:

- July 1993, Intercomparison Experiment in Davis, CA, sponsored by ARB (Zhao *et al.*, 1994)
- September 1993, LAFRS Experiment in Claremont, CA, sponsored by ARB (Zhao *et al.*, 1994)
- August, 1995, Ozone Transport Experiment in Victorville, CA, sponsored by ARB
- October–November 1995, Table Mountain Vertical Ozone Transport and Intercomparison Experiment in Boulder, CO, sponsored by NOAA.

This system is based on a solid state laser, the Nd:YAG laser with a fundamental wavelength of 1064 nm and a pulse repetition rate of up to 10 Hz. The third harmonic of this wavelength (i.e., 355 nm) with an operating pulse energy of 7–10 mJ is used for aerosol profiling with a range of about 9 km. The fourth harmonic of the fundamental (i.e., 266 nm) with an operating pulse energy of 20–30 mJ is used as "on-line" for the ozone measurement. The "off-line" for the ozone measurement is generated by Raman shifting the second harmonic (i.e., 532 nm) by the vibrational frequency of the deuterium molecule (i.e., 2987 cm^{-1}) to 632.5 nm, and subsequent sum-frequency mixing of 532 nm and 632.5 nm, yielding an "off-line" at 289 nm. This process takes place in a specially designed Raman cell, yielding a pulse energy of 1–2 mJ. This process utilizes the laser energy better than the more direct Raman shifting of the fourth harmonics (Ancellet *et al.*, 1989; Zhao *et al.*, 1994), while yielding the same wavelength.

The receiver section utilizes an 8"-diameter telescope to collect the backscattered light. Dichroic beamsplitters separate the light from the different laser lines for the detection by photomultiplier tubes. The signals are digitized by 12 bit A/D converters for the subsequent analysis. The aerosol channel currently has an 8 bit A/D which will be replaced by a 12 bit A/D.

Ozone measurements can be obtained for a range of up to 3 km under moderate to high surface ozone concentrations (< 150 ppb) while, for extremely high concentrations, a range of 2 km can still be achieved. The lower range limit is very good (≈ 50 m) due to the use of an innovative technique for the compression of the lidar dynamic range (Zhao *et al.*, 1992). The measurement direction of the lidar system can be scanned in one dimension from 30° to 150° yielding a two dimensional ozone measurement.

Sandia National Laboratories, Livermore (Sandia)

General sources of information: Personal communications with Dr. John Goldsmith in 1995 & 1996 and unpublished system descriptions.

The Laser Remote Sensing Group of the Sandia National Laboratory has recently developed a transportable UV-DIAL system for the measurement of a variety of atmospheric trace gases including ozone, sulfur dioxide, hydrocarbons (e.g., toluene), and nitrogen dioxide. So far the system has been used in two field tests:

- October 1994, Measurements in plumes at 0.5 km distance, Remote Sensor Test Range, Nevada Test Site
- July 1995, Measurements in plumes at 1.4 km distance, Remote Sensor Test Range, Nevada Test Site

These tests included measurements of sulfur dioxide, carbon disulfide, toluene, p-xylene, and m-xylene. Ozone was also detected, but during these tests it was only of interest as interference.

The system is based on two frequency doubled, broadly tunable solid state optical parametric oscillators (OPO), each pumped by its own frequency tripled Nd:YAG laser. The tuning range of both OPOs is 220–350 nm with 250–320 nm having been used so far. However, even this smaller tuning range fully covers the wavelength range needed for ozone measurements. Each of the OPOs emits a pulse energy of 5–15 mJ at a repetition rate of 30 Hz. Currently one of the OPOs runs only at 10 Hz; it hopefully will operate at 30 Hz again in the near future.

The receiver section utilizes an 30"-diameter telescope to collect the backscattered light. Dichroic beamsplitters separate the backscattered light from the two different lasers into two channels. Each of the two channels has two photomultiplier tubes for increased dynamic range. The scanning system utilizes a single mirror in conjunction with the upward pointing telescope and laser beams. This arrangement results in a 360° scanning angle in the horizontal plane and a vertical range from -20° (i.e., downward slanted) to 30°–40°. For vertical operation the scanning mirror would either have to be removed, resulting in a fixed zenith looking system, or have to be complemented by a second mirror. The signals are digitized by 12 bit A/D converters for the subsequent analysis.

Airborne System

National Oceanic and Atmospheric Administration (NOAA)

General sources of information: (Moosmüller, 1994) and personal communication with Dr. Raul Alvarez and Dr. Mike Hardesty 1995 & 1996.

The Atmospheric Lidar Division of NOAA's Environmental Technology Laboratory in Boulder is operating an airborne, downlooking UV-DIAL, which was originally developed by EPA's Environmental Monitoring Systems Laboratory – Las Vegas. This system is capable of measuring range resolved ozone concentrations and aerosol, nadir looking from its airborne platform to near the ground level. It has been tested and employed in several field experiments:

- July 1991, Initial Ground Tests at the Lake Mead National Recreation Area, Nevada (Moosmüller *et al.*, 1992)

- May 1992, Initial Airborne Tests in Southeastern Michigan (Moosmüller *et al.*, 1993; McElroy *et al.*, 1994; Moosmüller *et al.*, 1994)

- July–August 1993, COAST Study in Southeastern Texas (McElroy *et al.*, 1994; Moosmüller, 1994)

- June–July 1995, Southern Oxidant Study in Tennessee

- October–November 1995, Table Mountain Vertical Ozone Transport and Intercomparison Experiment in Boulder, CO, Ground Based Operation.

This system is based on a KrF excimer laser, which generates 700 mJ, 20 ns-long pulses at 248 nm with a maximum pulse repetition rate of 20 Hz. Raman cells produce transmitted laser beams at frequencies shifted from the KrF fundamental by integral multiples of the vibrational frequencies of hydrogen (4160 cm^{-1}) and deuterium (2987 cm^{-1}). The pulse power of the five utilized laser lines ranges from 5–12 mJ.

The receiver section consists of a 20"-diameter downlooking telescope for collection of the backscattered light and a spectrograph/detector system for the simultaneous detection of five individual laser lines (i.e., 276.9 nm, 291.6 nm, 312.9 nm, 319.4 nm, and 359.4 nm). Normally the 276.9 nm and 312.9 nm wavelengths are used as on- and off- lines for the ozone analysis. The 359.4 nm line is well suited for the measurement of aerosol profiles. The PMT signals are digitized by 12 bit A/D converters with a spatial resolution of 30 m. The resulting data together with the OMA spectra are stored on magnetic tape and simultaneously displayed on a monitor in real time to allow for optimization and control of the system operation.

The current measurement range for ozone is from about 0.8 km to 2.5–3 km, with the lower limit corresponding to the complete overlap of laser beams with the field of view of the telescope. The lower limit might be reduced somewhat in the future by applying the overlap correction in the data analysis and/or different alignment of the hardware. Generally, the DIAL data are analyzed for ozone concentrations down to about 90–150 m above ground.

3.4.2 Oxidized Nitrogen Species

Accurate measurements of NO and NO_2 in the atmosphere are of considerable importance because of the role of these compounds in the production of ozone and other photochemically derived air pollutants, such as peroxyacetyl nitrate (PAN), the nitrate radical (NO_3), and nitric acid (HNO_3). Proper evaluation and exercise of photochemical models require low detection limits (<1 ppbv) and interference-free measurements of these species. Routine monitoring techniques for measurement of NO and NO_2 and other oxides of nitrogen do not meet these requirements, thus, the photochemical models are unable to reproduce the measured atmospheric concentrations of these species accurately. Recent improvements in

routine monitors and the development of ultrasensitive and specific methods for measuring the nitrogen oxide species of interest (e.g., NO, NO_2, NO_X, NO_y, HONO, HNO_3, NO_3, and PAN) provide more accurate and reliable input data for photochemical models. Most of these methods were evaluated recently by Solomon (1995) during the SJVAQS/AUSPEX/SARMAP air quality study. Measurement of oxidized nitrogen species during SCOS97 will be made primarily by the commercially available instruments described below. Redundant measurements by alternative spectroscopic method such as a tunable diode laser absorption spectroscopy (TDLAS) or differential optical absorption spectroscopy (DOAS) would be desirable if sufficient funds are available.

Luminol Chemiluminescence Method

The Luminol NO_2 analyzer operates on the principle that gaseous NO_2 undergoes a surface reaction with a specially formulated solution containing water, luminol, sodium sulfate, sodium hydroxide, and alcohol ("Luminol II" solution). The luminol is oxidized and the product chemiluminesces in the 425 nm region. The luminol solution is presented to the air stream on a wick which is replenished with solution from a reservoir. The solution is introduced at the top of the wick and removed to a waste container by a two channel peristaltic pump. A 250 ml reservoir holds sufficient solution for about 3 days of operation. The light emitted by the chemiluminescence reaction is detected by a photomultiplier tube, amplified and output to a chart recorder and data logger. The signal is very sensitive, with a detection limit of 5 pptv if zeroed every 30 minutes or 50 ppt if zeroed daily.

Although luminol can produce chemiluminescence with other oxidants, these reactions usually require the presence of metal ion catalyst. Use of deionized water in the solution formulation prevents chemiluminescence from other oxidizers such as hydrogen peroxide. Only O_3 and PAN were found to produce luminescence, and addition of other substances to the solution, such as sodium sulfite, make the response to O_3 negligible for NO_2 mixing ratios above 1 ppbv. The interference by PAN is a constant fraction of the PAN mixing ratio, although the fraction may depend on the formulation, batch, and age of the luminol solution.

The LCM method has be adapted to measure PAN as well as NO_2. The Unisearch/Scintrex Model LPA-4 is the only commercial instrument for measuring PAN in the atmosphere. In this method, PAN is separated from NO_2 and other organonitrates by gas chromatography, thermally reduced to NO_2, and measured using the same luminol detector described above for the luminol chemiluminescence measurement of NO_2. The more reactive oxides of nitrogen, such as HNO_3, HONO, NO_3, and other reactive interfering species such as ozone are retained on the column. NO, while passing through the GC column, is not detected by the luminol detector. One major advantage of this method is that the instrument can be calibrated in the field with NO_2 rather than the thermally unstable PAN, which is required for the GC/electron capture detector method.

As a further modification to the LPA-4, the LNC-3 converter/sequencer can be used to enable the measurement of NO_X as well as NO_y. The NO_y converter in the model LNC-3M

converter/sequencer consists of a hot stainless steel tube operated at 400 °C. At this temperature, two otherwise difficult to measure NO_y species, namely HNO_3 and isopropyl nitrate, have been shown to convert at efficiencies approaching 100 percent. The resulting NO_X ($NO + NO_2$) is then measured by using a CrO_3 converter upstream of the LMA3 Luminox NO_2 analyzer. The cycle time between species is one minute each for NO_2, NO_X and NO_y, and five minutes for PAN. Detection limit for PAN is 30 ppt and 50 ppt for the other nitrogen species. NO and NO_z ($NO_y - NO_X$) are obtained from the difference. NO_z minus PAN yields an upper estimate for nitric acid. Because of the cycle time the modified LPA-4 cannot be used on-board an aircraft. A TEI 42S which has been modified to measure NO_y is now commonly used by contractors that perform airborne air quality measurements because of its high sensitivity and fast response (see Section 5.4 for additional details).

Tunable Diode Laser Absorption Spectroscopy

The TDLAS method takes advantage of the high monochromaticity and rapid tunability of a Pb salt diode laser to measure absorptions from single rotational-vibrational lines in the middle infrared spectrum of a molecule. Almost all gases absorb radiation in this spectral region. However, since many gases absorb in this region, very high spectral resolution is required to prevent interferences from other gases in the sampled air. The atmospheric sample is pumped rapidly at the reduced pressure through a White cell, which also provides the long optical path lengths required to achieve the desired detection limits. The tunable diode laser is a small Pb crystal with variable amounts of Sn, Se, Te or S. The wavelength region at which the laser emits radiation is governed by the proportions of the three elements in the crystal. Techniques of measuring NO, NO_2 and HNO_3 by TDLAS has been described by Hasties (1983) and Mackay (1993) and measuring H_2O_2 and HCHO by MacKay (1994).

The precision of the measurements is experimentally found to be better than ± 1 percent. The accuracy depends on the ability to accurately measure the various flows and on the ability to determine the mixing ratio of the calibration standard. The computed accuracy for H_2O_2, HCHO and HNO_3 is ± 15 percent (MacKay, 1994).

Differential Optical Absorption Spectroscopy (DOAS)

In this method, in situ atmospheric concentrations are determined by measuring the absorption of the species of interest in the ultraviolet/visible wavelength region. The DOAS is based on measuring the difference between the absorbance at a wavelength where the species of interest has a distinct peak, and another wavelength on either side of the peak. High sensitivities are obtained by combining the detector with a long-pathlength, multiple-reflectance system to yield optical pathlengths up to 10 km. Concentrations are determined from the pathlength and from absorption coefficients. Therefore, this is an absolute, highly specific, and nearly interference-free measurement that can be considered as a reference method.

The DOAS has been used to measure several pollutants in the atmosphere, including NO_2, HONO, NO_3, HCHO, SO_2, O_3 and OH. Several species can be monitored simultaneously. Detection limits as low as about 1 ppbv for NO_2, 0.020 ppbv for NO_3, 3.3 ppbv for HCHO, and 0.6 ppbv for HONO have been reported for pathlengths of 0.5 to 8 km (Finlayson-Pitts and Pitts, 1986; Plane, 1989; Winer and Biermann, 1989; Plane and Nien, 1991).

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4. PLANNING AND PRELIMINARY ANALYSES

For a large regional study of this type, the study plan must represent a consensus of technical and political input from a large number of sponsors, reviewers, and participants. The overall study objectives must be defined first, and the general modeling and analysis techniques that will be used to meet the objectives next. The data needs of the modeling and analysis approaches can then be defined. The field measurement and emission activities are then designed to meet the modeling and analysis needs. The development of these plans depends on a good understanding of the existing meteorology, air quality, and emission data. This understanding requires a review of the existing knowledge and often additional preliminary analysis and modeling activities. This section reviews elements of the two-year planning process for SCOS97 and planning considerations that have been important in recent large-scale air pollution studies. Projects that are currently in progress that are applicable to the planning and execution of SCOS97 are summarized, and additional preliminary and support studies are identified.

4.1 Planning Process

The development of a study plan is an iterative and interactive process. Development of the conceptual plan by the SCOS97 Technical Committee and Working Groups in October, 1995 was the first step in the process. This conceptual plan defined the study goals and objectives, and the scope of the study in terms of resources and approach. This draft field study plan is the next step in the planning process. It matches the program goals and objectives with the resources available to do the job, and evaluates tradeoffs between elements in light of the objectives and budget. It also serves as a strawman upon which to build the final program plan. During the planning phase of the study, a detailed set of integrated plans for the air quality modeling, data analysis, emission, measurement, and management components of the study should be developed. This field study plan specifies the field measurement, data analysis, and data management components of the study and lays out the overall structure of the study. Air quality modeling and emission components are discussed in the context of field measurement needs only, and separate, more detailed plans will be needed for these components of SCOS97. The three plans can be used by the sponsors for proposal requests and contracts.

The overall design process is iterative and the final plan will incorporate the input from sponsors, other stakeholders, knowledgeable peer reviewers, and users of the data. The following are some of the planning considerations that have been found to be important in past studies (Blumenthal and Watson, 1991; Lawson et al., 1993).

- Begin planning at least two years before the field program, and allow at least one year for incorporation of the results of pilot studies into the full program plan. Allow sufficient time for pre-field study activities (e.g., time required for the contracting process and lead time for the acquisition of expendables and for siting). Contracts should be in place for such activities as siting and QA long before the start of the field effort. There must be adequate time to develop plans or select sites, review the choices, and then modify them if necessary.

- Include all stakeholders and users of the data in the design and execution of the study. The uses of the data should be clearly defined during the planning stage, and the modelers and analysts who will use the data should be involved in the planning process. Changes in the study design should be evaluated in terms of their effects on the modeling and analysis tasks. To assist in the overall SCAQS planning phase, form several working groups (Meteorology, Emissions, Air Quality, and Modeling) to establish sampling protocols, and identify data needs for subsequent data analysis and modeling. Document results of the planning process in writing.

- Design the planning process to accommodate parallel planning and mid-course corrections. An initial scoping plan is required by sponsors so they can estimate the funding that will be needed. This step involves identifying the source(s) of funds for the study and the general level of funding available. Once the general funding level is identified, it is often necessary to revise the objectives and the scope to fit within the funding constraints. The elements of the plan and the design of the elements subsequently evolve throughout the planning process. It is important to build the capability for mid-course corrections into the planning process. Develop strawman plans early, and allow for changes and tradeoffs later. Identify design questions requiring additional information. If necessary, and if sufficient time is available, design and perform small pilot studies to answer the design questions. Maintain continuity between planning and management. Once the study plans are completed, they must be implemented by the sponsors. Proposal requests must be written and contractors selected. During the process of selecting contractors and implementing the study plan, many decisions and tradeoffs must be made. During this process, it is important to maintain continuity of the planning team in the management and decision process. In this way, the decisions made to change one element of the study will reflect an understanding of the study priorities and of how that change will affect other elements. Have a contingency plan for the field sampling program if meteorological conditions are not conducive for pollutant episode conditions.

- Before completing the plans, have the plans reviewed by a broad cross-section of interested and knowledgeable people. Modelers, analysts, potential measurement contractors, sponsors, and other knowledgeable scientists should be included in the review. One possible mechanism to accomplish the review is to convene a workshop. In addition, the costs of each component should be estimated and the plan reviewed in light of any funding limitations. Solicit evaluations by reviewers as to whether the plan will meet the objectives, whether the measurements are feasible and meet the needs of the modelers and analysts, whether the hardware and people resources are available in the required time frame, and whether the cost estimates are reasonable. Solicit suggestions for improvement. If changes are suggested which increase the cost, ask for suggestions to compensate for the changes to balance the budget. Assess the comments and recommendations in terms of the priorities and objectives, and revise the draft operational plan to reflect the changes due to budget and priority considerations as well as the input from the reviewers. After the resources and program objectives are reconciled, this information is compiled into the program (operational) plan.

- Integrate quality assurance (QA) into the planning process. The QA team should be chosen early and should be an integral part of the planning process. Allow enough funds to perform this task properly. Typically, about 5-10 percent of the total field and data processing budget is allocated to field QA, and additional QA resources are often provided directly by sponsoring agencies. Both quality control and quality assurance efforts for all program participants must be fully evaluated. Perform round-robin interlaboratory and intermethod comparisons before the field program begins. Build redundancy into all critical measurements. Use spectroscopic methods as "reference" methods where possible.

- Emphasize data archival as an integral part of the overall study. Data reporting conventions, site documentation, and units need to be established prior to delivery of data by the study participants. Funding and planning this activity up front (something that has not occurred in most studies) will greatly facilitate subsequent data analysis and modeling efforts. Recognize the need for extensive data management and "Level 2" data validation. The amount of effort required to get a database to a point where the validity of the numbers is understood is often greatly underestimated. Collecting data from many contractors into a single database is a tremendous task. To be reasonably confident in the data, temporal and spatial consistency checks (Level 2 validation) are useful. Aircraft and ground data and other collocated measurements should be compared. Screening tests should be performed to identify outliers and other inconsistencies (i.e., dew point higher than temperature, etc.). Analysts should quickly review the data to identify potential problems so that they can be resolved while the measurement personnel are still accessible.

- Provide sufficient funding for at least three types of data analysis: observation-based analyses; receptor modeling approaches; and airshed modeling. Provide for data to adequately evaluate the accuracy of emission inventory estimates and the performance of air quality models.

- Schedule symposia and workshops at appropriate intervals for presentation and discussion of data and results. Publish the results in peer-reviewed journals. Prepare a single volume that summarizes the study results. Allow several years for study results to be incorporated into policy. Five years elapsed between field measurements during the Southern California Air Quality Study (SCAQS) and formal presentation of data and modeling results. Scientific papers are still being published nearly 10 years after the field study. Shorter or legislatively mandated timelines must rely on interim results that are subject to revision.

4.2 Preliminary Analyses and Support Studies

This section describes the projects that are currently in progress that are applicable to the planning and execution of SCOS97 and additional preliminary and support studies that are needed in preparation for the SCOS97 field measurement program. These include developing and refining the forecast and decision protocol for SCOS97, conducting

measurement evaluations, developing detailed quality assurance and data management plans, and developing and improving emission inventory methods and databases.

4.2.1 Forecast and Decision Protocol

The intensive sampling days will be chosen using meteorological forecasting for the five scenarios of interest (see Section 2.6). The forecast team will include representatives from:

South Coast AQMD
San Diego APCD.
Ventura County and Santa Barbara County APCDs
California Air Resources Board
U.S. Navy
National Weather Service

The forecasts will be coordinated by telephone, with the SCAQMD serving as the focal point.

Specific criteria for each transport scenario of interest will be developed during the spring of 1996 by the Meteorology Working Group. Tests of the criteria (trial forecasting and evaluation) will be done during the summer of 1996, five days per week from June through October. The criteria will be evaluated on an ongoing basis and refined as appropriate during the summer 1996 trial.

Parameters that will likely be used to develop the criteria include:

- 500, 700, and 850 mb geopotential height field.
- Wind fields.
- 850 mb temperature (analysis and forecasted).
- Marine inversion base, top, and strength (observed and forecasted).
- SoCAB maximum temperature forecasts.
- Surface pressure field (gradients).
- General air quality forecasts for ozone and PM_{10}.
- Transport likelihood for each scenario of interest (high, medium, low, or none).

Each study day, the forecasters will provide a one-day and a two-day forecast to the decision makers with the following products:

- The meteorological classification (either one of the five scenarios of interest, or an "other" day not of interest).
- The forecasted air quality.
- The forecasted transport pattern.
- The probability of an eddy.
- Confidence level of the forecast.

The daily forecast will be completed in the early afternoon of each study day and will provide a one-day (go/no-go) forecast and a two-day (stand-by) forecast and, if feasible, a three-day (advisory) forecast. Due to the lead time of some operations, it is the two-day forecast that will be important for the decision makers to initiate a stand-by status for an IOP, while the one-day forecast, on the afternoon preceding the day of interest, represents a stand-down option. Because personnel will need to travel to southern California to conduct additional monitoring during the episodes of interest, special efforts will need to be made in the preliminary forecasting protocol to minimize the number of "false starts" during SCOS97.

4.2.2 Lidar Measurement, Development and Demonstration

For each lidar system described in Section 3.4 certain improvements should be implemented and certain testing should be performed before the start of the SCOS97 field study. It is likely that only one lidar system will be deployed during SCOS97 due to funding limitations. However, several available systems are discussed in this section in the event that funding and measurement priorities change.

All Ozone Lidars

Corrections for differential aerosol extinction and backscattering should be added to the data analysis algorithms. These procedures have been discussed and implemented previously (Browell et al., 1985) and newer variations have been described more recently (Zhao, 1991; Kovalev and McElroy, 1994). These correction algorithms should undergo preliminary testing and evaluation, which in the case of the already proven ozone lidar systems (i.e., NOAA ground based and NOAA airborne) could be done with already existing data sets. Final testing and fine- tuning of the correction algorithms will realistically take place during the analysis of the SCOS97 data set, as a large number of lidar and in situ data taken under typical SoCAB atmospheric conditions will be needed for this task.

Los Alamos National Laboratory (LANL) and Sandia National Laboratories (SNL)

Neither of these two ground-based lidar systems has previously been used for the measurement of range resolved ozone concentrations. Therefore, substantial hardware and software adaptation/development and testing are needed before the SCOS97 field season. In particular, the required effort includes the following items:

1. Theoretical analysis and optimization of differential absorption lidar (DIAL) operating parameters for ozone measurements:

   - Selection of operating wavelengths as a function of atmospheric conditions.
   - Error analysis including both statistical and systematic errors.
   - Determination of measurement range as function of atmospheric conditions and operating parameters.
   - Development of appropriate averaging procedures and selection of averaging intervals, in both space and time.

2. Adaptation/development and testing of hardware and software for ozone measurements:

   - Implementation of the procedures developed in the theoretical analysis resulting in software for the control of the lidar system including preliminary near-real-time data analysis and software for the post-field-study final analysis. The final analysis should result in spatially and temporally resolved concentration measurements with associated error ranges.
   - Testing of the hardware for ozone measurements, including tests for wavelength accuracy and stability, elimination and/or subtraction of background signal, proper operation of the photomultipliers (i.e., elimination of nonlinearities), proper utilization of the analog/digital converters' dynamic range, accurate recording of the scanning position.
   - Field test of the DIAL system and intercomparison with conventional in situ methods.

As the LANL can be used to measure both O_3 and NO_2, it is of great interest to be able to make sequential measurement of both species in a short time frame, i.e., well below one hour. This way the system could be used to study the spatially and time-resolved O_3–NO_X chemistry and dynamics, for example, in the vicinity of a major freeway (de Jonge et al., 1991). Of further interest is an improvement of the measurement range of this system, which is currently estimated to be from about 0.25 km to 1 km.

As described in Section 3.4, the scanning capability of the SNL system is currently rather limited and does not include the important zenith direction. Ideally, the system would be modified for 3-dimensional scanning over the full hemisphere.

National Oceanic and Atmospheric Administration (NOAA)

Both NOAA's ground-based and airborne systems have gone through iterative improvements along with their use in a number of field tests or studies. Therefore, most of the items mentioned above for the new systems have already been dealt with. However, a

critical analysis of past achievements and problems will be the basis of successful operation in SCOS97 even for these more mature systems.

A few improvements needed for better accuracy and more dependable operation of NOAA's ground based system are listed below:

- Scanner improvements: A better baffling system is required to block transmitted laser light that is scattered from the mirrors from reaching the detector. To avoid optical damage of the mirror coatings, the mirrors need to be cut smaller so they can be re-coated to stricter specifications. The frame of the scanner also needs to be redesigned to improve its flexibility. The seal between the sea-container and the scanner box requires improvement.

- Real-time display: A four-channel, 30-MHz, 12-bit digitizer and a QNX operation system need to be implemented to enable a real-time display of ozone mixing ratio and aerosol backscatter profiles.

- Environmental control: Replace the 20-year-old chiller and improve the container air-conditioning system.

The NOAA airborne DIAL system has performed well in its previous field use and no major improvements seem to be necessary. However, more work could be done to improve alignment and data analysis procedures to enhance the measurement range and especially the data analysis for the range cells close to the ground and close to the system.

There has been some interest in operating this system as a zenith-looking, mobile-ground-based system during SCOS97. For this mode of operation two issues have to be resolved:

- Laser beam direction and telescope field of view have to be reversed. This is a straightforward but not necessarily simple change in the mechanical setup. Actually, the system has already been operating in this configuration during the Table Mountain Vertical Ozone Transport and Intercomparison Experiment in Boulder, CO (October–November 1995).

- The lower boundary of the measurement range needs to be reduced drastically from the current value of about 800 m. Ground based measurements restricted to the region above 800 m above ground are of limited interest. Operating the system in a slanted direction rather than in the vertical direction might remedy this problem to some extent.

4.2.3 Measurement Comparisons and Evaluations

In addition to lidar, there are several measurement methods for which accuracy and validity cannot be fully assessed through standard quality auditing procedures. These measurements include hydrocarbon speciation, carbonyl compounds, PAN, NO_y, and upper air meteorology. For these measurements, measurement comparisons are an acceptable

means for estimating accuracy and validity. Section 6 describes the quality assurance issues related to these measurements and potential approaches for assessing data quality. The appropriate measurement comparisons and evaluations should be conducted well in advance of the SCOS97 field study, and coordinated through the quality assurance manager.

4.2.4 Emission Inventory Projects

Emission inventories are compiled and maintained by the APCDs and the ARB, and are regularly updated to incorporate improvements in emission models and input data. Many of the revisions and improvements are products of an on-going research program. Current studies in progress that could contribute to improvement in emission estimates for the SCOS97 emissions inventory are summarized in Section 8.2.

An emission inventory development plan for SCOS97 will identify significant data gaps and uncertainties in the inventory, and necessary studies. Collection of day-specific (including day-of-the-week variations) emissions and activity factors will be the main focus of these additional efforts (e.g., traffic counts, aircraft traffic).

As described in Section 2, an accurate emission inventory is an important prerequisite to good air quality model performance. Evaluations of the emission inventory include comparison of motor vehicle emission rates with "real-world" on-road measurements and top-down evaluation of the emission inventory using comparisons between ambient and emission inventory pollutant ratios and VOC composition, and application of source apportionment techniques. These and other data analysis approaches are described in Chapter 8.