### MEASUREMENTS OF DRY DEPOSITION PARAMETERS FOR THE CALIFORNIA ACID DEPOSITION MONITORING PROGRAM

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ABSTRACT

The concentrations of acidic gases and particles are measured at 10 sites throughout the State of California. Seven of these sampling sites represent urban areas (South Coast Air Basin, San Francisco Bay Area, Bakersfield, Santa Barbara, and Sacramento) and three represent forested areas (Sequoia, Yosemite, and Redwood National Parks). Several of these sampling sites are collocated with sites which are part of other air quality compliance and forest response monitoring networks.

Hourly average values for ozone, wind speed, wind direction, atmospheric stability, temperature, dew point, time of wetness, and solar radiation are obtained from continuous monitors. Daytime and nighttime measurements are taken every sixth day for sulfur dioxide, ammonia, nitrogen dioxide, and nitric acid gases on absorbing substrates. Mass, sulfate, nitrate, chloride, ammonium, sodium, magnesium, potassium, and calcium ion measurements are made on filter samples of particles in the  $PM_{2.5}$  and  $PM_{10}$  size ranges. The substrate-based measurements are taken following the EPA and ARB regulatory sampling schedules for suspended particulate matter. Weekly average wet deposition samples are taken at or near the dry deposition sampling sites.

The first year of the routine monitoring program included installation of the network, training of technicians, acquisition and validation of data, and transfer of the sampling and analysis technology to Air Resources Board (ARB) operating divisions. Data have been validated and catalogued for the period May, 1988 through September, 1989.

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#### 1.0 INTRODUCTION

#### 1.1 Background

The Kapiloff Acid Deposition Act of 1982 requires the Air Resources Board (ARB) to determine the regions in California where acid deposition is occurring, or might be expected to occur, in amounts which could be adverse to the environment, the economy, or the public health. The California Acid Deposition Monitoring Program (CADMP) was established to meet this need. This program consists of wet deposition sampling (rain and snow), fogwater sampling (Hoffman et al., 1989), and dry deposition sampling (Watson et al., 1990). This report describes the measurements obtained from the dry deposition component of CADMP.

These measurements are taken as input data for the concentration/deposition velocity model for estimating dry deposition fluxes. Using this method, ambient concentrations of acidic and other reactive species are measured over a period which assures an adequate amount of sample for analysis. These concentrations are multiplied by an assumed deposition velocity to calculate fluxes. The deposition velocities are estimated either theoretically or from micrometeorological measurements made under similar meteorological and surface conditions.

Atmospheric concentrations of reactive species in gaseous and particulate phases have been taken at 10 sites throughout California since the summer of 1988. Seven of these sampling sites represent urban areas (Fremont, Sacramento, Bakersfield, Santa Barbara, Long Beach, Downtown Los Angeles, and Azusa) and three represent forested areas (Gasquet, Yosemite, and Sequoia). Several of these sampling sites are part of other air quality compliance and forest response monitoring networks.

Hourly average values for ozone, wind speed, wind direction, atmospheric stability, temperature, dew point, time of wetness, and solar radiation are obtained from continuous monitors. Daytime (0601 to 1800 PST) and nighttime (1801 to 0600 PST) measurements are taken every sixth day for sulfur dioxide, ammonia, nitrogen dioxide, and nitric acid gases on absorbing substrates. Mass, sulfate, nitrate, chloride, ammonium, sodium, magnesium, potassium, and calcium ion measurements are made on filter samples of particles in the  $PM_{2.5}$  and  $PM_{10}$ The substrate-based measurements are taken on EPA and ARB size ranges. regulatory sampling schedules for suspended particulate matter. Weekly average CADMP wet deposition samples are taken at or near these dry deposition sampling Wherever possible, existing measurements have been identified and sites. integrated into the data base. Where necessary, new measurement equipment was procured or developed and installed at the sampling sites. As methods and procedures were perfected, the network operation was transferred to ARB monitoring staff in phases throughout the project.

#### 1.2 Objectives

The objectives of this measurement report are:

- To document the data bases acquired during the first 1½ years of monitoring.
- To evaluate monitoring hardware and procedures and formulate recommendations for improvements in data quality and efficiency of operation.
- To summarize measurements taken at the monitoring sites.

#### 1.3 Descriptions of Supporting Documents

This final report is one of five documents prepared for this project. The additional documents are:

- Program Plan for the California Acid Deposition Monitoring Program (Watson et al., 1990). This report describes the alternative monitoring methods which were considered in network design, the sampling sites and the reasons for their selection, the sampling and analytical methods, quality control and quality assurance procedures, data-base management, and the technology transfer plan. The plan is a companion to this measurement report.
- Field Operations Manual for the California Acid Deposition Monitoring Program: Meteorology, Ozone, and Dry Deposition (Bowen et al., 1990). This manual describes the operation of ambient air monitors which were installed as part of this project. It is intended as a training guide and reference for ARB site operators.
- Laboratory Operations Manual for the California Acid Deposition Monitoring Program: Dry Deposition Sample Preparation and Analysis (Chow et al., 1990). This manual specifies the preparation and handling of filter packs and the analysis methods to be applied to these samples upon receipt from the field sites. It is intended as a training guide and reference for the ARB laboratory staff.
- <u>Data Processing and Data Validation Operations Manual for the</u> <u>California Acid Deposition Monitoring Program: Meteorology, Ozone,</u> <u>and Dry Deposition Data (Frazier et al., 1990).</u> This manual describes the use of software which combines data from different sources into an integrated data base. Part of this processing includes the application of different validation criteria to define the quality level of the measurements. The manual is accompanied by programs and example data sets on IBM-PC compatible floppy disks. It is intended as a training guide and reference for the ARB data processing staff.

#### 1.4 Overview of Report

This introduction has provided the background for the measurement program, given an overview of the measurements taken, and stated the objectives of the

report. Section 2 describes the measurement network and its intended operation. Section 3 identifies the data available, the formats in which they are presented on IBM-PC compatible floppy disks, and the descriptions of the different field entries. Section 4 summarizes the data validation procedures and identifies their application to the data which accompany this report.

The first 1<sup>1</sup>/<sub>2</sub> years of network operations are evaluated in Section 5. The intention of this evaluation is to identify changes needed in instrument maintenance schedules and the limitations of current measurement methods. The attainment of the technology transfer objectives is evaluated in Section 6. Data from one year of measurements are analyzed in Section 7. A summary of the measurement program and recommendations for future work are given in Section 8.

#### 2.0 NETWORK DESCRIPTION

#### 2.1 Dry Deposition Measurements

The CADMP dry deposition observables are presented in Table 2-1, along with their averaging times, sampling frequencies, and measurement methods. Figure 2-1 shows the general locations of the dry deposition sampling sites throughout the State of California. Table 2-2 presents the street addresses, coordinates, elevations, and primary operators for each site. Sites are described in greater detail by Watson et al. (1990). These sites were selected to represent concentrations of reactive species in the varied emissions, meteorological, topographical, and exposure environments which typify California.

The three sites in the South Coast Air Basin (SoCAB) represent different emissions and aging times in a densely populated urban area. The Long Beach site is affected by fresh marine and industrial (oil refinery and power-plant) emissions which are generally transported inland by on-shore winds. The Downtown Los Angeles site is near the intersection of major freeways and represents a combination of fresh and partially aged emissions. The Azusa site is in the eastern portion of the SoCAB and receives the end-products of photochemical and other reactions, as well as fresh motor vehicle and some agricultural emissions.

The Santa Barbara site represents a coastal environment in the vicinity of light population densities and no major industries, aside from offshore oil operations and ship channel traffic. The Fremont site represents a densely populated coastal area with emissions and meteorology which are substantially different from those in the SoCAB.

The southern part of the Central Valley is represented by the Bakersfield site, which is affected by urban, agricultural, and oilfield emissions. During the summertime, this site lies along transport trajectories which originate in the San Francisco Bay Area and accumulate pollutants from up-valley sources. The northern part of the Central Valley is represented by the Sacramento site, which also experiences transport from the Bay Area as well as local urban emissions.

Forest exposures and non-urban concentrations are represented by the Sequoia, Yosemite, and Gasquet sites. Sequoia and Yosemite National Parks receive pollutants from the San Joaquin Valley transported by upslope flows. Gasquet, located adjacent to Redwoods National Park, is far removed from all emissions sources, and it probably offers the best estimate of reactive species concentrations in the absence of anthropogenic emissions.

The dry deposition portion of the CADMP is a permanent fixture in California's air quality monitoring program. California's air quality networks rely on a variety of agencies to operate monitoring sites, including the Air Resources Board (ARB), local air quality management districts, the National Park Service, and commercial entities, with coordination and data accumulation tasks performed by ARB. Table 2-3 shows responsibilities of the different parties involved in the dry deposition network and the periods of time for which they were responsible for network components. The Desert Research Institute (DRI)

# Table 2-1

## CADMP Dry Deposition Measurements

Measurement	Sampling 	Averaging <u>Time</u>	Sampling Frequency	Measurement Method /Instrument
$PM_{2.5}$ particle (0 to 2.5 $\mu$ m) chemistry and HNO <sub>3</sub> gas	All <sup>a</sup>	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	ATEC/DRI sequential filter sampler with PFA- coated Bendix 240 cyclone inlet and denuder difference method
$PM_{10}$ particle (0 to 10 $\mu$ m) chemistry, $SO_2$ , $NO_2$ , and $NH_3$ gases	All <sup>a</sup>	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	ATEC/DRI sequential filter sampler with SA-254 inlet and impregnated absorbing filters
PM <sub>2.5</sub> and PM <sub>10</sub> Mass	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Gravimetric analysis with microbalance of Teflon (Zefluor) filters
$PM_{2.5}$ and $PM_{10}$ Cl <sup>-</sup> , $NO_3^-$ , and $SO_4^-$	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Ion chromatography on Teflon filter extracts. Volatilized $NO_3^-$ measured on nylon backup filter from denuded $PM_{2.5}$ air stream by automated colorimetry
$PM_{2.5}$ and $PM_{10}$ $NH_4^+$	All <sup>a</sup>	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Automated colorimetry on Teflon filter extracts
$PM_{2.5}$ and $PM_{10}$ Na <sup>+</sup> , Mg <sup>++</sup> , K <sup>+</sup> , and Ca <sup>++</sup>	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Atomic absorption spectrophotometry on Telfon filter extracts
SO <sub>2</sub>	All <sup>a</sup>	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Ion chromatography for sulfate on particle-free potassium carbonate impregnated cellulose- fiber (ICF) filters

### Table 2-1 (continued)

#### CADMP Dry Deposition Measurements

<u>Measurement</u>	Sampling <u>Sites</u>	Averaging <u>Time</u>	Sampling Frequency	Measurement Method /Instrument
NO <sub>2</sub>	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Automated colorimetry for nitrate on triethanolamine (TEA) impregnated cellulose- fiber filters
NH <sub>3</sub>	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Automated colorimetry for ammonium on citric acid impregnated cellulose-fiber filters
HNO <sub>3</sub>	Allª	0601 to 1800, 1801 to 0600 PST	Two consecutive samples every sixth day	Ion chromatography for nitrate on non-denuded PM <sub>2.5</sub> Teflon and nylon filters minus PM <sub>2.5</sub> nitrate on denuded nylon filter
0 <sub>3</sub>	All <sup>a</sup>	l hour	Daily, 24 hr/day	Dasibi 1003 AH ultraviolet absorption monitor
Wind Speed	All <sup>a</sup>	1 hour	Daily, 24 hr/day	3-cup Anemometer
Wind Direction	All <sup>a</sup>	1 hour	Daily, 24 hr/day	Wind Vane
Sigma Theta	Allª	1 hour	Daily, 24 hr/day	Wind Vane
Temperature	Allª	1 hour	Daily, 24 hr/day	Thermistor
Dew Point	Allª	1 hour	Daily, 24 hr/day	Dew Cell
Solar Radiation	All <sup>a</sup>	1 hour	Daily, 24 hr/day	Pyranometer
Time of Wetness	Allª	1 hour	Daily, 24 hr/day	Electric Cell

a "All" includes: 1) Gasquet; 2) Fremont; 3) Sacramento; 3a) Collocated Sacramento;
4) Yosemite; 5) Sequoia; 6) Bakersfield; 7) Santa Barbara; 8) Long Beach; 9) Los Angeles; and 10) Azusa.





#### Table 2-2

#### Sampling Site Specifications in the CADMP Network

		Coord	inates		UTM Coordin	nates	<u> </u>	on	
Sampling 	Site Address	Longitude(W)	Latitude(N)	Zone	<u> </u>	<u>N(m)</u>	Above <u>Ground(m)</u>	Above <u>MSL<sup>a</sup>(m)</u>	Primary <sup>b</sup> <u>Operator</u>
Gasquet	9800 Highway 199 Gasquet, CA 95513	123*58'53"	41°50'43"	10	418,478	4,632,860	5.0	120	ARB
Fremont	40733 Chapel Way Fremont, CA 94538	121*57'40"	37*32'08"	10	591,780	4,154,573	6.5	16	BAAQMD
Sacramento	1309 T Street Sacramento, CA 95814	121 29 32"	38'34'07"	10	631,329	4,269,756	11.0	3	ARB
Yosemite	Turtleback Dome Yosemite National Park, CA	119'42'12"	37*42'47"	11	261,646	4,177,220	2.0	1,609	NPS
Sequoia	Lower Kaweah Sequoia National Park, CA	118*46'38"	36'34'01"	11	340,970	4,048,085	2.0	1,914	NPS
Bakersfield	225 Chester Ave., Rm. 309 Bakersfield, CA 93301	119.01,06"	35°21′27"	11	316,598	3,914,354	7.1	120	ARB
Santa Barbara	380 N. Fairview Ave. Goleta, CA 93117	119*49'30"	34*26'44"	11	240,170	3,814,939	4.7	20	SBAPCD
Long Beach	3648 N. Long Beach Ave. Long Beach, CA 90807	118°11'18"	33*49'23"	11	390,037	3,742,963	8.0	27	SCAQMD
Los Angeles	1630 N. Main Street Los Angeles, CA 90012	118*13'32"	34*03'59"	11	386,878	3,769,994	15.0	90	SCAQMD
Azusa	803 N. Loren Ave. Azusa, CA 91702	117°55'23"	34°08'11"	11	414,878	3,777,623	6.5	187	SCAQMD

<sup>a</sup> MSL = Mean Sea Level

b ARB = Air Resources Board

BAAQMD = Bay Area Air Quality Management District

NPS = National Park Service

SCAQMD = South Coast Air Quality Management District

SBAPCD = Santa Barbara County Air Pollution Control District

### Table 2-3

# Summary of CADMP Field Measurement Responsibilities

Agency	<u>Responsibilities</u>	<u>Calendar Periods</u>
Desert Research Institute	Program Management Network Design Site Installation Field Operation Supervision	12/86-4/90 12/86-6/87 3/88-4/89 6/88-4/90
	Data Processing	6/88-1/90
	Filter Pack Preparation	3/89-12/90
	Laboratory Analysis	9/88-9/89
	Maintenance and Repair	6/88-4/90
	Field Operation of Dry Deposition Sampler at Gasquet	5/88-4/90
	Field Operation of Meteorological Measurements at Gasquet	5/88-4/90
	Field Operation of Ozone Analyzer at Gasquet	5/88-4/90
ENSR Consulting and Engineering	Filter Pack Preparation Laboratory Analysis	3/88-3/89 5/88-9/88
South Coast Air Quality Management District	Field Operation of Dry Deposition Sampler at Long Beach, Los Angeles, and Azusa	5/88-current
	Field Operation of Meteorological Measurements at Long Beach, Los Angeles, and Azusa	2/89-current
	Field Operation of Ozone Analyzer at Long Beach, Los Angeles, and Azusa	5/88-current
Bay Area Air Quality Management District	Field Operation of Dry Deposition Sampler at Fremont	6/88-current

# Table 2-3 (continued)

### Summary of CADMP Field Measurement Responsibilities

<u>Agency</u>	<u>Responsibilities</u>	<u>Calendar Periods</u>		
Bay Area Air Quality Management District (continued)	Field Operation of Meteorological Measurements at Fremont	9/88-current		
	Field Operation of Ozone Analyzer at Fremont	6/88-current		
Santa Barbara Air Pollution Control District	Field Operation of Dry Deposition Sampler at Santa Barbara	2/89-current		
	Field Operation of Meteorological Measurements at Santa Barbara	4/89-current		
	Field Operation of Ozone Analyzer at Santa Barbara	4/89-current		
National Park Service	Field Operation of Dry Deposition Sampler at Yosemite and Sequoia	5/88-current		
	Field Operation of Meteorological Measurements at Yosemite and Sequoia	5/88-current		
	Field Operation of Ozone Analyzer at Yosemite and Sequoia	5/88-current		
California Air Resources Board	Field Operation of Dry Deposition Sampler at Sacramento	10/88-current		
	Field Operation of Meteorological Measurements at Sacramento	6/89-current		
	Field Operation of Ozone Analyzer at Sacramento	4/89-current		

# Table 2-3 (continued)

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# Summary of CADMP Field Measurement Responsibilities

<u>Agency</u>	<u>Responsibilities</u>	<u>Calendar Periods</u>
California Air Resources Board (continued)	Field Operation of Dry Deposition Sampler at Bakersfield	5/88-current
	Field Operation of Meteorological Measurements at Bakersfield	9/88-current
	Field Operation of Ozone Analyzer at Bakersfield	5/88-current
	Field Operation of Dry Deposition Sampler at Gasquet	5/90-current
	Field Operation of Meteorological Measurements at Gasquet	5/90-current
	Field Operation of Ozone Analyzer at Gasquet	5/90-current

of the University of Nevada and the ARB Research Division were charged with the initial responsibility of assembling existing resources into a coherent monitoring network, supplementing these resources with additional monitoring methods needed to meet the needs of dry deposition monitoring, operating the network for a one-year period, and transferring operations to ARB staff. The management of the CADMP dry deposition component is currently under the auspices of ARB's Monitoring and Laboratory Support Divisions.

#### 2.2 Field Measurement Systems

Watson et al. (1990) provide the rationale for the selection of monitoring methods and a summary of operating procedures. Each site is configured with: 1) a gas/particle sequential filter sampling system; 2) an ozone monitor; and 3) a meteorological monitoring system.

#### 2.2.1 Gas/Particle Sequential Filter Sampler

The gas/particle sequential filter sampling system consists of two units, one fitted with a  $PM_{10}$  inlet (for the collection of particles less than 10  $\mu$ m aerodynamic diameters) and another fitted with a  $PM_{2.5}$  inlet (for the collection of particles less than 2.5  $\mu$ m aerodynamic diameter). Air passes through these inlets into a conical plenum, then through filter substrates arranged in parallel and in series which remove the gases and particles specified in Table 2-1. All surfaces in the  $PM_{2.5}$  sampling system are coated with PFA Teflon which has been washed in dilute nitric acid to prevent atmospheric nitric acid from being adsorbed by the sampling system prior to contact with the collection substrates.

Four filter packs containing a total of eight substrates are needed for each sample. The eight filters are submitted to 21 different analysis processes to obtain 12-hour average concentrations of 24 separate species. Solenoid valves are triggered by a timer to switch between the daytime and nighttime samples. Filter packs for one month of sampling are prepared in a central laboratory and shipped to the field where they are loaded into and removed from the sampler by each site operator. Field blanks, through which no air is drawn, accompany each month's set of samples. These field blanks are used to evaluate contamination from sample handling and shipping.

#### 2.2.2 Ultraviolet Absorption Ozone Analyzer

Each sampling site is equipped with ultraviolet absorption spectrophotometers for the measurement of ozone. These units were already in place at all sites except Yosemite and Gasquet, where they were installed as part of CADMP. These instruments measure the amount of ultraviolet (UV) radiation absorbed by molecular ozone in a sample of ambient air. Greatest absorption occurs at a wavelength of 253.7 nm which is provided by a low pressure mercury vapor lamp.

Ambient air entering the monitor separates into two paths. One path leads directly into the absorption chamber, the other first passes through an ozone

filter or "scrubber" which selectively removes the ozone, and then into the chamber. A photodetector measures the amount of light absorbed by the ozone-laden air compared to the ozone-free air. The ozone concentration is then calculated electronically and recorded by a data acquisition system (DAS).

#### 2.2.3 Meteorological Measurements

To the greatest extent possible, use is made of existing measurements at the sampling sites. Several meteorological instruments were installed as part of the CADMP to supplement these existing units. The exact type of instrument varies from site to site. The following measurement principles are applied at most, but not all, of the sampling sites.

Wind speed is measured by a three-cup anemometer coupled to a wind-speed sensor which converts the rotational speed of the cups to a frequency proportional to wind speed. A transducer converts the frequency to direct current voltage (DCV) which is read by the data acquisition system.

Wind direction is measured by a wind vane coupled to a precision low torque potentiometer. Wind exerts pressure on the surface of the vane which rotates about a fulcrum. The angles of wind direction are measured clockwise from true north, which is 0°. Meteorological wind direction is defined as the direction from which the wind is coming. The 0-360° signal from the potentiometer is converted to 0-540° in a translator which is read by the data acquisition system.

The data acquisition system resolves the instantaneous wind-speed and winddirection signals into vector components, averages the components, and determines the average vector wind speed and direction. The data acquisition system computes the standard deviation of the instantaneous values from the winddirection sensor. These values are reported as sigma theta.

Ambient temperature is measured by a thermistor housed in an aspirated radiation shield. Voltage from the thermistor varies directly with temperature and is read by the data acquisition system.

Dew point is measured using a dew cell that consists of a heated wire-wound bobbin that is coated with lithium chloride (LiCl), a hygroscopic material. The bobbin is heated to drive off water vapor until a phase change occurs in the LiCl. This bobbin temperature is related to the dew point by a calibration curve that is built into a translator card, the output of which is recorded by the data acquisition system.

Two types of sensors are used to measure total direct and indirect solar radiation in the hemisphere above the horizon. At some sites, the sensor is a silicon solar cell that generates a voltage in the presence of sunlight. At other sites the sensor is a differential thermopile with black and white surfaces that develop a temperature difference. This difference produces a voltage proportional to the solar radiation. The generated solar radiation is translated into units of energy flux (watts/m<sup>2</sup>) and recorded by the data acquisition system.

Time of wetness is measured using an electrochemical sensor. Resistance across the sensor decreases as moisture collects on the sensor surface, leading to an increase in the current across the sensor. Output from the sensor is recorded by the data acquisition system.

#### 2.2.4 Data Acquisition System

The Dasibi SX444 and SumX SX445 data acquisition systems (SumX was acquired by Dasibi in 1988, and these designations represent the same instrument) are microprocessor-based instruments designed to collect and process air quality and meteorological data. An operating program is contained in read-only-memory (ROM), while data are stored in random-access-memory (RAM) of the data acquisition system and of a removable RAM storage module (RAM pack). Analog signals from sensors are converted to digital signals in an analog-to-digital converter. The digital signals are scaled, averaged over user-specified time scales, and saved in RAM. Calibration functions can be specified and initiated through several control outputs. Communications with the data acquisition system are accomplished via telephone and modem, an onsite Tandy 100 computer for Model SX444, and a front panel keyboard for Model SX445.

#### 2.3 Laboratory Operations

Laboratory operations support the gas/particle sequential filter sampling. Laboratory work consists of filter pack preparation, sample sectioning and extraction, and chemical analysis. Samples are submitted to gravimetric, ion chromatographic, atomic absorption spectrophotometric, and automated colorimetric analysis. Figure 2-2 shows the sequence of laboratory operations applied to these samples. Watson et al. (1990) describe the rationale for selecting the filter media, impregnation solutions, and analysis methods.

Four separate filter packs are assembled for each 12-hour sample. They are identified with an alphabetical prefix followed by an identification number. The prefixes identify the following configurations:

- A TCK prefix designates a filter pack containing a potassium carbonate impregnated cellulose filter on the bottom grid, preceded by a citric acid impregnated cellulose filter on a removable grid, preceded by a Teflon-membrane filter on a removable grid. The TCK filter pack samples particles, ammonia, and sulfur dioxide through the PM<sub>10</sub> inlet at 20 lpm.
- A GT prefix designates a filter pack containing a TEA impregnated cellulose filter on the bottom grid, preceded by a Teflon-coated glass-fiber filter on a removable grid. The GT filter pack samples nitrogen dioxide through the PM<sub>10</sub> inlet at 2 lpm. The Teflon-coated glass-fiber filter removes nitrate particulate matter and is discarded following sampling.



Figure 2-2. Flow Diagram of the CADMP Filter Processing Activities.

of transition energies and therefore absorbs light at different wavelengths. With the application of Beer-Lambert's Law, the amount of absorption is a function of the number of atoms which is proportional to analyte concentration. The light beam passes through a sample chamber (where the sample is heated with a burner) to a monochromator where an appropriate wavelength is focused on a photomultiplier tube. The amount of light absorbed at this wavelength is recorded by a data-acquisition computer and converted to concentration by comparison with the absorption by known standards. A separate analysis is performed for each species using a different light source and monochromator setting. An auto-injection system and computer-controlled data acquisition allow up to 120 samples per day to be analyzed for a single species.

Approximately 25% of all analyses are dedicated to standards, replicates, and blank samples to assure proper calibration and reproducibility. Sample extracts are re-analyzed when these quality control samples do not return values within pre-set limits. Samples with concentrations outside of the calibration range are diluted or are re-standardized using a calibration curve developed over a higher range of concentrations.

Detailed laboratory operations are documented in the standard operating procedures for this program (Chow et al., 1990).

#### 3.0 DATA-BASE DESCRIPTION

Validated data are presented in dBase III+ computer files which can be easily transferred on IBM-PC compatible floppy disks. dBase III+ formats can be read directly by many popular spreadsheet and data management programs, and it is not necessary to own dBase III+ software to access these data. ASCII blank or comma delimited text files can be produced from dBase files with a list command from the dBase III+ data management software.

Table 3-1 identifies the data which are delivered with this report and the file names which contain those data. The largest files are those which contain the hourly data, and these have been divided by site and year to make them more convenient to handle. The naming convention for these files uses a site code followed by the year of data acquisition. All of the gas/particle data are contained in a single file.

Tables 3-2 and 3-3 describe the data-base structures of the hourly and gas/particle files, respectively. Each record contains the sampling site, sample date, and sampling period. These fields can be used to group different records into sub-files for data interpretation purposes. Data validation flags for hourly data are defined in Tables 3-4, while validation flags for the gas/particle data are described in Tables 3-5 and 3-6. Each data record includes its own data validation summary. All missing or invalid data locations are represented by a -99 located in place of the absent measured value.

In Table 3-3, Fields 41 to 76 refer to particulate concentrations which are measured on extracts from the Teflon-membrane pre-filter. A nitric acid denuder which precedes the nylon filter (Field 77) removes nitric acid from the air stream prior to contact with the filter. Field 77 represents the total particulate nitrate which was in the atmosphere. This differs from the particulate nitrate measured on the Teflon filter (Field 69) because some of the particulate ammonium nitrate collected on the Teflon filter dissociates to gaseous nitric acid during sampling. The nylon backup filter (Field 79) absorbs Field 79 represents nitric acid, which is in the this evaporated nitrate. gaseous phase, plus ammonium nitrate which dissociated to nitric acid from particles collected on the Teflon-membrane pre-filter. Nitric acid in the atmosphere, reported in Field 87, results from adding the nitrate on the undenuded PM2 5 Teflon filter (Field 69) to the nitrate measured on the undenuded  $PM_{2,5}$  nylon backup filter (Field 79) and subtracting the nitrate measured on the  $PM_{2,5}$  denuded nylon filter (Field 77). This difference is multiplied by 1.016 to obtain the equivalent amount of nitric acid.

Tables 3-4 through 3-6 contain flags which describe the validation actions taken and the reasons for those actions. Most of these flags are of interest only for evaluating the measurement process, and they can be ignored by the typical data user. The most important flags are those which indicate the validation level of data: 1) valid at Level I or Level II; 2) suspect; or 3) invalid. Suspect data are retained because they may be useful for some situations but not for others. The dBase III+ data management system allows the data base to be sorted on these flags so that data can included or excluded depending on the desires of the investigator.

### Table 3-1

## Summary of CADMP Data-Base Files for Meteorological and Chemical Measurements

Sampling_Site	Descriptions	Start <u>Date</u>	End <u>Date</u>	Data-Base <u>File Name</u>
Gasquet	Hourly Meteorological Ozone Data	06/19/88 01/01/89	12/31/88 01/22/90	GA88.DBF GA8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>ª</sup> ) Data	06/20/88	09/25/89	CPCON.DBF
Fremont	Hourly Meteorological and Ozone Data	09/23/88 01/01/89	12/31/88 01/31/90	FR88.DBF FR8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	06/02/88	09/25/89	CPCON.DBF
Sacramento (13th & T St.)	Hourly Meteorological and Ozone Data	06/09/89	01/22/90	SA8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	10/06/88	09/25/89	CPCON.DBF
Collocated Sacramento	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	04/10/89	09/25/89	CPCON.DBF
Yosemite (Turtleback Dome)	Hourly Meteorological and Ozone Data	05/11/89	01/31/90	Y08990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	05/09/88	09/25/89	CPCON.DBF
Sequoia	Hourly Meteorological and Ozone Data	01/01/89	01/31/90	SB8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	05/15/88	09/25/89	CPCON.DBF
Bakersfield	Hourly Meteorological and Ozone Data	10/11/88 01/01/90	12/31/88 01/31/90	BA88.DBF BA8990.DBF
	Twelve-Hour Chemical (gas/particleª) Data	05/03/88	09/25/89	CPCON.DBF

### Table 3-1 (continued)

### Summary of CADMP Data-Base Files for Meteorological and Chemical Measurements

Sampling Site	<u>Descriptions</u>	Start <u>Date</u>	End <u>Date</u>	Data-Base <u>File_Name</u>
Santa Barbara (Goleta)	Hourly Meteorological and Ozone Data	06/20/89	01/22/90	<b>SB8990.</b> DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	04/22/89	09/25/89	CPCON.DBF
Long Beach	Hourly Meteorological and Ozone Data	02/01/89	01/31/90	LB8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	05/03/88	09/25/89	CPCON.DBF
Los Angeles	Hourly Meteorological and Ozone Data	02/01/89	01/31/90	LA8990.DBF
	Twelve-Hour Chemical (gas/particleª) Data	05/03/88	09/25/89	CPCON.DBF
Azusa	Hourly Meteorological and Ozone Data	02/01/89	01/31/90	AZ8990.DBF
	Twelve-Hour Chemical (gas/particle <sup>a</sup> ) Data	05/03/88	09/25/89	CPCON.DBF

<sup>a</sup>  $PM_{2.5}$  and  $PM_{10}$ .

# Table 3-2

### CADMP Data-Base Structure for Continuous Meteorological and Ozone Measurements (File ssmmyyHR.DBF)<sup>a</sup>

Number of data records	:	Varies with site
Date of last update	:	7/27/90
Missing value code	:	-99
Wind direction precision	:	1°
Wind speed precision	:	0.2 mps
Temperature precision	:	0.2°C
Insolation precision	:	2 watts/m <sup>3</sup>
Wetness precision	:	2%
Ozone precision <sup>.</sup>	:	5ppbv at 100ppbv

<u>Field</u>	<u>Field Name</u>	<u>Data Type</u>	<u>Width</u>	<u>Explanation</u>
1	SITE	Character	2	Sampling site
2	DATE	Date	8	Sampling date
3	STRTIM	Numeric	4	Begin time for average, 0000-2300
			_	hours
4	VWDDEGC	Numeric	3	Vector average wind direction,
c	TTINTAT	<b>01</b>	0	degrees
C	VWDVAL	Character	8	validation flag for vector average
6	STODECC	Numorio	3	Standard deviation of vector average
Ū	BIODIOO	Numeric	5	wind direction
7	SIGVAL	Character	8	Validation flag for standard
			-	deviation of vector average wind
				direction
8	VWSMPSC	Numeric	5.1	Vector average wind speed, m/s
9	VWSVAL	Character	8	Validation flag for vector average
				wind speed
10	SWSMPSC	Numeric	5.1	Scalar average wind speed, m/s
11	SWSVAL	Character	8	Validation flag for scalar average
				wind speed
12	TMPDGCC	Numeric	5.1	Temperature, °C
13	TMPVAL	Character	8	Validation flag for temperature
14	DPTDGCC	Numeric	5.1	Dew point temperature, °C
15	DPTVAL	Character	8	Validation flag for dew point
				temperature
16	SOLWM2C	Numeric	4	Solar insolation, watts/m <sup>2</sup>
17	SOLVAL	Character	8	Validation flag for solar insolation
18	WETPHRC	Numeric	3	Wetness, percent of sampling hour
19	WETVAL	Character	8	Validation flag for wetness
20	O3PPBC	Numeric	4	Ozone concentration, ppbv
21	03VAL	Character	8	Validation flag for ozone
				concentration

<sup>a</sup> ss = Site Code

mm = Month

yy = Year

### Table 3-3

CADMP Data-Base Structure for Ambient Chemical Concentrations (File CPCON.DBF)

<u>Field</u>	<u>Name</u>	<u>Data Type</u>	<u>Width</u>	Explanation
1	IDGT	Character	10	Sample ID, GT filter pack
2	IDTK	Character	10	Sample ID. TCK filter pack
3	IDDN	Character	10	Sample ID, DN filter pack
4	IDTN	Character	10	Sample ID. TN filter pack
5	SITE	Character	2	Sampling site, 'AZ'=Azusa.
				'BA'-Bakersfield, 'FR'-Fremont,
				'GA'=Gasquet, 'LB'=Long Beach,
				'LA'=Los Angeles, 'SA'=Sacramento,
				'SB'-Santa Barbara, 'SE'-Seguoia,
				'YO'=Yosemite
6	SAMPID	Numeric	2	Sampler ID number
7	DATE	Date	8	Sampling date
8	STRTIM	Numeric	4	Sample start time, HH:MM
9	PERIOD	Character	1	Sample period, D=Day, N=Night
10	FGTTFLG	Character	5	Field flag, GT filter pack
11	FTKTFLG	Character	5	Field flag, TCK filter pack
12	FDNFFLG	Character	5	Field flag, DN filter pack
13	FTNFFLG	Character	5	Field flag, TN filter pack
14	MAGTFF	Character	5	Analysis flag, PM <sub>2.5</sub> Teflon filter mass
15	MAGTTF	Character	5	Analysis flag, PM <sub>10</sub> Teflon filter mass
16	NAATFF	Character	5	Analysis flag, PM <sub>2.5</sub> Teflon filter Na
10	NAATTF	Character	5	Analysis flag, PM <sub>10</sub> Teflon filter Na
18	MGATFF	Character	5	Analysis flag, PM <sub>2.5</sub> Teflon filter Mg
19	MGATTF	Character	5	Analysis flag, PM <sub>10</sub> Teflon filter Mg
20	KPAIFF	Character	5	Analysis flag, $PM_{2.5}$ Teflon filter K
21	CAATEE	Character	5	Analysis flag, PM <sub>10</sub> ferion filter K
22	CAAIFF	Character	5	Analysis flag, $PM_{2.5}$ ferion filter (a
23	NACTEE	Character	5	Analysis flag, $PM_{10}$ ferror filter of $M_{10}$
24	NACTTE	Character	5	Analysis flag, $PM_{2.5}$ ferron filter $NH_4$
26	ANITEE	Character	5	Analysis flag, $M_{10}$ ferror filter $C_{11}$
20	MULLE.	Unaracter	2	NO. SO $=$
27	ANITTE	Character	5	Analysis flag PM., Teflon filter Cl
		ondradoor	3	No. So. $\mathbb{T}$
28	N3CNFF	Character	5	Analysis flag, nylon filter NO <sub>2</sub>
29	HNCNGF	Character	5	Analysis flag, nylon filter HNO <sub>2</sub>
30	NHCCGF	Character	5	Analysis flag, citric acid filter NH <sub>2</sub>
31	SOIKGF	Character	5	Analysis flag, K <sub>2</sub> CO <sub>2</sub> filter SO <sub>2</sub>
32	NOCEGF	Character	5	Analysis flag, TEA filter NO <sub>2</sub>
33	VOLGTC	Numeric	6.2	Volume, m <sup>3</sup> , GT filter pack
34	VOLGTU	Numeric	6.2	Volume uncertainty, m <sup>3</sup> , GT filter pack
35	VOLTKC	Numeric	6.2	Volume, m <sup>3</sup> , TCK filter pack
36	VOLTKU	Numeric	6.2	Volume uncertainty, m <sup>3</sup> , TCK filter
				pack
37	VOLDNC	Numeric	6.2	Volume, m <sup>3</sup> , DN filter pack
38	VOLDNU	Numeric	6.2	Volume uncertainty, m <sup>3</sup> , DN filter pack

,

# Table 3-3 (continued)

CADMP Data-Base Structure for Ambient Chemical Concentrations (File CPCON.DBF)

<u>Field</u>	<u>Name</u>	<u>Data Type</u>	<u>Width</u>	Explanation
39	VOLTNC	Numeric	6.2	Volume, m <sup>3</sup> , TN filter pack
40	VOLTNU	Numeric	6.2	Volume uncertainty, m <sup>3</sup> , TN filter pack
41	MAGTFC	Numeric	10.4	PM <sub>2</sub> , Teflon filter mass, $\mu g/m^3$
42	MAGTFU	Numeric	10.4	PM <sub>2.5</sub> Teflon filter mass uncertainty,
43	MAGTTC	Numeric	10.4	PG/m PM <sub>10</sub> Teflon filter mass, $\mu$ g/m <sup>3</sup>
44	MAGTTU	Numeric	10.4	PM <sub>10</sub> Teflon filter mass uncertainty, µg/m <sup>3</sup>
45	NAATFC	Numeric	10.4	$PM_2$ , Teflon filter Na <sup>+</sup> , $\mu g/m^3$
46	NAATFU	Numeric	10.4	$PM_{2.5}$ Teflon filter Na <sup>+</sup> uncertainty, $\mu g/m^3$
47	NAATTC	Numeric	10.4	$PM_{10}$ Teflon filter Na <sup>+</sup> , $\mu g/m^3$
48	NAATTU	Numeric	10.4	$PM_{10}$ Teflon filter Na <sup>+</sup> uncertainty, $\mu g/m^3$
49	MGATFC	Numeric	10.4	$PM_2$ , Teflon filter Mg <sup>++</sup> , $\mu g/m^3$
50	MGATFU	Numeric	10.4	$PM_{2.5}$ Teflon filter $Mg^{++}$ uncertainty, $\mu g/m^3$
51	MGATTC	Numeric	10.4	$PM_{10}$ Teflon filter Mg <sup>++</sup> , $\mu g/m^3$
52	MGATTU	Numeric	10.4	$PM_{10}$ Teflon filter $Mg^{++}$ uncertainty, $\mu g/m^3$
53	KPATFC	Numeric	10.4	$PM_{o}$ = Teflon filter K <sup>+</sup> . $\mu g/m^3$
54	KPATFU	Numeric	10.4	PM <sub>2</sub> f Teflon filter K <sup>+</sup> uncertainty, $\mu g/m^3$
55	KPATTC	Numeric	10.4	PM <sub>10</sub> Teflon filter $K^+$ . $\mu g/m^3$
56	KPATTU	Numeric	10.4	PM <sub>10</sub> Teflon filter K <sup>+</sup> uncertainty. $\mu g/m^3$
57	CAATFC	Numeric	10.4	$PM_2$ , Teflon filter $Ca^{++}$ , $\mu g/m^3$
58	CAATFU	Numeric	10.4	$PM_{2.5}$ Teflon filter Ca <sup>++</sup> uncertainty, $\mu g/m^3$
59	CAATTC	Numeric	10.4	$PM_{10}$ Teflon filter $Ca^{++}$ . $\mu g/m^3$
60	CAATTU	Numeric	10.4	$PM_{10}$ Teflon filter Ca <sup>++</sup> uncertainty,
61	N4CTFC	Numeric	10.4	$PM_{a}$ , Teflon filter NH <sup>+</sup> , $\mu g/m^3$
62	N4CTFU	Numeric	10.4	$PM_{2.5}$ Teflon filter $NH_4^+$ uncertainty,
63	N4CTTC	Numeric	10.4	$PM_{10}$ Teflon filter NH <sup>+</sup> , $\mu g/m^3$
64	N4CTTU	Numeric	10.4	$PM_{10}$ Teflon filter $NH_4^+$ uncertainty,
65	CLITFC	Numeric	10.4	$PM_{2}$ , Teflon filter Cl <sup>-</sup> , $\mu g/m^{3}$
66	CLITFU	Numeric	10.4	PMo, Teflon filter Cl uncertainty.
 (7)			10 /	$\mu g/m^3$
6/ ()	OLITIC OLITIC	Numeric	10.4	$rm_{10}$ Terion filter CL, $\mu g/m^{\circ}$
68	CLITTU	Numeric	10.4	$PM_{10}$ Terion filter Cl uncertainty, $\mu g/m^{\circ}$
69 70	NJITFC	Numeric	10.4	$PM_{2.5}$ Tetlon filter $NO_3$ , $\mu g/m^{\circ}$
70	NJITFU	Numeric	10.4	$\mu_{2.5}$ Tetion filter NO <sub>3</sub> uncertainty, $\mu_g/m^3$
71	N3ITTC	Numeric	10.4	$PM_{10}$ Teflon filter $NO_3$ , $\mu g/m^3$

.

## Table 3-3 (continued)

CADMP Data-Base Structure for Ambient Chemical Concentrations (File CPCON.DBF)

<u>Field</u>	<u>Name</u>	<u>Data Type</u>	Width	<u>Explanation</u>
72	N3ITTU	Numeric	10.4	PM <sub>10</sub> Teflon filter NO <sub>3</sub> <sup>-</sup> uncertainty, μg/m <sup>3</sup>
73	S4ITFC	Numeric	10.4	$PM_2$ , Teflon filter $SO_4^{\pm}$ , $\mu g/m^3$
74	S4ITFU	Numeric	10.4	$PM_{2.5}$ Teflon filter $SO_4^{=}$ uncertainty, $\mu g/m^3$
75	S4ITTC	Numeric	10.4	$PM_{10}$ Teflon filter $SO_{\mu}^{\pm}$ , $\mu g/m^3$
76	S4ITTU	Numeric	10.4	$PM_{10}$ Teflon filter $SO_4^{=}$ uncertainty, $\mu g/m^3$
77	N3CNFC	Numeric	10.4	$PM_{2.5}$ Total particulate nylon filter $NO_{2.5}$ $\mu g/m^3$
78	N3CNFU	Numeric	10.4	PM <sub>2.5</sub> Total particulate nylon filter
79	HNCNGC	Numeric	10.4	$PM_{2.5}$ Non-denuded nylon backup filter HNO <sub>2</sub> $\mu g/m^3$
80	HNCNGU	Numeric	10.4	$PM_{2.5}$ Non-denuded nylon backup filter
81	NHCCGC	Numeric	10.4	Citric acid filter NH <sub>2</sub> , $\mu g/m^3$
82	NHCCGU	Numeric	10.4	Citric acid filter $NH_3$ uncertainty, $\mu g/m^3$
83	SOIKGC	Numeric	10.4	$K_{0}CO_{2}$ filter SO <sub>2</sub> , $\mu g/m^{3}$
84	SOIKGU	Numeric	10.4	$K_2CO_3$ filter SO <sub>2</sub> uncertainty, $\mu g/m^3$
85	NOCEGC	Numeric	10.4	TEA filter NO <sub>2</sub> , $\mu g/m^3$
86	NOCEGU	Numeric	10.4	TEA filter NO <sub>2</sub> uncertainty, $\mu g/m^3$
87	HNDDGC	Numeric	10.4	Denuder difference HNO <sub>3</sub> , $\mu g/m^3$
88	HNDDGU	Numeric	10.4	Denuder difference $HNO_3$ uncertainty, $\mu g/m^3$
89	SUMIFC	Numeric	10.4	Sum of $PM_{2.5}$ chemical concentrations, $\mu g/m^3$
90	SUMIFU	Numeric	10.4	Sum uncertainty of $PM_{2.5}$ chemical concentrations $\mu_{3}/m^{3}$
91	SUMITC	Numeric	10.4	Sum of $PM_{10}$ chemical concentrations,
92	SUMITU	Numeric	10.4	Sum uncertainty of $PM_{10}$ chemical concentrations $ug/m^3$
93	NOTE	Character	60	Comments

# Table 3-4

### Hourly Data Validation Flags

Validation	Sub Flag	Description
<u>r_tag</u>	<u>Jub-Flag</u>	
<		Data are missing from the averaging period but not enough to invalidate the average - SumX DAS flag.
Р		Power failure. Used to explain invalid data.
D		Parameter marked down - SumX DAS flag. Used to explain invalid data.
В		Bad status input - SumX DAS flag. Used to explain invalid data.
#		Insufficient data during averaging period to produce valid data average - SumX DAS flag. Used to explain invalid data.
С		Calibration - SumX DAS flag. Used to explain invalid data.
М		Instrument malfunction. Invalidates data average.
F		All data acquisitions failure. Invalidates data average.
А		Audit. Invalidates data average.
1 ·		Valid at Level I Validation. Comparison tests have been made, data have been flagged, and invalid data have been removed.
2		Valid at Level II Validation. Performance test data have been examined and corrections have been made where needed.
3		Valid at Level III Validation. Data have been used in interpretation projects and anomalous values have been further investigated.
S	S0 S1 S2 S3 S4	Suspect: Suspect due to reason in memo field. Suspect due to wind blown dust. Suspect due to construction activity. Suspect due to rain. Suspect due to fire.

### Table 3-4 (continued)

# Hourly Data Validation Flags

Validation		
<u> </u>	<u>Sub-Flag</u>	Description
v		Invalid:
	VO	Invalid due to reason in memo field.
	V1	Invalid due to wind blown dust.
	V2	Invalid due to construction activity.
	V3	Invalid due to rain.
	₩4	Invalid due to fire.
	V5	Invalid but reason not needed. Sufficient valid data exist.
G		Data adjusted:
	GO	Adjustment explained in NOTE field. Data changed due to reason in memo field.
	G1	Data taken from strip chart.
	G2	Changed because data taken from backup recording device other than strip chart. Explanation in memo field.
	G3	Changed because of slope-intercept calibration correction.
	G4	Changed because of change of units. Explanation in memo field.
а		Failure of data lower limit test - produced by program SUMMARY.
b		Failure of data upper limit test - produced by program SUMMARY.
с		Failure of data jump test - produced by program SUMMARY.
đ		Failure of data standard deviation test - produced by program SUMMARY.
m		Missing data - produced by program SUMMARY.
e		Dew point temperature > ambient temperature.
f		Scalar wind speed > vector wind speed.

### Table 3-5

# CADMP Ambient Field Sampling Data Validation Flags

Validation	Sub	
Flag	Flag	Description
В		Field blank.
D		Sample dropped during loading/unloading.
Е		Filter holder broken after sampling.
F		Filter damaged or ripped.
	F1	Filter damaged in the field.
	F2	Filter damaged in the lab.
	F5	Scratch mark on filter.
	F6	Pinholes in filter.
G		Finger touched filter.
	G1	Finger touched filter without gloves.
	G2	Finger touched filter with gloves.
Н		Heavy sample loadings.
	H1	Deposit appears to have fallen off filter.
I		Inhomogeneous filter deposit.
	11	Evidence of impaction - spot in center of filter.
	12	Deposit density varies across filter surface.
	13	Lightly loaded sample with dark specks.
	<b>I</b> 4	Non-uniform appearance of citric acid impregnated
		filter.
	15	Non-uniform appearance of TEA impregnated filter.
	16	Non-uniform appearance of K2CO2 impregnated
		filter.
J		Filter pack assembly problems.
	J1	Filter wrinkled prior to sampling.
	J2	Filter wrinkled after sampling.
	J3	Filter pack loose in sampler.
	J4	Filter pack fell out of sampler.
	J5	Filter pack not tightened sufficiently - possible
		air leak.
	J6	Filter torn or misaligned, air leak around edge
		of filter.
K		Filter ID tag not on Field Data Sheet.
L		Light sample loading.
М		Sampler malfunction.
N		Pump not turned on after samples changed.
P		Power failure during sampling.
	P1	Circuit breaker tripped.
		* *

.

### Table 3-5 (continued)

# CADMP Ambient Field Sampling Data Validation Flags

Validation	Sub	
<u>    Flag    </u>	<u>Flag</u>	Description
Q		Flow rate deviation from nominal.
	Q1	Filter pack flow rate error. Magnehelic reading
		> 0.1 off setpoint (~10% error).
	Q2	Make-up flow rate error. Magnehelic reading
		> 0.1 off setpoint (~10% error).
	Q4	Flow rate was estimated.
R		Filter replaced with spare in the field.
S		Sample validity suspect.
Т		Sampling time or duration deviation from nominal.
	T1	Elapsed time error > +- $10$ % from nominal.
	Т2	Start time error $> 1$ hr. from nominal.
	Т4	Final elapsed time reading estimated.
	т5	Initial elapsed time reading estimated.
	Т7	Sampling duration estimated.
	Т9	Sample not taken on network sampling day.
U		Unusual filaments, ash, or other particles on
		filter.
	U1	Local construction activity.
	U2	Forest fire or field or slash burning.
v		Void sample, invalid.
W		Wet sample.
	Wl	Sample got wet before sampling.
	W2	Sample got wet after sampling.
	W3	Sample got wet during sampling.
Х		No sample taken this period.
	X1	Sample taken was not on network sampling day.

### Table 3-6

# CADMP Chemical Analysis Data Validation Flags

Validation	Sub	
Flag	<u>Flag</u>	Description
Ъ		Blank.
	b1	Field blank.
	b2	Laboratory control blank.
	b3	Distilled water blank.
	b4	Method blank.
	b5	Extract/solution blank.
f		Filter damaged.
	f1	Filter damaged, outside of analysis area.
	f2	Filter damaged, within analysis area.
	 £3	Teflon membrane separated from the ring.
	f5	Filter dropped during handling.
i		Abnormal deposit appearance.
	il	Inhomogeneous filter deposit.
	i2	Deposit smeared or scraped after sampling.
	i3	Deposit fallen off filter.
	i4	Foreign particles on filter.
	i6	Large particles on fine fraction filter.
a		Calibration standard.
r		Replicate analysis.
_	rl	Routine laboratory replicate analysis.
	r2	Second replicate analysis on the same sample.
	r3	Third replicate on the same sample.
S		Results suspect.
v		Void sample.
	<b>v1</b>	Sample void due to quality control standard check
		exceeded ±10% of specified concentration.
	<b>v</b> 2	Sample void due to replicate analysis exceeded
		±10% of specified concentration range.
	<b>v</b> 3	Sample void due to apparent contamination.
	<b>v</b> 4	PM <sub>2</sub> concentration statistically greater than the
		PM <sub>10</sub> .
	<b>v</b> 5	Concentration out of expected range.
w		Ouestionable gravimetric analysis.
	w1	Pre-weight is guestionable.
	w2	Post-weight is questionable.

#### 4.0 DATA PROCESSING AND VALIDATION

Data processing and validation systems, operating in dBase III+ on IBM-PC based microcomputers, have been implemented to prepare the data bases described in Section 3. There are separate systems for the hourly data and substrate data. Frazier et al. (1990) present the standard operating procedures for applying these systems to CADMP data.

#### 4.1 Meteorological and Ozone Data Processing and Validation

Figure 4-1 shows the process by which continuous hourly data are obtained from field monitoring instruments.

The software is menu driven for ease of operation. The menu contains the following options:

- 1. Download Met and Ozone Data from SumX. This command invokes a telecommunications program which automatically dials the data logger at each of the 10 sampling sites and transfers data to the computer. This feature can also be used in an automated mode to have a host computer interrogate sites at night when phone rates are lower. Data are typically downloaded twice per week.
- 2. Verify Data Transfer. This command presents a visual display of the downloaded file for the identification of recording or transmission errors. Minor corrections can be made to the data file. If phone transmission has been poor from a site, it is sometimes necessary to download the data again. This inspection also allows problems with instruments at the site to be identified and remedial actions to be defined.
- 3. Enter Transferred Data into dBase File. This step converts data from the SumX output formats into dBase III+ data-base files.
- 4. Graph Data. This command creates a time series plot of hourly data which can be scrolled across the computer screen. It is examined for sharp spikes, which may indicate invalid data, and for long-term trends, which may indicate shifts in baselines or spans.
- 5. Print Data. After a month of data have been accumulated, a paper copy for validation is produced by this command. This command executes a validation program entitled SUMMARY.EXE which reads through the data file and calculates averages, standard deviations, highs, and lows for each specified observable. It also flags the following items: 1) missing data; 2) data which are less than a specified lower bound; 3) data which are greater than a specified amount from one hour to the next; 5) data with standard deviations over a specified period which are less than a specified amount, i.e., flat; 6) dew point temperature (DPT) which is greater than ambient temperature (TMP); and 7) scalar wind speed (SWS) which is less than


Figure 4-1: Flow Diagram of Hourly Data Processing Steps.

vector wind speed (VWS). Validation flags are inserted to alert the operator that remedial action may be needed and to qualify the data for future use.

- 6. Edit Data. This allows data to be changed in response to validation flags or quality control tests. The same change (e.g., zero offsets or span drifts) can be made to blocks of data with a single operation.
- 7. Delete a Selected Range of Data. When instruments are found to be defective, or if validation criteria are exceeded by too wide a margin, it is sometimes necessary to remove the invalid data. This command allows a range of hourly averages to be specified for replacement with the missing value parameter (-99).
- 8. Assign Validation Flags. Ranges of data are classified as valid, suspect, or invalid with the appropriate validation flag using this command.
- 9. Help. This command provides instructions on the use of the data processing and validation software.
- 10. Exit. This command terminates the data processing session.

Table 4-1 defines the programs, data files, and specification files which constitute this system. Using this system, it is possible to acquire and validate data for all sites in a few hours per week. The quasi real-time access to on-site instruments allows problems to be rapidly identified and corrected, thereby minimizing data loss.

#### 4.2 Chemical Data Processing and Validation

Data processing and validation of the gas/particle filter data involve the following six steps: 1) transcription of data from field and chemical analysis data sheets into data-base files; 2) calculation of measurement precisions for each chemical species from replicate analysis data; 3) merging of data from the various measurements into a unified data base; 4) calculation of field blank concentrations; 5) calculation of ambient concentrations; and 6) preparation of validation summaries. Figure 4-2 shows a flow diagram of the data processing and validation process and Table 4-2 summarizes the computer programs and files which constitute the system. Operations are described in detail by Frazier et al. (1990).

This system is menu-driven and operates in a manner similar to the hourly data processing system. The menu commands and their functions are as follows:

# Table 4-1

# Summary of Computer Software Developed for Hourly Meteorological and Ozone Data Processing and Data Validation in CADMP

(I) dBase III+ Programs:

MET.PRG	Main controlling program - runs all other programs.
CPMETHLP.PRG	Display help screens.
CPMETFIL.PRG	Get site, month, and year of data to process.
CPDNLOAD.PRG	Download data from SumX.
CPVERIFY.PRG	Verify data transfer from SumX.
CPTXTDB3.PRG	Convert data from text file to dBase III+ file.
CPMETGRA.PRG	Graph met data.
CPMETEDT.PRG	Edit data.
CPMETDEL.PRG	Delete selected data.
CPMETFLG.PRG	Assign validation flags.
CPMETPRT.PRG	Print met data.
SAVECOR.PRG	Determine if OK to save corrected data.
SETPRNT.PRG	Set up printer.
STOPPRNT.PRG	Abort printing.
NOFILE.PRG	Display message if wrong file selected.

(II) DOS Programs (Run by dBase III+ program MET.PRG):

SUMXHR1.EXE	Conver	t Su	mΧ	format	text	: file	e to	dBase	III+	format.
SUMMARY.EXE	Apply	data	va	lidatio	on te	sts a	ind j	print	data	summary.
GRAPH.EXE	Graph	met	dat	a.			-			-

(III) SumX Parameter Files:

SUMXPAR.AZ SUMXPAR.BA SUMXPAR.FR SUMXPAR.GA SUMXPAR.LA SUMXPAR.LB SUMXPAR.SA SUMXPAR.SB SUMXPAR.SB	SumX parameters for Azusa. Bakersfield. Fremont. Gasquet. Los Angeles. Long Beach. Sacramento. Santa Barbara. Sequoia
SUMXPAR.SB	Santa Barbara.
SUMXPAR, SE	Yosemite
	1000002000

(IV) Data Validation Parameter Files:

STATPAR.AZ	Data validation	parameters	for	Azusa.
STATPAR.BA	Bakersfield.	-		
STATPAR.FR	Fremont.			
STATPAR.GA	Gasquet.			
STATPAR.LA	Los Angeles.			
STATPAR.LB	Long Beach.			
STATPAR.SA	Sacramento.			
STATPAR.SB	Santa Barbara.			
STATPAR.SE	Sequoia.			
STATPAR.YO	Yosemite.			

# (V) Procomm Plus Files (in PROCOMM directory):

CADMP.ASP	Script file for automated SumX data access.
CPCALL.ASP	Script file to dial each site in turn.
CPREAD.ASP	Script file to generate SumX data listings.
CPMKFILE.ASP	Script file to create disk file of SumX data.
PCPLUS.KEY	Keyboard macros.
PCPLUS.PRM	Procomm configuration.





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# Table 4-2

Summary of Computer Software Developed for Chemical Data Processing and Data Validation in CADMP

(I) dBase III+ Programs:

DRYDEP.PRG	Main controlling program - runs all other programs.
DEMO, PRG	Run this program before DRYDEP to use demo data set.
CPCON.PRG	Calculate field blanks, ambient concentrations.
CPHLP.PRG	Display help screens.
CPMERGE . PRG	Integrate individual chemical measurement files.
CPFLOW.PRG	Enter flow calibration data.
CPCHEM, PRG	Enter chemical measurement data.
CPFIELD.PRG	Enter field data.
CPREP.PRG	Calculate replicate measurement precision.

(II) dBase III+ Structure Files:

CPFLOW00.DBF	Flow calibration.
CPFIEL00.DBF	Field data.
CPMAGT00.DBF	Mass data.
CPANITO0.DBF	Teflon filter Cl <sup>-</sup> , $NO_3^-$ , $SO_4^-$ data.
CPN4CT00.DBF	NH <sup>+</sup> <sub>4</sub> data.
CPNAAT00.DBF	Na <sup>+</sup> data.
CPMGAT00.DBF	Mg <sup>++</sup> data.
CPKPATO0.DBF	$K^{+}$ data.
CPCAATOO.DBF	Ca <sup>++</sup> data.
CPNTCN00.DBF	Nylon filter $NO_3^-$ data.
CPSOIK00.DBF	$SO_2$ data.
CPNHCC00.DBF	$NH_3$ data.
CPNOCE00.DBF	NO <sub>2</sub> data.
RPMAGT00.DBF	Mass replicate data.
RPCLITO0.DBF	Teflon filter Cl <sup>-</sup> replicate data.
RPN3ITOO.DBF	Teflon filter $NO_3$ replicate data.
RPS4IT00.DBF	Teflon filter $SO_4^{=}$ replicate data.
RPN4CT00.DBF	NH4 <sup>+</sup> replicate data.
RPNAATOO.DBF	Na <sup>+</sup> replicate data.
RPMGAT00.DBF	Mg <sup>++</sup> replicate data.
RPKPATOO.DBF	K <sup>+</sup> replicate data.
RPCAATOO.DBF	Ca <sup>++</sup> replicate data.
RPNTCNOO.DBF	Nylon filter $NO_3^-$ replicate data.
RPSOIK00.DBF	$SO_2$ replicate data.
RPNHCCOO.DBF	NH <sub>3</sub> replicate data.
RPNOCE00.DBF	NO <sub>2</sub> replicate data.
CPCHM00.DBF	Integrated data set.
CPVAL00.DBF	Validation ratios.

# Table 4-2 (continued)

Summary of Computer Software Developed for Chemical Data Processing and Data Validation CADMP

(III) dBase III+ Screen Entry Format Files:

ry.

(V) dBase III+ Printing Format Files:

CPFIEL1.FRM	Field data, page 1.
CPFIEL2.FRM	Field data, page 2.
CPFLOWM.FRM	Flow calibration, magnehelic setpoints.
CPFLOWC.FRM	Flow calibration, coefficient 'C'.
CPFLOWD.FRM	Flow calibration, exponent 'D'.
CPCONF.FRM	Concentration summary, $PM_{2.5}$ and $HNO_3$ data.
CPCONT.FRM	Concentration summary, $PM_{10}$ , $NH_3$ , $SO_2$ , and $NO_2$ data.

(VI) Installation Batch Files:

INSTALL.BAT	To instal	L1 DRYDEP	software	on	hard	disk.
INSCADMP.BAT	Called fr	com INSTAI	LL.BAT.			
INSEXIT.BAT	Called fr	com INSCAI	DMP.BAT.			

- 1. Enter Flow Calibration Data. This command establishes the relationship between the pressure gauge readings recorded on the field data sheet and the flow rates through the sampling system. These data are entered only when units are re-calibrated, i.e., once per year or when performance test tolerances are exceeded.
- 2. Enter Field Data. This command presents a screen display which mimics the data sheet filled out by the field technician. The field data are punched into appropriate positions on this display. The data entry program applies limits to the data entered and will not accept data which exceed these limits. This feature is intended to minimize major data transcription errors.
- 3. Enter Mass and Chemical Data. This command allows manual entry of data from chemical analysis systems which do not have automated data acquisition systems. The data entry program also tests entries against ranges established for each observable.
- 4. Calculate Replicate Precision. This interactive command associates original and replicate analyses with each other and calculates the standard deviation of their differences. The program allows the operator to select different concentration ranges and to eliminate outliers from the calculation.
- 5. Merge Field, Mass, and Chemical Data. This command associates data from the individual analysis files with the information in the field file.
- 6. **Calculate Concentrations**. This command calculates concentrations and propagates precisions. The calculations performed are given below.

The following formulae describe the calculation of ambient concentrations and the precision propagation:

 $C_i = (M_i - B_i)/V$  (4-1)

- $V = Fxt \tag{4-2}$
- $B_{i} = -\frac{1}{n} \sum_{\substack{n \\ j=1}}^{n} B_{ij} \qquad \text{for } B_{i} > \sigma_{Bi} \qquad (4-3)$
- $B_i = 0 \qquad \text{for } B_i \le \sigma_{\text{Bi}} \qquad (4-4)$

 $\sigma_{\rm Bi} = {\rm STD}_{\rm Bi} = \left[\frac{1}{n^{-1}} \sum_{j=1}^{n} (B_{ij} - B_{i})^2\right]^{1/2} \text{ for } {\rm STD}_{\rm Bi} > {\rm SIG}_{\rm Bi}$  (4-5)

$$\sigma_{\text{Bi}} = \text{SIG}_{\text{Bi}} = \left[\frac{1}{n^{-1}} \sum_{j=1}^{n} (\sigma_{\text{Bij}})^2\right]^{1/2} \text{ for STD}_{\text{Bi}} \le \text{SIG}_{4\text{Bi}}$$
(4-6)

$$\sigma_{\rm Ci} = \left[\frac{(\sigma_{\rm Mi}^2 + \sigma_{\rm Bi}^2)}{V^2} + \frac{\sigma_{\rm V}^2(M_{\rm i} - B_{\rm i})^2}{V^4}\right]^{1/2}$$
(4-7)

$$D_{Mij} = M_{ijf} - M_{ijr}$$
(4-8)

$$D_{Vj} = (F_{jf} - F_{jr}) \times t$$
(4-9)

$$D_{Mi} = -\sum_{\substack{n \\ j=1}}^{1} D_{Mij}$$
 (4-10)

$$D_{v} = -\sum_{\substack{n \\ n \\ j=1}}^{1} D_{v_{j}}$$
(4-11)

$$\sigma_{\rm Mi} = \left[\frac{1}{n^{-1}} \sum_{j=1}^{n} (D_{\rm Mij} - D_{\rm Mi})^2\right]^{1/2}$$
(4-12)

$$\sigma_{\rm V} = 0.05$$
 (4-13)

,

where

= average amount of species i on field blanks	
= the amount of species i found on field blank j	
= the ambient concentration of species i	
= flow rate throughout sampling period	
- flow rate performance test made before sampling	
= flow rate performance test made after sampling	
= amount of species i on the substrate	
= amount of species i on sample j from analysis	
= amount of species i on sample j from replicate analysis	
= sample duration	
- volume of air sampled	
= blank precision for species i	
= propagated precision for the concentration of species i	
= precision of amount of species i on substrate	
= precision of sample volume	
	<pre>= average amount of species i on field blanks = the amount of species i found on field blank j = the ambient concentration of species i = flow rate throughout sampling period = flow rate performance test made before sampling = flow rate performance test made after sampling = amount of species i on the substrate = amount of species i on sample j from analysis = amount of species i on sample j from replicate analysis = sample duration = volume of air sampled = blank precision for species i = propagated precision for the concentration of species i = precision of amount of species i on substrate = precision of sample volume</pre>

Nitrate in nitric acid is determined by subtracting the total particulate nitrate determined by the denuded nylon filter from the total nitrate determined on the non-denuded Teflon/nylon sample. The precision of this measurement is determined by addition in quadrature of the precisions of these two observables as specified in Bevington (1969).

#### 5.0 NETWORK PERFORMANCE

Different parts of the CADMP dry deposition network were functioning for up to two years at the time of this report. The purpose of this section is to evaluate the instrumentation and procedures to determine their effectiveness and efficiency in acquiring the desired measurements.

#### 5.1 New Equipment Procurement

When the dry deposition component of the CADMP was first envisioned, it was assumed that most of the hourly measurements were already being taken at existing sampling sites, and that these would only require supplementation by new instrumentation for a few key variables. An initial survey of the proposed network in 1987 showed that this assumption was incorrect. Table 5-1 compares the anticipated number of units with the number of units which were found necessary for successful attainment of the project objectives.

In the case of meteorological instrumentation, it was found in many cases that existing sites did not take the needed measurements, used antiquated (and unreliable) hardware, or could not interface with modern data acquisition systems. Where appropriate, agreements were made with the site operating agency to upgrade equipment to CADMP specifications, with the operating agency taking ownership in exchange for long-term maintenance of the hardware. This arrangement has worked well, with benefits to both the CADMP and the operating agency.

In the case of ozone monitors, all sites except Yosemite and Gasquet had existing monitors. Since Yosemite and Gasquet are remote sites which are difficult to service, two additional ozone analyzers were located at each site. In normal operating mode, one unit serves as a calibration unit to verify the values returned by the primary unit. When the primary unit needs repair, data acquired by the second unit can be used in place of the primary unit. This arrangement has worked well at these sites. The investment in two units has more than paid for itself by eliminating the need for emergency repair trips to these sites. One of the units can be shipped by the site operator to the repair laboratory for remedial action.

It was anticipated that on-site data loggers would be needed only at the Yosemite and Gasquet sites, with a third unit used by the data processing technician to read solid-state data modules (RAM packs) from those without phone lines. Telephone lines were eventually installed at all sites. The hourly data at other sites were intended to be acquired by the site operating agencies' data acquisition systems for extraction from their data bases and merging with the CADMP data base. This works well for ozone data, which are validated by standard criteria and are eventually reported to ARB in consistent formats. It is a simple matter to obtain these data from ARB's archives and integrate them into the CADMP file structures. This is not the case for meteorological data, which are often used instantaneously for forecasting without validation or archiving for later

# Summary of Equipment Acquired for CADMP

	Equipment	Anticipated Units	Number of Units <u>Procured and Installed</u>
(I)	Meteorological Instruments		
	Wind-Speed Sensor	3	7
	Wind-Direction Sensor	3	7
	Ambient Temperature Sensor	4	5
	Dew Point Sensor	7	8
	Radiation Sensor	5	8
	Time of Wetness Sensor	10	10
	Translator Box with Cards	3	5
(11)	Air Quality Instruments		
	Dasibi 1003 AH Ozone Analyzer	2	2
	Dasibi 1008 PC Ozone Analyzer	0	2
(111)	Data Acquisition and Processors Systems		
	SumX Data Acquisition System with Modems	3	11
	286 Desktop Computer with Modem and Software	1	2
	386 Desktop Computer with Modem and Software	0	1
(IV)	Dry Deposition Instruments		
	Gas/Particle Sampling System	10	11

retrieval. Additional data loggers were procured and installed for the CADMP so that continuous records could be acquired, validated, and included in the data base. The investment in data logging hardware is once again small compared to the cost of labor which would be required to obtain these data by other means.

It was originally anticipated that a single desktop computer would be adequate to handle CADMP dry deposition data processing needs. As the procedures developed, it became clear that dedicated computers were needed for field operations, laboratory operations, and data interpretation. IBM-compatible 286 systems with fast disk drives were procured for the data processing tasks, since these are time limited by disk access rather than processor speed. An IBMcompatible 386 system was procured for data interpretation and display, since several of the models associated with the concentration/velocity measurements require substantial central processor time.

The hourly meteorological, air quality, and data acquisition systems were commercially available and had proven their reliability in previous programs. There was no such commercial instrument capable of acquiring the gas/particle measurements, so one was designed, tested, and installed as part of this project. Watson et al. (1990) and Chow et al. (1991) describe this instrument and its testing. Ten units were constructed and installed, and the prototype unit was upgraded for collocated operation at the Sacramento site. These units have proven to be reliable and practical to operate in a long-term program.

#### 5.2 Network Operations Experience

Most of the equipment has operated reliably throughout the first 1-2 years of monitoring. Table 5-2 lists the new parts which were procured and installed during that period, and this list is no longer than that found in other, less demanding aerometric monitoring networks. Telemetered data retrieval and dedicated site operators have ensured a high rate of data recovery after initial installation problems were solved.

DRI made a final maintenance and calibration visit to each site during the period 4/9/90 through 4/21/90 to identify and correct any network deficiencies as part of the final transfer of responsibilities to ARB. The activities conducted on this visit and a summary of the results are reported in the following sub-sections. A similar visit should be made to each site at least annually, in addition to repair visits which are needed in response to instrument failure.

#### 5.2.1 Gas/Particle Sampling System

Gas/particle samplers were inspected and tubing was replaced when it appeared worn, cracked, or kinked. The inlets, solenoid valves, and flow control lines were cleaned. Pump exhaust filters were replaced. No major operational failures were found.

# Summary of Repairs and Replacement of Hardware at CADMP Field Sites

Sampling Site	Equipment	Date	Observation	<u>Action</u>						
Gasquet	Met Equipment									
	Ozone Analyzer Pump	10/04/89	Malfunction	Installed New Shaft						
	Data Acquisition System									
	SumX	03/30/89	Malfunction	Installed New Unit						
Fremont	Dry Deposition Samples	~								
	bly beposition Sample	<b>L</b>								
	PFA Tubing	03/10/89	Line Broken	Replaced Lines to PM <sub>2.5</sub> and PM <sub>10</sub>						
	Fiber Exhaust Filter	04/18/89	Checked	Changed						
	Capsule Exhaust Filter	05/03/89	Checked	Changed						
	Capsule Exhaust Filter	10/05/89	Checked	Changed						
	0-ring	11/21/89	Loose in TCK Port	Replaced O-ring						
	Data Acquisition Syste	em								
	Ram pack	02/16/89	Malfunction	Changed to Modem						
Sacramento										
	Dry Deposition Sampler	r								

Polyethylene Tubing 07/17/89 Broken Line Replaced

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# Table 5-2 (continued)

# Summary of Repairs and Replacement of Hardware at Field Sites

Sampling 	Equipment	Date	<u>Observation</u>	Action
Yosemite	Dry Deposition Sample	er		
	0-ring	10/17/89	Filter holders loose in ports	Replaced O-rings
	Met Equipment			
	Wind-Sensor Cups	5/11/89	Broken	Replaced
	Data Acquisition Syst	tem		
	Ram pack	2/13/89	Malfunction	Replaced
	SumX	5/9/89	Malfunction	Replaced
	Ram pack	5/11/89	Malfunction	Replaced
	Ram pack	11/9/89	Malfunction	Replaced
Sequoia				
	Dry Deposition Sample	er		
	0-ring	9/18/89	Loose on Port #7	Replaced O-ring
	0-ring	7/8/89	Loose on Port #3	Replaced O-ring
	Timer	8/14/89	Malfunction	Replaced
	Met Equipment			
	Wet Sensor Control Box	6/6/89	Lack of Sensitivity	Replaced
	Wind Direction/ Temperature	8/9/89	Lightning Hit	Repaired
	Wind Direction	9/5/89	Bearings Worn	Replaced
	PC Board in Wet Sensor	10/3/89	Malfunction	Replaced

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# Table 5-2 (continued)

# Summary of Repairs and Replacement of Hardware at Field Sites

Sampling <u>Site</u>	Equipment	<u>Date</u>	Observation	Action
Bakersfield	Dry Deposition Sampler			
	PFA Tubing	9/12/88	Broken	Replaced
	ÝFA Tubing	4/6/89	Broken	Replaced
	Capsule Exhaust Filters	3/9/90	Checked	Changed
	Fiber Exhaust	3/9/90	Checked	Changed
Santa Barbara	Dry Deposition Sampler			
	PFA Tubing	11/29/89	Broken Line	Repaired
Long Beach	Dry Deposition Sampler			
	Capsule Exhaust Filter	12/13/88	Checked	Replaced
	Fiber Exhaust Filters	12/13/88	Checked	Replaced
	PFA Tubing	5/1/89	PM <sub>10</sub> GT Line Broken	Replaced
	Pump Vanes	7/6/89	Unknown	Replaced
	PFA Tubing	7/6/89	Broken	Replaced
	PFA Tubing	7/25/89	PM <sub>2.5</sub> Line Broken	Replaced
	PFA Tubing	7/28/89	PM <sub>2.5</sub> Line Broken	Replaced
	PFA Tubing	8/7/89	Broken	Replaced

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# Table 5-2 (continued)

# Summary of Repairs and Replacement of Hardware at Field Sites

Sampling Site	Equipment		Date	<u>Observation</u>	<u>Action</u>		
Los Angeles	Dry	Deposition Sampler					
		Fiber Exhaust Filters	12/12/88	Checked	Replaced		
		Capsule Exhaust Filters	12/12/88	Checked	Replaced		
		PFA Tubing	7/21/89	Broken	Replaced		
Azusa	Dry	Deposition Sampler					
		Pump Box	12/12/88	Blew off Roof	Replaced, Secured		
	Data Acquisition System						
		SumX	2/28/89	Malfunction	Replaced		

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Flow rates were checked against the original calibration, and on-site flow meters were re-calibrated. The results of these checks are given in Table 5-3. The total inlet flow rates were compared to the sum of the individual flow rates, and these are compared with actual flows in Table 5-4. For most samplers, the total flow rates were 5 to 8% lower than the sums. Several samplers had greater differences caused by leaks in the plena after they were replaced following cleaning. Leaks were found in the Bakersfield  $PM_{2.5}$  and  $PM_{10}$  units and the Azusa  $PM_{10}$  unit. These leaks were located and plugged. The Fremont  $PM_{10}$ , Sequoia  $PM_{2.5}$ , and Los Angeles  $PM_{10}$  units had differences greater than 10% but no leaks were apparent during leak tests after calibration.

New setpoints for the sampler magnehelics were determined. Flow rates are at their specified levels when these setpoints are achieved. The samplers at Gasquet, Sacramento (both primary and collocated), and Yosemite were adjusted to the new setpoints. The other samplers were not adjusted. The new setpoints were generally within  $\pm 0.10$  inches of water of the old ones, which corresponds to less than a 5% deviation from specified flow rates. The old and new setpoints are given in Table 5-5.

The gas/particle samplers have operated reliably and most of them held their calibrations within  $\pm 10$ % for a year or more.

#### 5.2.2 Ozone Measurements

The analyzers at Gasquet and Yosemite were audited with DRI's transfer standard. Maintenance on the Gasquet analyzer had been done by ARB personnel prior to this visit. At Yosemite, sample chamber tubes were cleaned, and the control and sample frequencies were adjusted after the audit. At Gasquet, the average percent deviation after subtracting the zero offset for the 1003 AH was  $0.16 \pm 1.32$ %. At Yosemite, the average percent deviation for the 1003 AH before maintenance was  $5.26 \pm 2.18$ %. Monitors at the other sites were not examined, since their maintenance, operation, and auditing are covered in other air monitoring programs.

The 1008 PC calibration units at Gasquet and Yosemite were verified against DRI's transfer standard. The Gasquet calibration unit had just been returned to the site following certification tests by ARB at Sacramento. At Gasquet, the average percent deviation after subtracting the zero offset was  $0.31 \pm 1.16$ % and at Yosemite it was  $-4.23 \pm 1.06$ %.

The ozone monitors have operated reliably throughout the first years of CADMP operation.

#### 5.2.3 Wind-Speed Measurements

All wind-speed sensors were checked either directly (at Gasquet, Yosemite, Sequoia, and Long Beach) or indirectly (at the remaining sites). During direct checks, synchronous motors with different rotation rates were attached to the sensors and the sensor outputs were compared to the manufacturers' expected

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				_ <u>PM</u> 10-	Flow F	<u>lates</u>				_ <u>PM</u> 2.5	<u>Flow R</u>	ates_
Site	Date	Filter <sup>a</sup> Pack	Port Id	Site <u>(lpm</u> )	Test (lpm)	DIFF <sup>c</sup> _(%)		Filter Pack	Port ID	Site ( <u>lpm)</u>	Test ( <u>lpm)</u>	DIFF (%)
Gasquet	4/13	GT	1	1.60 <sup>b</sup>	2.02	26.3		DN	1	19.6	19.7	0.5
		Blue	2	57.4	55.8	-2.8		Blue	2	38.3	37.8	-1.3
		GT	3	2.05	2.02	-1.5		DN	3	20.7	20.3	-1.9
		TCK	5	20.4	20.5	0.5		TN	5	23.4	21.5	-8.1
		Black	6	36.6	35.4	-3.3		Black	6	38.0	37.9	-0.3
		TCK	7	19.3	20.2	5.0		TN	7	22.8	20.4	-10.5
		SUM		116.5	113.7	-2.4		SUM		119.3	116.9	-2.0
Fremont	4/10	GT	1	1.88	2.02	7.5		DN	1	21.0	19.7	-6.4
		Blue	2	51.5	54.6	6.0		Blue	2	36.8	37.2	1.1
		GT	3	1.88	2.02	7.5		DN	3	20.8	19.6	-5.8
		TCK	5	20.8	20.0	-3.9		TN	5	20.8	20.2	-2.9
		Black	6	37.1	37.9	2.2		Black	6	37.5	37.4	-0.3
		TCK	7	20.9	19.5	-6.7		TN	7	20.6	20.2	-1.9
		SUM		111.3	114.5	2.9		SUM		116.1	114.0	-1.8
Sacramento	4/9	GT	1	2.20	2.15	-2.3		DN	1	20.0	19.6	-2.0
		Blue	2	46.9	52.0	10.9		Blue	2	37.7	36.8	-2.4
		GT	3	2.20	2.17	-1.4		DN	3	19.8	19.8	0.0
		TCK	5	21.2	20.3	-4.3		$\mathbf{TN}$	5	21.6	20.7	-4.2
		Black	6	39.9	38.6	-3.3		Black	6	37.6	37.4	-0.5
		TCK	7	21.0	20.3	-3.3		TN	7	21.8	20.7	-5.1
		SUM		110.2	113.1	2.6		SUM		117.1	114.5	-2.2
Collocated Sacramento		Flow se	tting	gs char	nged be	fore au	ıdit					
Yosemite	4/16	GT	1	1.88	1.82	-3.2		DN	1	18.9	19.8	4.8
	·	Blue	2	53.9	53.8	-0.2		Blue	2	37.1	36.5	-1.6
		GT	3	1.94	1.84	-5.2		DN	3	18.9	19.6	3.7
		TCK	5	21.2	20.1	-5.2		TN	5	23.1	19.3	-16.5
		Black	6	36.6	36.3	-0.8		Black	6	36.1	37.2	3.1
		TCK	7	21.3	20.1	-5.6		TN	7	23.1	19.0	-17.8
		SUM		113.6	112.0	-1.4		SUM		115.2	112.8	-2.1
Sequoia	4/19	GT	1	2.28	2.13	-6.6		DN	1	20.3	20.6	1.5
		Blue	2	51.6	50.9	-1.4		Blue	2	36.5	36.0	-1.4
		GT	3	2.28	2.13	-6.6		DN	3	20.1	20.6	2.5
		TCK	5	21.5	19.6	-8.8		TN	5	22.0	20.0	-9.1
		Black	6	40.7	36.9	-9.3		Black	6	32.3	32.6	0.9
		TCK	7	21.0	19.6	-6.7		TN	7	22.2	19.9	-10.4
		SUM		116.1	109.3	-6.9		SUM		111.0	109.3	-1.5

# Summary of Flow Rate Test Results for Gas/Particle Sampling Performed in April, 1990

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## Table 5-3 (continued)

## Summary of Flow Rate Test Results for Gas/Particle Sampling Performed in April, 1990

				<u>PM</u> 10_	Flow F	<u>lates</u>			<u>PM</u> 2.5	<u>Flow R</u>	<u>ates</u>
Site	Date	Filter <sup>a</sup> Pack	Port Id	Site (lpm)	Test (lpm)	DIFF <sup>c</sup> (%)	Filter Pack	Port ID	Site (lpm)	Test (1pm)	DIFF (%)
<u>.</u>				·							
Bakersfield	4/13	GT	1	1.78	2.04	14.6	DN	1	19.0	20.0	5.3
		Blue	2	53.8	54.3	0.9	Blue	2	35.8	35.8	0.0
		GT	<u> </u>	1.78	2.04	14.6	DN	3	20.4	20.0	-2.0
		TCK	5	20.8	19.7	-5.3	TN	5	20.6	20.2	-1.9
		Black	6	36.4	36.1	-0.8	Black	6	35.5	36.2	2.0
		TCK	7	20.8	19.7	-5.3	TN	7	20.6	20.2	-1.9
		SUM		112.8	112.0	-0.7	SUM		110.9	112.2	1.1
Santa	4/13	GT	1	2.17	2.02	-6.9	DN	1	22.7	23.6	4.0
Barbara		Blue	2	51.6	53.1	2.9	Blue	2	32.7	32.7	0.0
		GT	3	2.17	2.02	-6.9	DN	3	22.7	23.6	4.0
		TCK	5	24.0	23.8	-0.8	TN	5	24.4	23.4	-4.1
		Black	6	33.8	32.5	-3.9	Black	6	33.7	33.7	0.0
		TCK	7	24.0	23.8	-0.8	TN	7	24.1	23.4	-2.9
		SUM		111.5	111.4	-0.1	SUM		113.4	113.3	-0.1
Long Beach	4/13	GT	1	2.06	1.96	-4.9	DN	1	21.2	20.5	-3.3
		Blue	2	53.4	58.4	9.4	Blue	2	36.9	36.1	-2.2
		$\mathbf{GT}$	3	2.06	1.96	-4.9	DN	3	21.2	19.8	-6.6
		TCK	5	21.2	20.4	-3.8	TN	5	20.7	19.8	-4.4
		Black	6	37.3	35.0	-6.2	Black	6	38.9	38.6	-0.8
		TCK	7	21.2	20.4	-3.8	TN	7	20.7	19.8	-4.4
		SUM		114.0	115.7	1.5	SUM		117.7	115.0	-2.3
Los Angeles	4/13	GT	1	2.06	1.84	-10.2	DN	1	21.7	20.1	-7.4
		Blue	2	49.8	52.4	5.2	Blue	2	35.0	34.8	-0.6
		GT	3	2.06	1.84	-10.7	DN	3	21.5	20.0	-7.0
		TCK	5	21.2	19.9	-6.1	TN	5	20.7	19.7	-4.8
		Black	6	37.4	36.2	-3.2	Black	6	36.0	37.1	3.1
		TCK	7	21.2	19.9	-6.1	TN	7	20.7	19.7	-4.8
		SUM		110.2	110.4	0.2	SUM		113.4	115.8	2.1
Azusa	4/13	GT	1	2.19	2.02	-7.8	DN	1	21.9	20.1	-8.2
		Blue	2	51.3	53.7	4.7	Blue	2	35.4	34.8	-1.7
		GT	3	2.19	2.02	-7.8	DN	3	21.4	19.8	-7.5
		TCK	5	20.5	19.8	-3.4	TN	5	21.0	19.6	-6.7
		Black	6	35.4	36.1	-2.0	Black	6	35.9	35.3	-1.7
		TCK	7	20.5	19.8	-3.4	TN	7	20.5	19.8	-3.4
		SUM		109.4	111.5	1.9	SUM		114.1	109.8	-3.8

<sup>a</sup> GT=TEA Filter, TCK=Teflon/citric acid/potassium carbonate, DN=Denuded nylon TN=Non-denuded Teflon/nylon, Blue=Makeup Air, Black=Makeup Air, and SUM=sum of flows through Ports 1,2,5 and 6.

<sup>b</sup> Filter holder leaking.

° Percent difference.

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Comparison of Total Inlet Flow Rates to Sum of Filter Flow Rates

	<u>PM<sub>10</sub> Inlet Flow Rate</u>					PM <sub>2.5</sub> Inlet Flow Rate				
Sampling Site	Measured (1pm)	Sum (1pm)	Diffe (lpm)	rence (%)		Measured (lpm)	Sum (1pm)	Diffe: (1pm)	rence (%)	
Gasquet	107.7	116.5	8.8	7.6		110.6	119.3	8.7	7.3	
Fremont	97.8	111.3	13.5	12.1		106.7	116.1	9.4	8.1	
Sacramento	103.6	110.1	6.5	5.9		112.2	117.1	4.9	4.2	
Yosemite	_a	-	-	-		108.0	115.2	7.2	6.3	
Sequoia	109.9	116.1	6.2	5.3		97.7	111.1	13.4	12.1	
Bakersfield	93.7	112.8	19.1	16.9		80.5	110.8	30.2	27.4	
Santa Barbara	104.5	111.5	7.0	6.3		105.7	113.4	7.7	6.8	
Long Beach	106.1	114.0	7.9	6.9		109.7	117.7	8.0	6.8	
Los Angeles	97.7	110.2	12.5	11.3		104.2	113.4	9.2	8.1	
Azusa	79.0	109.4	30.4	27.8		105.3	114.1	8.8	7.7	

 $^{\rm a}$  Inlet flow rates on  ${\rm PM}_{\rm 10}$  module at Yosemite were not measured.

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Sampling		Filter	Setp	Setpoints		
Site	Size	Pack <sup>a</sup>	New <sup>b</sup>	01d		
Gasquet	PM <sub>10</sub>	GT	1.10	1.10		
-	10	Blue	1.50	1.45		
		TCK	0.60	0.60		
	`	Black	1.00	1.05		
	PM <sub>2.5</sub>	DN	0.55	0.60		
		Blue	1.10	1.20		
		TN	0.60	0.75		
		Black	1.10	1.05		
Fremont	PM <sub>10</sub>	GT	1.20	1.05		
		Blue	1.75	1.65		
		TCK	0.55	0.55		
		Black	1.25	1.25		
	PM <sub>2.5</sub>	DN	0.50	0.50		
		Blue	1.25	1.20		
		TN	0.55	0.60		
		Black	1.30	1.30		
Sacromonto	ЪМ	С <b>Т</b>	1 10	1 15		
Sacramento	F <sup>H</sup> 10	Blue	1.10	1.15		
		DIUE	1.50	0.95		
		Plack	1 00	0.60		
		DIACK	1.00	1.05		
	PM <sub>2.5</sub>	DN	0.65	0.65		
		Blue	1.10	1.15		
		TN	0.60	0.70		
		Black	1.10	1.05		
0-11	DV	<b></b>	1 10	1 10		
Collocated	$PM_{10}$	Gr	1.15	1.15		
Sacramento		Blue	1.65	1.70		
			0.50	0.55		
		DIACK	1.20	1.25		
	PM <sub>2.5</sub>	DN	0.60	0.65		
		Blue	1.30	1.35		
		TN	0.60	0.65		
		Black	1.15	1.20		

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# CADMP Dry Deposition Sampler Setpoints

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# Table 5-5 (continued)

# CADMP Dry Deposition Sampler Setpoints

Sampling		Filter	r Setpoints			
Site	Size	Pack <sup>a</sup>	New <sup>b</sup>	Old		
Yosemite	PM <sub>10</sub>	GT Blue TCK Black	1.10 0.90 0.50 0.90	1.15 1.00 0.60 0.95		
	PM <sub>2.5</sub>	DN Blue TN Black	0.50 0.85 0.50 0.90	0.50 0.90 0.75 0.90		
Sequoia	PM <sub>10</sub>	GT Blue TCK Black	1.00 0.65 0.55 0.80	1.00 0.60 0.55 0.90		
	PM <sub>2.5</sub>	DN Blue TN Black	0.60 0.75 0.60 0.95	0.55 0.75 0.65 0.95		
Bakersfield	PM <sub>10</sub>	GT Blue TCK Black	1.40 1.60 0.45 1.15	1.10 1.70 0.50 1.20		
	PM <sub>2.5</sub>	DN Blue TN Black	0.60 1.20 0.60 0.90	0.60 1.25 0.65 0.95		
Santa Barbara <sup>c</sup>	PM <sub>10</sub>	GT Blue TCK Black	1.15 1.85 0.90 1.70	1.25 1.75 1.00 1.75		
	PM <sub>2.5</sub>	DN Blue TN Black	1.00 1.80 0.85 1.50	0.90 1.75 0.95 1.50		

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# Table 5-5 (continued)

Sampling		Filter	Setpoints		
Site	Size	Pack <sup>a</sup>	New <sup>b</sup>	01d	
Long Beach	PM <sub>10</sub>	GT	1.15	1.10	
		Blue	1.20	1.00	
		TCK	0.50	0.60	
		Black	1.00	1.00	
	PM <sub>2.5</sub>	DN	0.55	0.65	
		Blue	1.10	1.15	
		TN	0.60	0.60	
		Black	1.20	1.15	
Los Angeles	DM	<b>CT</b>	1 20	1 10	
	PPI <sub>10</sub>	Blue	1.20	1.10	
		TCV	1.40	1.55	
		Plaal	0.30	0.55	
		DIACK	0.75	0.85	
	PM <sub>2.5</sub>	DN	0.60	0.70	
		Blue	1.00	1.00	
		TN	0.60	0.65	
		Black	1.20	1.15	
Azusa	PM <sub>10</sub>	GT	1.00	1.10	
		Blue	1.10	1.30	
		TCK	0.70	0.55	
		Black	1.00	0.95	
	PM2.5	DN	0.50	0.60	
		Blue	1.00	0.90	
		TN	0.60	0.70	
		Black	1.00	1.05	

## CADMP Dry Deposition Sampler Setpoints

<sup>a</sup> GT=TEA filter, TCK=Teflon/citric acid/potassium carbonate, DN=Denuded nylon TN=Non-denuded Teflon/nylon, Blue=Makeup air, Black=Makeup air, and SUM=sum of flows through Ports 1,2,5 and 6.

<sup>b</sup> April, 1990.

<sup>c</sup> Nominal set points for sampler at Santa Barbara are different from those of other sites, because this is the original prototype sampler and has different plumbing from other samplers. The actual flow rates are the same as for the other samplers.

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values. Indirect checks were made at sites where the sensors could not be reached; the wind speed was estimated by the technician from the motion of nearby objects, such as flags or trees, and then categorized as calm (< 0.5 m/sec), light (0.5-2 m/sec), or strong (> 5 m/sec). The sensor output was compared to the estimated value. The sensors were operating well in all cases. The test results for wind-speed measurements are summarized in Table 5-6.

#### 5.2.4 Wind-Direction Measurements

All wind-direction sensors were checked either by aiming the vane at targets having known bearings (Gasquet and Long Beach), sighting the orientation of the crossarm (Fremont, Yosemite, Sequoia, Bakersfield, Los Angeles, and Azusa), or estimating wind direction from vane orientation (Sacramento and Santa Barbara). The sensors at Yosemite and Sequoia malfunctioned and were returned to Reno. A new sensor had been ordered for Sequoia but did not arrive before the site visit. These sensors have since been installed and are operating.

Test results for wind-direction measurements are summarized in Table 5-7. Most sensors were within a few degrees of the correct values. The sensor at Gasquet was reading about 6° higher than the audit value. The crossarm at Bakersfield was along a 165-345° true line instead of north-south. This information was communicated to ARB for remediation.

#### 5.2.5 Temperature Measurements

Temperature sensors were checked with an aspirated thermometer placed as close to the sensor as possible. The audit results are summarized in Table 5-8. Most sensors were within  $\pm 1$  °C of the standard thermometer.

The sensor at Gasquet was found to provide data which corresponded to the standard but the data acquisition system returned readings which were approximately 5 °C higher. After running the internal calibration routine, the deviation decreased to 0.2 °C. This offset has not been observed with this type of data acquisition system at any other site. The output from the sensor should be compared with that acquired by the data acquisition system at this site at regular intervals to verify whether or not this is a long-term problem. The temperature sensor at Fremont was operating improperly and was replaced.

#### 5.2.6 Dew Point Measurements

Dew point sensors were checked with an aspirated psychrometer placed as close to the sensor as possible. Results are reported in Table 5-9. At most sites, the audit dew point was higher than the site dew point by 2 °C or more. Fremont, Sequoia, Bakersfield, and Long Beach had better agreement.

At Gasquet, the sensor measured 5 °C low. The bobbin was found to have a bad solder joint. After replacing the bobbin, the sensor was 2 °C low. The SumX reading was consistently 0.5 °C higher than the sensor value both before and after recalibrating the data acquisition system.

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# Summary of Wind-Speed Tests Performed in April, 1990

			_	Difference		
	Audit	Sensor	DAS <sup>d</sup>	Sensor	DASd	
Site	<u>(m/s)</u>	(m/s)	<u>(m/s</u> )	(m/s)	(m/s)	
Gasquet	0	0.2	0.2	0.2	0.2	
	8.3	8.2	8.2	-0.1	0.0	
	16.3	16.2	16.3	-0.1	0.0	
	48.3	48.4	a	0.1	a	
Fremont	2 est	b	2.0		c	
Sacramento	l est	1.4	1.5			
Yosemite	0	0.2	0.5	0.2	0.5	
	8.3	8.5	8,6	0.2	0.3	
	16.3	16.2	16.4	-0.1	0.1	
	48.3	48.2	a	-0.1	а	
Sequoia	0	b	0.5	b	0.5	
	8.3		8.2		-0.1	
	16.3		16.2		-0.1	
	48.3		а		a	
Bakersfield	0	b	0.6			
	4 est		3.7			
Santa	0	ь	0.6			
Barbara	5 est		43			
barbara	5 656		4.5			
Long Beach	0	b	0.5	b	0.5	
	7.3		7.4		0.1	
	14.3		14.4		0.1	
	42.5		42.4		-0.1	
Los Angeles	0	ь	0.5			
-	3 est		2.7			
Azusa	0	Ъ	0.6			
	2 est		2.2	·		

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<sup>&</sup>lt;sup>a</sup> 48 m/s is greater than range of Met One.
<sup>b</sup> Sensor voltage not recorded.
<sup>c</sup> Differences between estimated speed and site values not computed.
<sup>d</sup> Data Acquisition Systems.

# Summary of Wind-Direction Tests Performed in April, 1990

					Diff	erence
Sampling Site	Audit (deg)	Sensor (deg)	DAS <sup>c</sup> (deg)		Sensor (deg)	DAS <sup>c</sup> (deg)
Gasquet	42 222 222 402	48 228 229 408	47 228 228 409		6 6 7 6	5 6 7
	156 336 336 515	163 345 344 521	163 346 344 522		7 9 8 6	7 10 8 7
Fremont	270 est		265			
Sacramento	Crossarm	bearing 360	deg true	north		
Yosemite <sup>a</sup>	Sensor bu	shing set to	o due nort	th <sup>b</sup>		
Sequoiaª	Crossarm	bearing 360	deg true	north		
Bakersfield	Crossarm	bearing 345	deg true	north		
Santa Barbara	SE (140)		137			
Long Beach	Crossarm Vane rela 360 450 90 180 270 360 450 180	bearing 360 ative to cros 358 447 90 177 266 355 451 181	deg true ssarm		-2 -3 0 -3 -4 -5 1	
Los Angeles	Crossarm Sensor al	bearing 360 Ligned along	deg true crossarm	north 357		
Azusa	Crossarm	bearing 360	deg true	north		

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<sup>&</sup>lt;sup>a</sup> Sensor not working. <sup>b</sup> Bushing lined up due south after checks. <sup>c</sup> Data Acquisition Systems.

# Summary of Temperature Tests Performed in April, 1990

				Difference					
Sampling Site	Audit (°C)	Sensor (°C)	DAS <sup>f</sup> (°C)	Sensor (°C)	DAS <sup>f</sup> (°C)				
Gasquet	9.5	9.7	 14.7ª	0.2	5.7				
Fremont	14.5	5.4 <sup>b</sup>							
Sacramento	18.0	17.3	17.5	-0.7	-0.5				
Yosemite	4.4	4.2	5.3°	-0.2	0.9				
Sequoia	7.7	7.5	d	-0.2					
Bakersfield	28.0	27.6	27.9	-0.4	-0.1				
Santa Barbara	16.3	15.3	15.5	-1.0	-0.8				
Long Beach	22.8	e	20.8		-2.0				
Los Angeles	20.8	e	21.0		0.2				
Azusa	14.5	e	13.4		-1.1				

- <sup>a</sup> SumX about 5 °C high before recalibrating.
  <sup>b</sup> Sensor broken.
  <sup>c</sup> SumX about 8 mv (0.8 °C) high before ground loop fixed.
  <sup>d</sup> SumX reading not entered.
  <sup>e</sup> Sensor voltage not entered.
  <sup>f</sup> Data Acquisition Systems.

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# Summary of Dew Point Tests Performed in April, 1990

				Difference					
Sampling Site	Audit (°C) 	Sensor (°C)	DAS° (°C) 	Sensor (°C)	DAS° (°C)				
Gasquet <sup>a</sup>	6.1 9.7	-0.9 6.8	-0.3 7.5	-7.0 -2.9	-6.4 -2.2				
Fremont	11.3	11.0	11.1	-0.3	-0.2				
Sacramento	10.1 9.4	1.1 3.6	b	-9.0 -5.8					
Yosemite <sup>c</sup>	1.8 5.8	-1.1 3.5	-0.5 3.9	-2.9 -2.3	-2.3 -1.9				
Sequoia	6.4	d	5.9	-0.5					
Bakersfield	6.8	7.9	7.5	1.1	0.7				
Santa Barbara	11.5	9.2	9.2	-2.3	-2.3				
Long Beach	11.9	đ	10.7		-1.2				
Los Angeles	6.6	đ	4.9		-1.7				
Azusa	11.9	đ	9.4		-2.5				

<sup>a</sup> First reading prior to replacing bobbin. Second with new bobbin. <sup>b</sup> SumX value not entered.

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<sup>&</sup>lt;sup>c</sup> First reading prior to retreatment. Second after treatment. <sup>d</sup> Sensor value not entered.

<sup>&</sup>lt;sup>e</sup> Data Acquisitions System.

The dew point sensor is the least reliable component in the entire monitoring system. ARB is currently evaluating new instruments to measure relative humidity or dew point. The CADMP units should be replaced with these more reliable units when the evaluation has been completed.

#### 5.2.7 Solar Radiation Measurements

Solar radiation sensors were checked by placing an Eppley Precision Spectral Pyranometer as close to the sensors as possible. Yosemite, Sequoia, Santa Barbara, and Azusa sensors were not checked because of clouds and rain during the visits, or because the test instrument could not be located near the sensor. The test results are summarized in Table 5-10.

#### 5.2.8 Time of Wetness Measurements

The wetness sensors were found to turn on when they became wet either from natural causes or by artificial means. At some sites these units stayed on after the water evaporated. The sensitivity of the sensor to wetness was adjusted but the adjustment is sensitive and needs to be done about every two weeks.

#### 5.2.9 Data Acquisition System

The SumX at Gasquet added an offset to the temperature and dew point channels. The SumX temperature reading was about 5 °C higher than that of the sensor. The dew point reading was about 0.5 °C higher than that of the sensor. After recalibration of the SumX, the temperature reading showed better agreement but the dew point reading was still 0.5 °C high. The other data collected as double-ended inputs (solar, wetness, and ozone calibrator) were also reading 3 to 5 mv higher than their inputs on this data acquisition system, but these offsets are not significant.

All channels of the SumX at Yosemite read ~8 mv higher than their inputs. The modem that had recently been installed had a ground that was not common to the instruments. The resulting ground loop caused the difference in readings. After putting the modem on a common ground, the SumX readings for single-ended inputs were within 1 mv of their inputs, while the readings for double-ended inputs were 2 to 3 mv higher than their inputs.

The data acquisition systems at all other sites were found to perform reliably.

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# Summary of Solar Radiation Tests Performed in April, 1990

				Difference					
Sampling Site	Audit w/m <sup>2</sup>	Sensor w/m <sup>2</sup>	DAS <sup>d</sup> w/m <sup>2</sup>	Sensor w/m <sup>2</sup>	DAS <sup>d</sup> w/m <sup>2</sup>				
Gasquet	864	826	835	- 38	-29				
Fremont	892	818	823	-74	-69				
Sacramento	a								
Yosemite	b								
Sequoia	b								
Bakersfield	923	728	725	-195°	-198°				
Santa Barbara	b								
Long Beach	990	с	893		- 97				
Los Angeles	1057	c	826		-231				
Azusa	b								

<sup>a</sup> Not done because of sensor location. <sup>b</sup> Not done because of rain and clouds.

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 <sup>&</sup>lt;sup>c</sup> Sensor output not recorded.
 <sup>d</sup> Data Acquisition System.
 <sup>e</sup> Cause of the differences is unknown.

## 6.0 TECHNOLOGY TRANSFER

A major goal of the dry deposition component of the CADMP was to transfer the operations of the long-term monitoring network to ARB staff. This was done in phases over a two-year period. Major milestones in this technology transfer are identified in Table 6-1. The major components of technology transfer were: 1) network design; 2) procedures development; 3) technology transfer workshops; 4) phased takeover of network operations; and 5) long-term technical advisement.

#### 6.1 Network Design

As noted in previous sections and explained in detail by Watson et al. (1990), the network was designed with technology transfer in mind. A careful study was undertaken to provide the greatest benefit for the least expenditure of labor. This resulted in the assignment of much initial effort to develop effective data acquisition and processing systems which would allow many manual operations to be performed by computer.

## 6.2 Procedures Development

Procedures were performed by DRI staff, then documented for feedback from field operations and laboratory staff within DRI and at ARB. Several drafts of procedures were prepared and implemented. Incremental improvements were identified and recorded as they became known. Through this process, the operating procedures have evolved into an efficient and integrated system, as documented by Bowen et al. (1990), Chow et al. (1990), and Frazier et al. (1990).

## 6.3 Technology Transfer Workshops

ARB field and laboratory operations staff were already well-versed in the use of most of the instruments and analytical methods used in this study. Major emphasis was placed on the integration of field and laboratory operations and on the processing and validation of data from both program components. These workshops offered an opportunity for feedback to DRI staff on certain practices unique to ARB for which the standard operating procedures required adjustment.

## 6.4 Phased Takeover of Operations

By phasing in ARB's takeover of certain monitoring sites, an orderly transition of responsibility was effected. This phase-in period allowed ARB staff the time needed to become proficient with the individual procedures before being inundated with the responsibility for the entire network. Deficiencies in operating procedures, or in their documentation, were identified and corrected as part of this phased takeover.

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#### Table 6-1

Summary of the CADMP Technology Transfer Activities

Technology Transfer Activities <u>Date</u> 11/87 First draft, CADMP Program Plan. 9/1/88 Site operator training at Sacramento. and 9/2/88 2/28/89 Second revision of field, laboratory, and data processing procedures completed. 3/1/89 One-day training of field operations supervisors and assistant in sampler operation and continuous data processing at Sacramento. 3/2/89 and Two-day training of laboratory personnel in filter 3/3/89 impregnation, filter loading, chain of custody, and laboratory data processing at El Monte. 8/1/89 ARB's El Monte laboratory began analysis of dry deposition samples for Teflon filters. Two-day training of field and laboratory personnel in 12/7/89 and 12/8/89 continuous and laboratory data processing procedures at El Monte. 2/1/90 ARB took over continuous data operations of all sampling sites. 2/2/90 ARB's El Monte laboratory began analysis of dry deposition samples for Teflon, nylon, and citric acid impregnated filters. 2/27/90 One-day training of laboratory sample chain of custody at El Monte. 3/5/90 ARB's El Monte laboratory began analysis of all dry deposition samples. 4/9/90 One-day training of field operations and final progress report meeting at Sacramento. 4/10/90 ARB took over operation of all sampling sites. 4/9/90 to Final site inspection and maintenance by DRI at all sites. 4/21/90 5/21/90 One-day training of laboratory sample processing staff at El Monte. 7/31/90 Revised program plan and draft measurement reports completed.

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## 6.5 Long-Term Technical Advisement

The dry deposition component of the CADMP provides data to ARB's research program on acid deposition. Although it is a routine monitoring program, it is expected that changes will be made in its operation as new knowledge is gained. These changes may be made to increase efficiency of operation, to better meet the needs of those using the data for decision-making, or to improve the measurement process. DRI scientists remain on call to answer any questions regarding the methods and procedures.

#### 7.0 SUMMARY OF DRY DEPOSITION DATA

It is not within the scope of work for this project to interpret the acquired measurements with respect to deposition fluxes, chemical and meteorological causes, or relationships to emissions sources. Nevertheless, the data have been thoroughly examined as part of the evaluation and validation process, and some interesting similarities and differences among sampling sites, sampling periods, and chemical concentrations have been observed. This section describes several of those observations and their implications with respect to the dry deposition measurement process.

## 7.1 Lower Quantifiable Limits

Watson et al. (1990) estimated concentration levels for the dry deposition species when designing the gas/particle sampling system. Flow rates and sample durations were selected using these estimates to obtain a sufficient deposit for chemical analysis. The current data base allows the accuracy of those estimates to be evaluated.

Table 7-1 compares the concentration ranges found over more than a year of monitoring with minimum detectable concentrations and lower quantifiable limits for each species measured during daytime and nighttime. The table has stratified samples by urban (Fremont, Sacramento, Bakersfield, Santa Barbara, Long Beach, Los Angeles, and Azusa) and non-urban (Gasquet, Yosemite, and Sequoia) sampling sites.

Minimum detectable concentrations (MDC) are those for which instrument response equals the standard deviations of the response to a known concentration of zero. The MDC in Table 7-1 are always smaller than the lower quantifiable limit (LQL), which is defined as one standard deviation of the field blank concentrations. Field blanks account for contamination acquired during sample handling and passive deposition. The sensitivity of the selected laboratory methods is not the limiting factor for quantifying any of the species in this program. Any needed improvements must be made in the sampling component, not in the laboratory component.

The LQLs are approximately twice the MDCs for the particulate species, but they are typically 10 times the MDCs for the gaseous species (with the exception of  $NH_3$ , for which the LQL/MDC ratio is approximately 4). This difference between particle and gas arises since the impregnated substrates are passive absorbers of their respective gases, and the only way to minimize this passive absorption is to minimize the time period of passive exposure by reducing time in the field and by storage in cold, pollutant-free atmospheres. Both of these methods are applied to the extent practical in the monitoring program as it is currently designed.

For the urban sites, in excess of 90% of all values measured during the first 1½ years of monitoring were detectable above the LQLs for all species except  $PM_{2.5}$  potassium, calcium, and chloride. These species are soil- or seasalt-related and are usually more abundant in the coarse particle size fraction

7-1

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## Table 7-1

# Analytical Specification for Urban and Non-Urban Samples Collected from California Acid Deposition Monitoring Program (CADMP) Between May 3, 1988 and September 25, 1989

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# I. <u>Urban Sites</u>

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					Daytime Range of		Total	Perc	Nightti	me Ra	ange of	Total	Percent			
Chemical		Analysis	MDC <sup>D</sup>	LQL <sup>C</sup>	Urban C	oncei	nt <u>r</u> ation <sup>d</sup>	No. of	Samp	le Exceed	Urban Con	cent	ration <sup>d</sup>	No. of	Samp le	e Exceed
<u>Species</u>	<u>Size</u>	<u>Method<sup>a</sup></u>	<u>(µg/m<sup>3</sup>)</u>	( <u>µq/m<sup>3</sup>)</u>	·	(µq,	/m <sup>3</sup> )	<u>Samples</u>	MDCb	LQL <sup>C</sup>	(	μg/m	s <sub>)</sub>	<u>Samples</u>	MDC <sup>D</sup>	<u>lql</u> °
Particle Mass	PM2.5	Gravimetry	0.67	1.70	0.50	to	132.54	479	100	99	0.00	to	187.53	474	89	98
Particle Mass	PM10	Gravimetry	0.67	1.70	0.00	to	213.17	479	100	99	0.00	to	196.74	478	100	100
Sodium (Na <sup>+</sup> )	PM2.5	AA	0.004	0.040	0.00	to	1.92	478	96	90	0.00	to	2.25	475	96	89
Sodium (Na <sup>+</sup> )	PM10	AA	0.004	0.052	0.00	to	6.27	487	99	97	0.00	to	6.49	484	99	97
Magnesium (Mg <sup>++</sup>	) PM2.5	AA	0.0027	0.0083	0.00	to	0.35	485	98	92	0.00	to	0.35	477	97	90
Magnesium (Mg <sup>++</sup> )	) PM <sub>10</sub>	AA	0.0027	0.0063	0.002	to	0.85	488	100	99	0.003	to	0.85	484	100	99
Potassium (K+)	PM2.5	AA	0.0066	0.024	0.00	to	0.69	485	92	80	0.00	to	1.13	476	91	76
Potassium (K <sup>+</sup> )	PM10	AA	0.0066	0.034	0.00	to	1.76	478	89	96	0.00	to	1.51	475	99	96
Calcium (Ca <sup>++</sup> )	PM2.5	AA	0.033	0.046	0.00	to	2.00	485	72	59	0.00	to	2.34	477	51	38
Calcium (Ca <sup>++</sup> )	PM10	AA	0.033	0.041	0.001	to	2.39	489	99	99	0.00	to	3.50	484	96	95
Ammonium (NH <sub>4</sub> )	PM2.5	AC	0.066	0.096	0.00	to	18.46	467	95	94	0.00	to	24.64	467	87	96
Ammonium (NH <sub>4</sub> )	PM10	AC	0.066	0.15	0.00	to	26.43	468	99	96	0.00	to	24.09	467	98	96
Chloride (Cl <sup>-</sup> )	PM2.5	IC	0.066	0.13	0.00	to	3.24	419	28	17	0.00	to	2.30	417	37	26
Chloride (Cl <sup>-</sup> )	PM10	IC	0.066	0.13	0.00	to	4.55	407	65	51	0.00	to	9.74	406	77	67
Sulfate $(SO_4^{=})$	PM2.5	IC	0.066	0.36	0.00	to	21.92	467	99	97	0.00	to	21.91	472	99	96
Sulfate (S0 <mark>‡</mark> )	PM10	IC	0.066	0.18	0.00	to	29.43	467	100	100	0.00	to	27.44	469	99	99
Sulfur																
Dioxide (SO <sub>2</sub> )	Gas	IC	0.022	0.29	0.00	to	28.45	441	99	98	0.00	to	41.06	443	98	87
Nitrogen -																
Dioxide (NO <sub>2</sub> )	Gas	IC	0.025	0.39	0.00	to	370.00	477	99	98	0.00	to	254.98	471	98	98
Ammonia (NH <sub>3</sub> )	Gas	AC	0.032	0.14	0.00	to	38.33	497	99	99	0.00	to	30.09	490	99	99
Nitrate (NOz)	PM10	IC	0.066	0.10	0.00	to	37.91	469	99	98	0.00	to	51.23	469	99	99
Nitrate (NOz)	PM2.5	IC	0.066	0.12	0.00	to	27.64	470	95	94	0.00	to	31.28	472	95	94
Nitrate (NO <sub>3</sub> )	Undend	luded														
Nitrate (NO-)	PM2.5 Denude	DI Di	0.034	0.41	0.004	to	54.48	471	100	95	0.00	to	31.64	473	97	66
HILLARE (1103)	PM2.5	IC	0.034	0.34	0.00	to	49.27	464	100	99	0.00	to	51.67	462	100	98
Nitric																
Acid (HNO <sub>3</sub> )	Gas	IC	0.066	0.41	0.00	to	37.28	429	82	78	0.00	to	12.35	437	39	25

# Table 7-1 (continued)

# Analytical Specification for Urban and Non-Urban Samples Collected from California Acid Deposition Monitoring Program (CADMP) Between May 3, 1988 and September 25, 1989

#### II. Non-Urban Sites

Chemical Ana Species Size Me		Analysis Method <sup>a</sup>	Analysis MDC <sup>b</sup> LQL <sup>C</sup> Method <sup>a</sup> (µg/m <sup>3</sup> ) (µg/m <sup>3</sup> )		Daytime Range of <sup>e</sup> Nonurban Concentration <sup>f</sup> (µg/m <sup>3</sup> )		Total No. of Samples	Percent Sample Exceed MDC <sup>b</sup> LOL <sup>C</sup>		Nightti Nonurban (	me Ra Conce μg/m <sup>3</sup>	nge of <sup>e</sup> ntration <sup>f</sup> )	Total No. of Samples	Percen Sample MDC <sup>D</sup>	t Exceed	
<u></u>		<u></u>		<u> </u>							. <u> </u>					
Particle Mass	PM2.5	Gravimetry	0.67	1.70	0.00	to	48.82	179	87	79	0.00	to	177.87	172	84	80
Particle Mass	PM10	Gravimetry	0.67	1.70	0.00	to	90.55	172	97	93	0.00	to	182.30	163	92	87
Sodium (Na <sup>†</sup> )	PM2.5	AA	0.004	0.040	0.00	to	1.50	183	73	60	0.00	to	0.96	178	70	52
Sodium (Na <sup>+</sup> )	<sup>₽М</sup> 10	AA	0.004	0.052	0.00	to	2.93	177	87	77	0.00	to	2.48	170	84	64
Magnesium (Mg <sup>++</sup>	) PM <sub>2.5</sub>	AA	0.0027	0.0083	0.00	to	0.16	183	87	66	0.00	to	0.12	178	83	63
Magnesium (Mg <sup>++</sup>	) PM <sub>10</sub>	AA	0.0027	0.0063	0.00	to	0.47	177	92	85	0.00	to	0.48	170	88	81
Potassium (K+)	PM2.5	AA	0.0066	0.24	0.00	to	0.55	182	80	60	0.00	to	0.91	177	78	60
Potassium (K <sup>+</sup> )	PM10	AA	0.0066	0.034	0.00	to	2.39	173	89	68	0.00	tp	1.81	166	93	64
Calcium (Ca <sup>++</sup> )	PM2.5	AA	0.033	0.046	0.00	to	0.38	183	42	29	0.00	to	0.75	178	38	28
Calcium (Ca <sup>++</sup> )	PM <sub>10</sub>	AA	0.033	0.041	0.00	to	0.76	177	79	75	0.00	to	1.34	170	71	66
Ammonium $(NH_4^+)$	PM2.5	AC	0.066	0.096	0.00	to	2.33	178	78	71	0.00	to	1.96	172	78	74
Ammonium $(NH_4^+)$	PM10	AC	0.066	0.149	0.00	to	7.50	167	92	78	0.00	to	2.63	159	90	78
Chloride (Cl <sup>°</sup> )	PM2.5	IC	0.066	0.128	0.00	to	2.59	158	23	16	0.00	to	1.84	151	25	13
Chloride (Cl <sup>-</sup> )	PM10	IC	0.066	0.131	0.00	to	3.15	148	38	26	0.00	to	1.85	134	36	23
Sulfate $(SO_4^{=})$	PM2.5	IC	0.066	0.36	0.00	to	4.27	178	94	78	0.00	to	6.12	171	92	78
Sulfate (S0₄)	PM10	IC	0.066	0.18	0.00	to	3.60	166	97	92	0.00	to	4.85	155	94	88
Sulfur																
Dioxide (SO <sub>2</sub> )	Gas	IC	0.022	0.29	0.00	to	2.96	158	73	46	0.00	to	3.90	154	71	42
Nitrogen																
Dioxide (NO <sub>2</sub> )	Gas	IC	0.025	0.39	0.00	to	18.11	170	15	14	0.00	to	30.91	162	22	20
Ammonia (NH <sub>3</sub> )	Gas	AC	0.032	0.14	0.00	to	13.96	179	98	89	0.00	to	15.69	172	88	80
Nitrate $(NO_{3})$	PM10	IC	0.066	0.104	0.00	to	6.00	166	85	80	0.00	to	4.91	155	79	75
Nitrate $(NO_{\overline{3}})$	PM2.5	IC	0.066	0.116	0.00	to	4.98	178	64	56	0.00	to	4.47	171	57	52
Nitrate $(NO_{\overline{3}})$	Undend	luded														
	PM2.5	IC	0.034	0.41	0.00	to	7.79	183	89	58	0.00	to	3.38	177	80	44
Nitrate (NU3)	PM <sub>2.5</sub>	IC	0.034	0.34	0.00	to	8.41	180	99	59	0.00	to	10.63	173	97	55
Nitric	2.0															
Acid (HNO <sub>3</sub> )	Gas	IC	0.066	0.41	0.00	to	9.80	171	63	47	0.00	to	2.64	163	44	21

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# Analytical Specification for Urban and Non-Urban Samples Collected from California Acid Deposition Monitoring Program (CADMP) Between May 3, 1988 and September 25, 1989

<sup>a</sup> IC: Ion Chromatography

AC: Automated Colorimetry

AA: Atomic Absorption Spectrophotometry

<sup>b</sup> Minimum Detectable Concentration (MDC) is the concentration at which instrument response equals the standard deviation of the response to a known concentration of zero.

<sup>c</sup> Lower Quantifiable Limit (LQL) equals the standard deviation of dynamic field blanks as determined from the CADMP sampling program.

<sup>d</sup> Urban sites include: Fresno, Sacramento, Collocated Sacramento, Bakersfield, Santa Barbara, Long Beach, Los Angeles, and Azusa.

e Assumes extractions of half filter in 10 ml for particle samples and extractions of entire filter in 10 ml for impregnated filters with an nominal volume of 15.5 m<sup>3</sup>.

<sup>f</sup>Non-urban sites include: Gasquet, Yosemite, and Sequoia.

between  $PM_{10}$  and  $PM_{2.5}$ . In the  $PM_{10}$  size fraction, only chloride was found to be below LQLs for more than 90% of the measurements. Since the major source of chloride is sea salt, the chloride contribution is usually low at inland sites such as Sacramento, Bakersfield, and Azusa.

Among the gases, urban nitric acid was measured in excess of the LQL for nearly 80% of the samples during daytime, but in only 25% of the samples during nighttime. For the nighttime samples, the measured concentrations exceeded the  $0.07 \ \mu g/m^3$  MDC for only 39% of the samples. Nitric acid is a photochemical endproduct with high deposition and reaction rates. This species appears to be present at very low levels after the sun sets. This is also reflected in the undenuded nylon backup filter data from which the nitric acid concentration is calculated, which exceeds the LQL for only 66% of the analyzed samples.

At the non-urban sites, the concentrations are substantially lower than at the urban sites and LQLs are exceeded for 60 to 90% of the samples for most species. Nitrogen dioxide is rarely detectable at these sites, presumably owing to the paucity of local motor vehicle traffic in the vicinity of the sampling sites. Sulfur dioxide,  $PM_{2.5}$  calcium,  $PM_{2.5}$  chloride, and  $PM_{10}$  chloride concentrations are not found above LQLs in more than 50% of the daytime or nighttime samples taken at these non-urban sites.

The implication of the results presented in Table 7-1 is that the sampling system is living up to expectations for most of the species measured. Nighttime nitric acid, some geologically related species in  $PM_{2.5}$ , and chloride in both  $PM_{2.5}$  and  $PM_{10}$  size fractions are found above the current LQLs in less than 50% of the measurements. The LQLs are still quite low, however, generally much less than 1  $\mu$ g/m<sup>3</sup>, and these species are not detected because their sources are distant from the sampling site, or because the relevant atmospheric chemistry does not produce them during the specified time period. Unless a case is made that lower LQLs are needed to assess adverse effects or to better understand the causes of the higher concentrations, there is no need to change sampling methods.

# 7.2 Collocated Sampling

The Sacramento monitoring site is equipped with an additional gas/particle sampling system which can be used to evaluate the reproducibility of the entire sampling and analysis process. This collocated sampling system is operated in a manner identical to that of the primary system. The two systems are located within 4 m of each other on the roof of the ARB monitoring laboratory at 13th and T Streets. Scatterplots, with linear regression statistics, are presented in Figures 7-1 through 7-4 to show the reproducibility which can be expected for Level II validated data as a function of different chemical species. The four scatterplots in each figure are grouped to facilitate the evaluation of differences between the collocated and primary values.

Reproducibility is considered to be acceptable when the correlation coefficient (r) exceeds 0.9, the slope is within two or three standard errors of unity, and the intercept is within two or three standard errors of zero. When a few points were identifiable as obvious outliers, the regression statistics



Figure 7-1. Comparison of Collocated Measurements of PM<sub>2.5</sub> and PM<sub>10</sub> Mass and Sodium Concentrations at Sacramento. Linear regression coefficients in parentheses were calculated with outliers removed.



Figure 7-2. Comparison of Collocated Measurements of PM<sub>2.5</sub> and PM<sub>10</sub> Calcium and Magnesium Concentrations at Sacramento.



Figure 7-3. Comparison of Collocated Measurements of PM<sub>2.5</sub> and PM<sub>10</sub> Teflon Nitrate, PM<sub>2.5</sub> Particulate Nitrate, and Nitric Acid Concentrations at Sacramento. Linear regression coefficients in parentheses were calculated with outliers removed.



Figure 7-4. Comparison of Collocated Measurements of PM<sub>2.5</sub> Sulfate, Sulfur Dioxide, Nitrogen Dioxide, and Ammonia Concentrations at Sacramento.

were re-calculated without these points, and the re-calculated values are displayed in parentheses. Most of the comparisons in Figures 7-1 through 7-4 meet these criteria for acceptable reproducibility. The exceptions reveal limitations in the measurement process.

All of the  $PM_{10}$  measurements are more reproducible than the  $PM_{2.5}$  measurements, as evidenced by a greater degree of scatter and lower correlation coefficients for  $PM_{2.5}$ . These samples are taken according to identical sampling and analysis procedures; these cannot be the cause of the discrepancy. Potential causes may be one or more of the following: 1) less precise flow rates in the non-denuded  $PM_{2.5}$  air stream of one or both sampling systems; 2) lower concentrations of the measured species; 3) different large particle penetration through the  $PM_{2.5}$  inlet; and/or 4) instability of the sample deposit.

The flow rate tests presented in Section 5 showed no biases on the nondenuded  $PM_{2.5}$  sampling ports for either the primary or the collocated sample. If such a bias did exist, it would affect all concentrations on the corresponding sampler in the same way, and the scatter in Figures 7-1 through 7-4 would exhibit similar patterns, which they do not. While less precise flow rates may be a cause, the evidence does not support this.

The  $PM_{2.5}$  calcium values have already been identified as being close to or less than LQLs, and this is evident in the comparison of data in Figure 7-2. The  $PM_{10}$  calcium values are not present at sufficient levels in the  $PM_{2.5}$  fraction to be reliably reproduced. This may also be a cause of variability at the lower concentrations of  $PM_{2.5}$  magnesium and sodium.

The size-selective inlet on the  $PM_{2.5}$  sampler is Teflon-coated and is not greased. Though it should be cleaned monthly, there were periods when this maintenance was not performed. This could allow some of the coarse particles to become re-entrained into the air stream and sampled on the filter. This may have caused some of the decrease in precision with respect to  $PM_{10}$ , which has an inlet with a much higher loading capacity than the Teflon-coated cyclone.

Stability of the deposit is probably a major cause of discrepancies between the collocated and primary  $PM_{2.5}$  nitrate concentrations, as shown in Figure 7-3. The first three panels in this figure show: 1)  $PM_{10}$  Teflon nitrate, which is nitrate on a Teflon filter through an aluminum  $PM_{10}$  inlet; 2)  $PM_{2.5}$  Teflon nitrate, which is nitrate on a Teflon filter through a Teflon-coated  $PM_{2.5}$  inlet; and 3)  $PM_{2.5}$  particulate nitrate, which is nitrate measured on a nylon filter after having been drawn through a Teflon-coated  $PM_{2.5}$  inlet and an aluminum nitric acid denuder.

The  $PM_{2.5}$  Teflon nitrate comparison shows much more scatter than any of the other comparisons, yet the  $PM_{2.5}$  particulate nitrate and  $PM_{10}$  Teflon nitrate values show good comparisons between primary and collocated measurements. This comparison confirms the suspicion that particulate nitrate dissociates from the Teflon filters in the primary and collocated samplers in different amounts, and that the deposit on the  $PM_{2.5}$  Teflon pre-filter is unstable with respect to nitrate, and possibly with respect to other species (such as ammonium and sodium) which react with nitrate. On the other hand, the  $PM_{10}$  Teflon nitrate appears to be very stable, and is approximately equivalent in concentration to the  $PM_{2.5}$ 

particulate nitrate. The alkaline soil particles present in the coarse particle fraction may serve the same purpose as the  $PM_{2.5}$  nylon filter by reacting with volatilized nitric acid, and the aluminum  $PM_{10}$  inlet may serve the same purpose as the  $PM_{2.5}$  denuder in removing nitric acid.

The nitric acid comparison shown in the last panel of Figure 7-3 shows four major outliers and a large number of samples near zero. As explained in Section 3, the nitric acid concentration is calculated from three separate measurements. If any one of these measurements is incorrect, or if any one of the samples has been mislabeled as day or night, then the nitric acid value will be affected. The nighttime nitric acid values congregate about the origin and are fairly randomly distributed, confirming the observation that many nighttime values are close to LQLs and are therefore inherently imprecise. Aside from the four outliers, the daytime values demonstrate a reasonably good reproducibility between the primary and collocated samplers.

Figure 7-4 presents the sulfate, sulfur dioxide, nitrogen dioxide, and ammonium comparisons. The sulfate scatter is similar to that observed for other measurements made on the  $PM_{2.5}$  Teflon filter. The gaseous data are repeatable, based on these collocated measurements.

These collocated analyses include samples taken between April 16 and September 25, 1989. These samplers are still being operated, and further analysis of new data along the lines presented here should be done at six-month intervals to determine the general applicability of these results. The collocated sampling plots presented in Figures 7-1 through 7-4 are similar to those observed for routine collocated sampling of  $PM_{10}$  using high volume samplers, even though the sampling system is more complex and the filter media are more difficult to handle. These data indicate that, for the most part, CADMP gas/particle data are precise, equivalent, and repeatable.

## 7.3 Statistical Summaries of CADMP Gas/Particle Data

The CADMP gas/particle data base contains over 30,000 individual chemical measurements. Table 7-2 presents annual arithmetic averages, standard deviations, maxima, and minima at each site for the measured species, particle size range, and diurnal sampling periods. The beginning and ending dates for samples included in each average are given since several sites were not on line by October, 1988. The chemical concentrations in these tables can be examined for similarities and differences among particle sizes, daytime and nighttime periods, and sampling sites.

#### 7.3.1 Particle Size

As expected,  $PM_{10}$  averages exceed the  $PM_{2.5}$  averages for those species with 50% or more samples which exceed LQLs. The  $PM_{10}$  maxima do not always exceed the  $PM_{2.5}$  maxima because there are different numbers of samples included in each data

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### Table 7-2

# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

# Site Name: Gasquet (Measurement Period: March 17, 1989 through September 25, 1989)

							Conc	entrations	in μq/m <sup>3</sup>						
				Davtime ((	)601-180	0 PST)	)				Niahttii	me (1801	-0600	PST)	
<u>Species</u>	<u>Size</u>	Average	e ±	Std. Dev.	Min	Max	Number (	of Samples	Average	±	Std. Dev.	Min	<u>Max</u>	Number of	Samples
Particle Mass	PM2.5	3.84	±	3.06	0.00	15.60	)	29	4.55	±	3.73	0.00	16.82	2 30	
Particle Mass	PM <sub>10</sub>	7.78	±	3.62	2.90	16.88	3 <sup>-</sup> 3	29	7.43	±	4.93	0.00	22.29	9 27	
Sodium (Na <sup>+</sup> )	PM2.5	0.18	±	0.21	0.00	1.03	3 ;	29	0.14	±	0.20	0.00	0.96	5 30	
Sodium (Na <sup>+</sup> )	PM <sub>10</sub>	0.64	±	0.56	0.056	2.93	3 1	29	0.49	±	0.42	0.0043	1.47	7 28	
Magnesium (Mg <sup>++</sup> )	PM2.5	0.025	±	0.028	0.0041	0.13	3 :	29	0.022	±	0.030	0.00	0.12	2 30	
Magnesium (Mg <sup>++</sup> )	PM10	0.090	±	0.086	0.013	0.47	' :	29	0.069	±	0.058	0.00	0.21	l 28	
Potassium (K <sup>+</sup> )	PM2 5	0.031	±	0.039	0.00	0.16	i 1	29	0.061	±	0.133	0.00	0.66	5 30	
Potassium (K <sup>+</sup> )	PM10	0.071	±	0.072	0.00	0.38	3 1	29	0.089	±	0.134	0.0072	0.70	) 28	
Calcium (Ca <sup>++</sup> )	PM2 5	0.027	±	0.027	0.00	0.12	2 :	29	0.027	±	0.026	0.00	0.14	4 30	
Calcium (Ca <sup>++</sup> )	PM10	0.089	±	0.134	0.00	0.76	5 1	29	0.057	±	0.045	0.00	0.16	5 28	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2 5	0.15	±	0.12	0.00	0.44	<b>ب</b> ا	28	0.16	±	0.18	0.00	0.79	9 29	
Ammonium (NH <sub>4</sub> )	PM10	0.21	±	0.15	0.00	0.55	5 1	26	0.22	±	0.19	0.00	0.83	3 27	
Chloride (Cl <sup>2</sup> )	PM2 5	0.14	±	0.24	0.00	0.90	) :	28	0.078	±	0.165	0.00	0.8	29	
Chloride (Cl <sup>-</sup> )	PM10	0.53	±	0.46	0.00	1.75	5 :	27	0.49	±	0.51	0.0006	1.78	3 25	
Sulfate $(SO_{4}^{-})$	PMos	0.84	±	0.45	0.071	1.84	i :	28	0.80	±	0.58	0.00	2.62	2 29	
Sulfate $(SO_{\lambda}^{\pm})$	PM10	0.88	±	0.46	0.14	2.08	3 3	27	0.83	±	0.72	0.012	2.97	7 25	
Sulfur	10														
Dioxide (SO <sub>2</sub> )	Gas	0.057	±	0.053	0.00	0.16	5 ;	28	0.10	±	0.20	0.00	0.99	9 27	
Nitrogen															
Dioxide (NO <sub>2</sub> )	Gas	2.34	±	3.60	0.00	18.11	. :	27	4.29	±	5.92	0.00	30.93	27	
Ammonia (NH <sub>z</sub> )	Gas	0.83	±	1.45	0.0018	5.76	; ;	30	0.20	±	0.30	0.00	0.99	9 29	
Nitrate (NO <sub>7</sub> )	PMan	0.32	±	0.20	0.0017	0.82	2	27	0.23	±	0.18	0.00	0.60	) 25	
Nitrate (NO <sub>7</sub> )	PMa s	0.12	±	0.15	0.00	0.60	)	27	0.11	±	0.14	0.00	0.44	4 29	
Nitrate (NO <sub>7</sub> )	Undenuded														
	PMo c	0.12	+	0.11	0.00	0.36	; ;	28	0.055	ŧ	0.087	0.00	0.30	5 31	
Nitrate $(NO_{\overline{2}})$	Denuded		_							-					
	PMa r	0.32	+	0 14	0 14	<b>7</b> 3 0	۰ ۲	31	0 27	+	0.16	0.042	0.7	5 31	
Nitric		0102	-	0141	V· 4 1	0.00		~ •		-	0.10				
Acid (HNO <sub>3</sub> )	Gas	0.031	±	0.052	0.00	0.16	5 3	28	0.017	±	0.044	0.00	0.13	7 29	

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# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### <u>Site Name:</u> <u>Yosemite (Measurement Period: October 6, 1988 through September 25, 1989)</u>

							<u>Concentrations</u>	in µg/m <sup>3</sup>						_
				Daytime ((	)601-18	00 PST)				Nighttime	(1801-06	500 PST	)	
<u>Species</u>	Size	Averag	e ±	Std. Dev.	<u>Min</u>	<u>Max Num</u>	ber of Samples	Average	±	Std. Dev.	<u>Min</u>	<u>Max</u>	Number of Samp	les
Particle Mass	PM2.5	6.08	±	7.19	0.00	40.07	51	6.97	±	13.79	0.00	90.29	51	
Particle Mass	PM <sub>10</sub>	10.32	±	8.54	0.00	35.77	45	10.46	±	15.60	0.00	99.31	45	
Sodium (Na <sup>+</sup> )	PM2.5	0.059	±	0.079	0.00	0.24	52	0.059	±	0.086	0.00	0.42	52	
Sodium (Na <sup>+</sup> )	PM10	0.12	±	0.12	0.00	0.51	46	0.12	±	0.19	0.00	0.95	i 46	
Magnesium (Mg <sup>++</sup> )	PM2_5	0.012	±	0.015	0.00	0.098	52	0.011	±	0.011	0.00	0.05	i9 52	
Magnesium (Mg <sup>++</sup> )	PM <sub>10</sub>	0.025	±	0.022	0.00	0.084	46	0.024	±	0.023	0.00	0.12	46	
Potassium (K <sup>+</sup> )	PM2.5	0.049	±	0.052	0.00	0.18	51	0.053	±	0.063	0.00	0.28	51	
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.057	±	0.063	0.00	0.24	43	0.088	±	0.224	0.00	1.44	43	
Calcium (Ca <sup>++</sup> )	PM2_5	0.042	±	0.057	0.00	0.38	52	0.041	±	0.046	0.00	0.25	52	
Calcium (Ca <sup>++</sup> )	PM10	0.089	±	0.084	0.00	0.37	46	0.078	±	0.067	0.00	0.22	46	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2 5	0.21	±	0.18	0.00	0.66	50	0.28	±	0.22	0.00	0.76	51	
Ammonium (NH <sup>+</sup> )	PM10	0.48	±	1.12	0.00	7.50	43	0.37	±	0.30	0.037	1.59	44	
Chloride (Cl <sup>-</sup> )	PM2.5	0.16	±	0.41	0.00	1.77	51	0.07	±	0.20	0.00	1.34	50	
Chloride (Cl <sup>-</sup> )	PM10	0.13	±	0.38	0.00	1.53	43	0.057	±	0.131	0.00	0.79	41	
Sulfate (SO <sub>4</sub> )	PM2.5	0.69	±	0.59	0.00	2.12	50	0.87	±	0.96	0.00	6.12	51	
Sulfate (SO <sub>4</sub> <sup>±</sup> )	PM10	0.72	±	0.57	0.00	2.41	41	0.82	±	0.62	0.025	2.35	42	
Dioxide (SO <sub>2</sub> )	Gas	0.42	±	0.59	0.00	2.76	41	0.32	±	0.34	0.00	1.08	41	
Nitrogen														
Dioxide (NO <sub>2</sub> )	Gas	0.00	±	0.00	0.00	0.00	42	0.017		0.110	0.00	0.71	41	
Ammonia (NH <sub>3</sub> )	Gas	1.54	±	2.26	0.09	13.96	46	0.67	±	0.80	0.037	4.70	46	
Nitrate $(NO_{\overline{3}})$	PM10	0.25	±	0.24	0.00	1.11	41	0.28	±	0.36	0.00	1.90	42	
Nitrate $(NO_{\overline{3}})$	PM2.5	0.17	±	0.15	0.00	0.67	50	0.20	±	0.30	0.00	1.51	51	
Nitrate $(NO_{\overline{3}})$	Undenuded													
Nitrate (NOz)	<sup>PM</sup> 2.5 Denuded	0.76	±	0.71	0.00	2.56	51	0.36	±	0.31	0.00	1.23	51	
- بر	PM2.5	0.58	±	1.18	0.00	8.41	50	0.44	±	0.37	0.00	1.62	50	
Nitric														
Acid (HNO <sub>3</sub> )	Gas	0.58	±	0.66	0.00	2.42	49	0.18	±	0.28	0.00	1.16	50	

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# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

# Site Name: Sequoia (Measurement Period: October 6, 1988 through September 25, 1989)

							Concentrations	in µg/m <sup>3</sup>					<u>.</u>	
				Daytime ((	601-180	00 PST)				Nighttir	ne (180	1-0600	PST)	
<u>Species</u>	<u>Size</u>	<u>Averaq</u>	e ±	<u> Std. Dev.</u>	<u>Min</u>	<u>Max Nu</u>	mber of Samples	Average	±	Std. Dev.	Min	Max	Number of	Samples
Particle Mass	PM2.5	9.21	±	9.17	0.00	47.29	50	14.59	±	29.37	0.00	157.18	49	
Particle Mass	PM10	16.00	±	14.45	0.00	72.25	52	19.56	±	33.28	0.00	176.60	) 51	
Sodium (Na <sup>+</sup> )	PM2.5	0.072	±	0.12	0.00	0.65	51	0.052	±	0.072	0.00	0.26	5 51	
Sodium (Na <sup>+</sup> )	PM10	0.16	±	0.18	0.00	0.86	52	0.10	±	0.13	0.00	0.52	2 52	
Magnesium (Mg <sup>++</sup> )	PM2.5	0.012	±	0.012	0.00	0.048	51	0.01	±	0.01	0.00	0.03	3 51	
Magnesium (Mg <sup>++</sup> )	PM10	0.032	±	0.028	0.00	0.098	52	0.025	±	0.025	0.00	0.12	2 52	
Potassium (K <sup>+</sup> )	PM2.5	0.077	±	0.079	0.00	0.33	51	0.12	±	0.17	0.00	0.91	. 51	
Potassium (K <sup>+</sup> )	PM10	0.15	±	0.34	0.00	2.39	51	0.15	±	0.22	0.00	0.99	51	
Calcium (Ca <sup>++</sup> )	PM2.5	0.048	±	0.049	0.00	0.21	51	0.057	±	0.11	0.00	0.75	5 51	
Calcium (Ca <sup>++</sup> )	PM <sub>10</sub>	0.14	±	0.14	0.00	0.72	52	0.12	±	0.20	0.00	1.34	52	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM <sub>25</sub>	0.52	±	0.55	0.00	2.33	50	0.40	±	0.36	0.00	1.41	. 47	
Ammonium (NH <sub>4</sub> )	PM10	0.60	±	0.59	0.00	2.80	49	0.43	±	0.34	0.00	1.32	46	
Chloride (Cl <sup>T</sup> )	PM2.5	0.14	±	0.45	0.00	2.59	48	0.097	±	0.28	0.00	1.84	45	
Chloride (Cl <sup>°</sup> )	PM10	0.054	±	0.077	0.00	0.46	50	0.074	±	0.190	0.00	1.22	. 47	
Sulfate (S0⊈)	PM2.5	1.15	±	1.01	0.00	4.27	50	1.03	±	0.79	0.00	3.24	46	
Sulfate (SO <sub>4</sub> <sup>I</sup> ) Sulfur	PM10	1.24	±	0.90	0.069	3.50	49	1.01	±	0.77	0.00	2.77	46	
Dioxide (SO <sub>2</sub> ) Nitrogen	Gas	0.74	±	0.82	0.00	2.58	49	0.47	±	0.59	0.00	2.55	5 49	
Dioxide (NO <sub>2</sub> )	Gas	0.007	±	0.051	0.00	0.36	51	0.21	±	0.70	0.00	3.87	50	
Ammonia (NH <sub>z</sub> )	Gas	1.66	±	1.86	0.00	8.31	54	1.18	±	2.46	0.00	15.69	53	
Nitrate (NOz)	PM <sub>10</sub>	0.54	±	0.92	0.00	6.00	49	0.44	±.	0.51	0.00	2.12	46	
Nitrate $(NO_3)$	PM2.5	0.47	±	0.92	0.00	4.98	50	0.39	±	0.74	0.00	4.47	46	
Nitrate $(NO_{\overline{x}})$	PM2.5 Denuded	0.93	±	0.86	0.00	3.28	51	0.36	±	0.35	0.00	1.27	51	
· J·	PM2.5	1.24	±	1.64	0.088	8.22	50	0.87	±	1.56	0.00	10.63	49	
Acid (HNO <sub>3</sub> )	Gas	0.47	±	0.61	0.00	2.04	47	0.14	±	0.27	0.00	1.35	42	

# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### Site Name: Santa Barbara (Measurement Period: April 22, 1989 through September 25, 1989)

							Concentrations	<u>in μg/m<sup>3</sup></u>					
				Davtime ((	0601-180	O PST)	ł			Nightti	ne (1801	-0600	PST)
<u>Species</u>	Size	Averag	e ±	Std. Dev.	Min	Max	Number of Samples	Average	ŧ	Std. Dev.	Min	Max	Number of Samples
Particle Mass	PM2.5	9.88	±	4.36	3.35	23.59	25	7.88	±	5.01	0.00	18.1	6 22
Particle Mass	PM10	25.17	±	10.75	2.33	45.36	5 25	20.28	±	7.68	6.04	35.5	1 27
Sodium (Na <sup>+</sup> )	PM2.5	0.48	±	0.39	0.022	1.40	) 27	0.30	±	0.27	0.00	0.8	1 22
Sodium (Na <sup>+</sup> )	PM10	2.23	±	1.76	0.21	6.00	26	2.14	±	1.42	0.42	5.5	9 27
Magnesium (Mg <sup>++</sup> )	PM2.5	0.060	±	0.047	0.0074	0.17	27	0.038	±	0.031	0.00	0.0	96 22
Magnesium (Mg <sup>++</sup> )	PM10	0.27	±	0.19	0.025	0.62	26	0.26	ŧ	0.16	0.069	0.5	6 27
Potassium (K <sup>+</sup> )	PM2.5	0.047	±	0.026	0.011	0.10	) 27	0.035	±	0.026	0.00	0.0	91 22
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.13	±	0.07	0.0038	0.28	26	0.13	±	0.078	0.029	0.3	2 27
Calcium (Ca <sup>++</sup> )	PM2.5	0.045	±	0.032	0.0079	0.13	27	0.031	±	0.024	0.00	0.1	0 22
Calcium (Ca <sup>++</sup> )	PM10	0.28	±	0.13	0.083	0.48	26	0.18	±	0.091	0.032	0.3	3 27
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2.5	0.97	±	0.64	0.21	2.96	26	0.94	±	0.74	0.00	2.3	9 21
Ammonium (NH <sub>4</sub> )	PM10	0.90	±	0.57	0.091	2.25	26	0.92	±	0.70	0.15	2.9	7 27
Chloride (Cl <sup>°</sup> )	PM2.5	0.18	±	0.63	0.00	3.24	26	0.15	±	0.48	0.00	2.3	0 22
Chloride (Cl <sup>-</sup> )	PM10	1.09	±	1.21	0.00	3.72	25 <sup>·</sup>	1.53	±	1.52	0.019	4.4	2 27
Sulfate (SO <sub>4</sub> <sup>=</sup> )	PM2.5	2.95	±	1.62	0.60	7.85	5 26	2.33	±	1.68	0.00	6.1	1 22
Sulfate (SO₄ <sup>±</sup> )	PM10	3.89	±	1.88	0.32	9.62	25	3.16	±	1.73	0.26	6.5	1 27
Sulfur													
Dioxide (SO <sub>2</sub> )	Gas	0.74	±	0.50	0.042	1.92	27	0.21	±	0.20	0.00	0.8	6 27
Nitrogen													
Dioxide (NO <sub>2</sub> )	Gas	12.46	±	9.66	0.00	39.70	24	14.82	±	13.31	0.00	61.4	2 24
Ammonia (NH <sub>3</sub> )	Gas	2.59	±	1.64	0.00	5.89	27	1.34	±	0.97	0.19	4.7	4 27
Nitrate $(NO_{3})$	PM10	2.78	±	2.27	0.16	8.48	25	2.63	±	1.71	0.49	6.4	9 27
Nitrate $(NO_{3})$	PM2.5	0.52	±	0.61	0.00	1.87	26	0.56	±	0.72	0.00	3.1	7 22
Nitrate $(NO_{3})$	Undenude	d											
-	PM2.5	2.35	±	1.35	0.36	6.58	27	0.56	±	0.62	0.00	2.8	5 27
Nitrate (NO3)	Denuded												
	PM2.5	1.60	±	0.78	0.41	3.46	27	1.51	±	1.40	0.33	7.3	8 27
Nitric													
Acid (HNO <sub>3</sub> )	Gas	1.34	±	0.70	0.00	3.18	26	0.25	±	0.74	0.00	2.8	6 22

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# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

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#### Site Name: Fremont (Measurement Period: October 6, 1988 through September 25, 1989)

							Concentrations	in μg/m <sup>3</sup>					
				_Daytime (C	601-180	0 PST	)			Nighttime	(1801-06	00 PS	T).
<u>Species</u>	Size	Averag	e ±	Std. Dev.	<u>Min</u>	Max	Number of Samples	Average	±	<u>Std. Dev.</u>	Min	Max	Number of Samples
Particle Mass	PM2.5	16.31	±	14.54	0.55	68.62	2 53	14.20	±	14.04	0.49	58.8	9 55
Particle Mass	PM10	29.48	±	17.98	4.55	82.14	4 55	26.94	±	18.39	3.28	89.78	8 55
Sodium (Na <sup>+</sup> )	PM2.5	0.30	±	0.27	0.00	1.14	4 53	0.29	±	0.30	0.00	1.3	7 55
Sodium (Na <sup>+</sup> )	PM10	1.28	±	1.01	0.00	3.91	L 55	1.48	±	1.40	0.00	5.0	56 55
Magnesium (Mg <sup>++</sup> )	PM2.5	0.038	±	0.032	0.00	0.13	3 53	0.036	±	0.037	0.00	0.1	6 55
Magnesium (Mg <sup>++</sup> )	PM <sub>10</sub>	0.18	±	0.13	0.0033	0.49	9 55	0.20	±	0.18	0.0051	0.78	8 55
Potassium (K <sup>+</sup> )	PM2.5	0.067	±	0.069	0.00	0.27	7 53	0.083	±	0.089	0.00	0.3	5 55
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.14	±	0.089	0.00	0.38	3 54	0.17	±	0.13	0.00	0.6	4 54
Calcium (Ca <sup>++</sup> )	PM2.5	0.050	±	0.034	0.00	0.14	53	0.034	±	0.030	0.00	0.1	7 55
Calcium (Ca <sup>++</sup> )	PM10	0.31	±	0.17	0.0011	0.66	5 55	0.20	±	0.13	0.019	0.5	2 55
Ammonium (NH <sub>4</sub> )	PM2.5	0.72	±	1.10	0.014	4.38	3 53	0.88	±	1.15	0.00	5.4	1 55
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM <sub>10</sub>	1.19	±	1.60	0.074	6.58	3 53	1.11	±	1.44	0.084	7.30	8 53
Chloride (Cl <sup>-</sup> )	PM2.5	0.16	±	0.17	0.00	0.67	52	0.26	±	0.32	0.00	1.4	5 54
Chloride (Cl <sup>^</sup> )	PM <sub>10</sub>	0.96	±	1.18	0.00	4.39	53	1.98	±	2.38	0.00	9.74	4 54
Sulfate $(SO_4^{=})$	PM2.5	1.58	±	1.21	0.00	5.02	2 53	1.43	±	0.97	0.20	4.7	4 55
Sulfate $(SO_4^{\pm})$	PM <sub>10</sub>	2.10	±	1.40	0.40	6.28	3 53	1.93	±	1.21	0.00	6.4	2 53
Sulfur													
Dioxide (SO <sub>2</sub> )	Gas	1.73	±	1.30	0.24	5.58	52	0.57	±	0.56	0.11	2.58	8 51
Nitrogen													
Dioxide (NO <sub>2</sub> )	Gas	33.33	±	23.00	0.16	103.32	2 56	33.24	±	22.98	0.00	99.43	3 57
Ammonia (NH3)	Gas	5.14	±	3.01	0.00	12.44	57	2.98	±	2.68	0.77	17.93	2 57
Nitrate $(NO_3)$	PM10	3.82	±	4.48	0.00	21.52	2 53	3.30	±	3.99	0.00	22.03	3 53
Nitrate $(NO_3)$	PM2.5	2.52	±	3.64	0.00	16.48	3 53	2.07	±	3.14	0.00	16.89	9 55
Nitrate $(NO_{3})$	Undenuded	1											
Nitrate (NO <sup>2</sup> )	PM2.5 Denuded	2.14	±	2.39	0.15	12.86	5 55	0.40	t	0.65	0.00	4.8	6 57
· • • •	PM2 5	3.89	±	4.18	0.00	21.65	5 53	2.77	±	3.33	0.33	16.0	2 56
Nitric	<b>L</b> .J												
Acid (HNO <sub>3</sub> )	Gas	1.00	±	2.36	0.00	15.55	5 50	0.15	±	0.63	0.00	4.3	2 53

# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### Site Name: Sacramento (Measurement Period: October 6, 1988 through September 25, 1989)

<u>Concentrations in  $\mu g/m^3$ </u>

				Daytime ((	601-180	0 PST)				Nighttime (	1801-00	500 PS1	r)
<u>Species</u>	Size	<u>Averag</u>	e ±	Std. Dev.	<u>Min</u>	<u>Max</u>	Number of Samples	Average	_ <u>±</u>	<u>Std. Dev.</u>	<u>Min</u>	<u>Max</u>	Number of Samples
Particle Mass	PM2.5	14.96	±	14.02	1.80	85.62	2 52	16.05	±	19.35	0.70	87.57	7 56
Particle Mass	PM10	28.04	±	18.62	6.42	114.86	5 52	29.46	±	27.04	2.06	119.23	3 52
Sodium (Na <sup>+</sup> )	PM2.5	0.21	±	0.23	0.00	0.84	50	0.21	±	0.25	0.00	1.06	5 54
Sodium (Na <sup>+</sup> )	PM10	0.63	±	0.79	0.00	3.63	52	0.81	±	0.91	0.00	3.39	50
Magnesium (Mg <sup>++</sup> )	PM2.5	0.028	±	0.028	0.00	0.09	9 55	0.028	±	0.028	0.00	0.13	3 55
Magnesium (Mg <sup>++</sup> )	PM10	0.10	±	0.09	0.0051	0.37	52	0.12	±	0.11	0.006	0.48	3 50
Potassium (K <sup>+</sup> )	PM2.5	0.10	±	0.12	0.00	0.69	55	0.11	±	0.15	0.00	0.80	) 55
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.16	±	0.13	0.019	0.57	50	0.19	±	0.15	0.014	0.70	) 48
Calcium (Ca <sup>++</sup> )	PM2.5	0.054	±	0.052	0.00	0.28	55	0.033	±	0.033	0.00	0.17	54
Calcium (Ca <sup>++</sup> )	PM10	0.20	±	0.12	0.0012	0.53	52	0.16	±	0.10	0.00	0.48	3 50
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2.5	1.12	±	1.71	0.066	10.13	52	1.17	±	1.58	0.069	6.60	) 54
Ammonium (NH₄)	PM10	1.33	±	2.18	0.00	12.28	46	1.44	±	2.39	0.00	11.88	3 44
Chloride (Cl <sup>®</sup> )	PM2.5	0.11	±	0.28	0.00	1.48	51	0.14	±	0.27	0.00	1.27	51
Chloride (Cl <sup>-</sup> )	PM10	0.28	±	0.47	0.00	2.03	47	0.75	±	1.09	0.00	5.67	46
Sulfate (SO <sub>4</sub> <sup>=</sup> )	PM2.5	1.39	±	0.90	0.00	4.09	52	1.41	±	1.00	0.00	4.53	3 54
Sulfate (S0₄) Sulfur	<sup>PM</sup> 10	1.64	±	0.94	0.44	4.38	45	1.85	ŧ	1.21	0.00	5.14	43
Dioxide (SO <sub>2</sub> )	Gas	2.30	±	2.05	0.24	12.39	48	1.70	±	1.83	0.12	7.28	5 49
Nitrogen													
Dioxide (NO <sub>2</sub> )	Gas	29.12	±	16.00	0.59	62.11	51	39.26	t	26.88	1.41	127.25	5 49
Ammonia (NH <sub>3</sub> )	Gas	12.01	±	5.86	4.63	32.12	54	9.61	±	5.42	1.41	30.09	9 54
Nitrate (NO <sub>3</sub> )	<sup>PM</sup> 10	3.70	±	6.34	0.00	37.91	46	4.29	±	6.56	0.29	33.68	3 43
Nitrate (NOz)	PM2.5	2.32	±	4.73	0.00	27.64	53	2.62	±	4.46	0.014	18.86	5 54
Nitrate $(NO_{\overline{3}})$	Undenudeo	ł											
Nitrate (NO <sub>z</sub> )	PM2.5 Denuded	2.53	±	2.24	0.024	9.08	54	0.48	±	0.76	0.031	5.75	5 54
· · · ·	PM2.5	3.71	±.	5.06	0.27	29.02	52	3.24	±	5.21	0.11	30.51	51
Nitric												_	
Acid	Gas	1.08	±	1.17	0.00	4.21	49	0.45	±	1.28	0.00	7.2	51

# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

## Site Name: Collocated Sacramento (Measurement Period: April 16, 1989 through September 25, 1989)

							Concentrations	in µg/m <sup>3</sup>						
				Daytime ((	)601-180	0 PST	)			Nighttime	(1801-06)	00 PST	)	
<u>Species</u>	<u>Size</u>	<u>Average</u>	±	<u>Std. Dev.</u>	<u>Min</u>	Max	Number of Samples	Average	ţ	Std. Dev.	<u>Min</u>	<u>Max</u>	<u>Number of</u>	Samples
Particle Mass	PM2.5	9.94	±	4.66	3.88	18.4	25	8.32	±	3.92	2.01	17.22	23	
Particle Mass	PM <sub>10</sub>	24.26	±	12.80	8.10	57.89	27	17.88	±	7.53	2.44	35.36	25	
Sodium (Na <sup>+</sup> )	PM2.5	0.34	±	0.29	0.0081	0.94	22	0.40	±	0.34	0.031	1.13	21	
Sodium (Na <sup>+</sup> )	PM10	1.00	±	0.82	0.00	2.8	5 25	1.42	±	1.00	0.22	3.54	24	
Magnesium (Mg <sup>++</sup> )	PM2.5	0.045	±	0.032	0.011	0.11	25	0.051	±	0.039	0.0087	0.14	22	
Magnesium (Mg <sup>++</sup> )	PM10	0.15	±	0.099	0.035	0.39	25	0.19	±	0.12	0.049	0.43	24	
Potassium (K <sup>+</sup> )	PM2.5	0.083	±	0.072	0.00	0.26	5 25	0.075	±	0.092	0.00	0.41	22	
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.13	±	0.098	0.00	0.34	25	0.13	±	0.11	0.00	0.47	24	
Calcium (Ca <sup>++</sup> )	PM2.5	0.077	±	0.052	0.021	0.29	25	0.050	±	0.048	0.0039	0.24	22	
Calcium (Ca <sup>++</sup> )	PM10	0.24	±	0.13	0.074	0.51	26	0.17	±	0.07	0.059	0.28	24	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2.5	0.59	±	0.44	0.00	1.59	23	0.63	±	0.32	0.17	1.15	20	
Ammonium (NH <sub>4</sub> )	PM10	0.49	±	0.31	0.033	1.40	26	0.51	±	0.33	0.00	1.27	26	
Chloride (Cl <sup>2</sup> )	PM2 5	0.064	±	0.084	0.00	0.30	) 23	0.15	±	0.23	0.00	1.02	22	
Chloride (Cl <sup>-</sup> )	PM10	0.34	±	0.40	0.004	1.56	5 25	1.01	±	0.94	0.012	3.65	24	
Sulfate (S0₄)	PM2 5	1.54	±	0.64	0.55	3.09	23	1.75	±	0.83	0.66	3.17	23	
Sulfate (SO <mark>≟</mark> ) Sulfur	PM10	2.02	±	1.21	0.51	6.33	25	1.97	±	0.91	0.60	3.74	25	
Dioxide (SO <sub>2</sub> ) Nitrogen	Gas	2.98	±	1.84	0.87	8.35	5 25	2.25	±	1.76	0.34	7.16	26	
Dioxide (NO <sub>2</sub> )	Gas	21.28	±	16.64	0.00	57.99	23	29.24	±	20.36	0.00	70.35	21	
Ammonia (NHz)	Gas	13.39	±	5.85	5.16	33.05	5 27	9.74	±	5.10	1.52	23.96	26	
Nitrate (NOz)	PM10	1.58	±	1.25	0.39	4.77	25	1.73	±	1.22	0.29	4.93	25	
Nitrate (NO <sub>z</sub> )	PMos	0.55	±	0.35	0.056	1.42	25	0.63	±	0.44	0.16	1.56	23	
Nitrate (NOz)	Undenuded													
Nitrate (NO <sub>2</sub> )	PM2.5 Denuded	3.40	t	2.41	0.55	10.56	5 25	0.44	±	0.26	0.058	1.19	23	
	PM2.5	1.77	±	1.26	0.47	5.54	24	1.23	±	0.49	0.52	2.15	22	
Nitric Acid (HNO-)	Gas	2 23	+	1 63	0 00	5.64	25	0 16	+	0.32	0 00	1 56	24	
Acia (moz)	uas	6.60	I	1.05	v. vv	5.04	- 25	0.10	T	0.02	0.00	1.00	۴.4	

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## Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### <u>Site Name:</u> <u>Bakersfield (Measurement Period: October 6, 1988 through September 25, 1989)</u>

					<u></u> "		Concentrations	in µg/m <sup>3</sup>						
				Daytime (C	601-180	O PST)				Nighttime	(1801-0	600 PST	)	
<u>Species</u>	<u>Size</u>	Averag	e ±	Std. Dev.	<u>Min</u>	Max	Number of Samples	Average	±.	Std. Dev.	Min	Max	Number of Sa	mples
Particle Mass	PM2.5	37.50	±	28.31	1.10	132.54	47	40.92	±	37.97	4.27	187.53	48	
Particle Mass	PM <sub>10</sub>	56.28	±	32.97	1.32	154.92	51	69.06	±	44.73	7.81	196.74	50	
Sodium (Na <sup>+</sup> )	PM2.5	0.25	±	0.31	0.00	1.92	48	0.22	±	0.26	0.00	1.43	49	
Sodium (Na <sup>+</sup> )	PM10	0.44	±	0.33	0.019	1.79	52	0.48	±	0.32	0.072	1.50	51	
Magnesium (Mg <sup>++</sup> )	PM2.5	0.072	±	0.068	0.00	0.35	48	0.073	±	0.083	0.00	0.35	49	
Magnesium (Mg <sup>++</sup> )	PM <sub>10</sub>	0.13	±	0.095	0.0022	0.57	52	0.17	±	0.13	0.011	0.71	51	
Potassium (K <sup>+</sup> )	PM2.5	0.17	±	0.12	0.00	0.48	47	0.22	±	0.22	0.00	0.99	48	
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.24	±	0.16	0.011	0.74	48	0.36	±	0.29	0.00	1.51	47	
Calcium (Ca <sup>++</sup> )	PM2 5	0.44	±	0.45	0.00	2.00	48	0.43	±	0.57	0.00	2.34	49	
Calcium (Ca <sup>++</sup> )	PM <sub>10</sub>	0.75	±	0.52	0.03	2.16	52	1.02	±	0.70	0.053	3.50	51	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2 5	2.50	±	3.90	0.00	18.46	46	2.62	±	4.28	0.11	24.64	48	
Ammonium (NH <sub>4</sub> )	PM10	3.08	±	5.24	0.039	26.43	47	2.95	±	4.63	0.26	22.47	48	
Chloride (Cl <sup>7</sup> )	PM2 5	0.083	±	0.13	0.00	0.63	43	0.17	±	0.38	0.00	1.88	46	
Chloride (Cl <sup>®</sup> )	PM10	0.16	±	0.30	0.00	1.83	47	0.32	±	0.58	0.00	2.94	49	
Sulfate (SO₄)	PM2 5	3.00	±	2.12	0.095	11.03	44	2.88	±	1.75	0.12	10.65	47	
Sulfate (SO <sub>4</sub> ) Sulfur	PM10	3.39	±	2.92	0.00	15.53	47	3.08	±	2.15	0.00	10.36	48	
Dioxide (SO <sub>2</sub> )	Gas	7.19	±	3.77	0.00	16.68	46	5.54	±	3.99	1.06	18.78	46	
Nitrogen														
Dioxide (NO <sub>2</sub> )	Gas	28.09	±	15.85	0.76	79.44	50	52.89	±	29.22	0.83	143.04	50	
Ammonia (NHz)	Gas	16.09	±	7.58	1.80	38.33	51	13.31	±	6.91	1.52	25.98	51	
Nitrate (NOz)	PM10	3.90	±	6.19	0.00	31.56	47	4.91	±	7.07	0.00	39.57	48	
Nitrate (NO <sub>7</sub> )	PMas	3.31	±	5.10	0.00	21.83	44	3.62	±	5.22	0.00	29.95	47	
Nitrate (NO <sub>2</sub> )	Undenudeo	1												
Nitrate $(NO_{\overline{2}})$	PM2.5 Denuded	6.48	±	4.78	0.25	22.23	49	2.48	±	5.45	0.11	31.64	46	
۰. ر.	PM2 5	7.85	±	10.04	0.27	49.27	48	6.41	±	9.68	0.38	51.67	46	
Nitric	2.3													
Acid (HNO <sub>3</sub> )	Gas	3.37	±	3.01	0.00	10.60	41	0.72	t	1.13	0.00	4.21	41	

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# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### Site Name: Long Beach (Measurement Period: October 6, 1988 through September 25, 1989)

							Concentrations	in $\mu g/m^3$					
				Daytime (	0601-18	<u>00 PST</u>	)			Nighttime	(1801-06	500 <u>PS</u> 1	[]
<u>Species</u>	Size	<u>Averaq</u>	e ±	Std. Dev.	<u>Min</u>	Max	Number of Samples	<u>Average</u>	t	Std. Dev.	<u>Min</u>	Max	Number of Samples
Particle Mass	PM2.5	24.48	±	17.25	2.60	78.11	L 56	22.80	±	19.31	3.76	93.92	2 56
Particle Mass	PM <sub>10</sub>	48.78	±	23.24	10.72	115.87	7 56	42.62	±	26.98	0.00	137.03	3 56
Sodium (Na <sup>+</sup> )	PM2.5	0.28	±	0.26	0.00	1.47	/ 55	0.24	±	0.21	0.00	1.10	) 55
Sodium (Na <sup>+</sup> )	PM <sub>10</sub>	1.71	±	1.33	0.17	6.27	/ 56	1.65	±	1.29	0.10	6.49	56
Magnesium (Mg <sup>++</sup> )	PM2.5	0.044	±	0.031	0.006	2 0.18	3 55	0.03	±	0.024	0.00	0.13	55
Magnesium (Mg <sup>++</sup> )	PM <sub>10</sub>	0.25	±	0.15	0.04	0.8	5 56	0.23	±	0.15	0.021	0.85	5 56
Potassium (K <sup>+</sup> )	PM2.5	0.056	±	0.040	0.00	0.17	/ 55	0.094	±	0.11	0.00	0.54	55
Potassium (K <sup>+</sup> )	PM10	0.18	±	0.12	0.039	0.86	5 55	0.20	±	0.14	0.0097	0.75	5 55
Calcium (Ca <sup>++</sup> )	PM2.5	0.073	±	0.085	0.00	0.51	55	0.041	±	0.040	0.00	0.19	55
Calcium (Ca <sup>++</sup> )	PM10	0.59	±	0.38	0.10	2.39	56	0.32	±	0.26	0.00	1.39	56
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2.5	2.53	±	2.27	0.25	10.60	54	2.17	±	1.85	0.17	7.38	3 54
Ammonium $(NH_4^{4})$	PM10	2.90	±	2.83	0.00	13.00	) 55	2.61	±	2.38	0.17	10.41	56
Chloride (Cl <sup>2</sup> )	PM2 5	0.077	±	0.154	0.00	0.93	3 54	0.32	±	0.47	0.00	1.75	5 53
Chloride (Cl <sup>-</sup> )	PM10	0.70	±	0.99	0.016	4.27	52	1.40	±	1.26	0.00	4.87	52
Sulfate (SO <sub>4</sub> <sup>=</sup> )	PM2 5	4.32	±	4.11	0.00	20.99	) 55 <sup>.</sup>	3.45	±	3.13	0.35	14.54	55
Sulfate (S0₄)	PM10	6.00	±	5.22	0.98	27.63	3 55	4.94	±	4.14	0.76	21.80	) 56
Sulfur													
Dioxide (SO <sub>2</sub> )	Gas	8.30	±	5.78	0.60	21.78	53	3.94	±	4.87	0.40	25.06	5 54
Nitrogen													
Dioxide (NO <sub>2</sub> )	Gas	61.15	±	35.31	2.79	170.86	5 54	54.93	±	33.58	2.26	150.03	53
Ammonia (NH <sub>z</sub> )	Gas	7.97	±	4.04	0.93	18.04	58	4.66	±	2.67	0.00	11.82	2 58
Nitrate (NOz)	PM10	6.90	±	5.84	0.32	23.58	55°	5.89	±	5.42	0.00	29.01	56
Nitrate (NOz)	PM2.5	3.40	±	5.05	0.00	20.78	3 55	2.85	±	4.29	0.00	21.50	) 55
Nitrate (NOz)	Undenuded	I											
5	PM2 5	5.59	±	4.10	0.08	18.30	) 54	1.13	±	1.86	0.00	12.37	54
Nitrate (NOz)	Denuded												
J	PM <sub>25</sub>	6.48	±	5.85	0.66	22.76	5 53	4.00	±	4.33	0.40	25.24	53
Nitric	L.,												
Acid (HNO <sub>3</sub> )	Gas	2.59	±	2.17	0.00	9.59	50	0.55	±	1.57	0.00	7.52	2 50

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## Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### Site Name: Los Angeles (Measurement Period: October 6, 1988 through September 25, 1989)

					······		Concentrations	<u>in μg/m<sup>3</sup></u>					
				Daytime (	0601-18	00 PST)				Nighttime	(1801-06	00_PST	)
<u>Species</u>	<u>Size</u>	Averag	e ±	Std. Dev.	<u>Min</u>	Max	Number of Samples	Average	±	Std. Dev.	<u>Min</u>	Max	Number of Samples
Particle Mass	PM2.5	30.25	±	19.42	3.78	95.46	56	28.34	±	18.62	3.57	80.54	55
Particle Mass	PM <sub>10</sub>	64.60	±	30.99	19.16	166.77	56	53.34	±	27.21	11.59	154.15	56
Sodium (Na <sup>+</sup> )	PM2.5	0.24	±	0.21	0.00	1.14	56	0.24	±	0.33	0.00	2.25	56
Sodium (Na <sup>+</sup> )	PMto	1.50	t	1.12	0.098	5.56	56	1.45	±	1.15	0.033	6.15	56
Magnesium (Mg <sup>++</sup> )	PM2 5	0.037	±	0.027	0.00	0.14	56	0.030	±	0.023	0.0045	0.12	56
Magnesium (Mg <sup>++</sup> )	PM10	0.25	±	0.15	0.032	0.74	56	0.22	±	0.15	0.0025	0.80	56
Potassium (K <sup>+</sup> )	PM2 5	0.066	±	0.044	0.00	0.19	56	0.077	±	0.051	0.00	0.21	56
Potassium (K <sup>+</sup> )	PM <sub>10</sub>	0.19	±	0.093	0.016	0.46	55	0.18	±	0.12	0.00	0.79	55
Calcium (Ca <sup>++</sup> )	PM2 5	0.083	±	0.12	0.00	0.82	56	0.057	±	0.089	0.00	0.65	56
Calcium (Ca <sup>++</sup> )	PM10	0.75	±	0.39	0.12	1.85	56	0.37	±	0.22	0.00	0.96	56
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2 5	3.00	±	2.57	0.16	12.75	56	2.75	±	2.22	0.052	12.38	55
Ammonium $(NH_4^{+})$	PM10	3.77	±	3.46	0.31	19.76	55	3.46	±	3.26	0.00	20.67	55
Chloride (Cl <sup>7</sup> )	PM2 5	0.058	±	0.091	0.00	0.46	54	0.11	±	0.16	0.00	0.67	54
Chloride (Cl <sup>-</sup> )	PM <sub>10</sub>	0.39	±	0.65	0.00	4.55	53	0.98	±	1.19	0.00	4.44	52
Sulfate $(SO_4^{=})$	PM2 5	4.37	±	3.71	0.43	16.20	56	3.87	±	3.41	0.36	16.56	56
Sulfate $(SO_4^{\pm})$	PM10	6.69	±	5.38	0.85	29.43	56	5.67	±	5.30	0.00	26.54	56
Dioxide (SO <sub>2</sub> )	Gas	6.00	±	3.96	1.08	16.90	54	3.68	ŧ	4.41	0.00	20.27	52
Dioxide (NO <sub>2</sub> )	Gas	76.30	±	57.21	2.51	358.04	54	70.69	±	37.95	5.90	177.81	54
Ammonia (NH-)	Gas	10.42	±	4.50	0.74	24.27	57	5.66	±	3.77	0.19	18.86	56
Nitrate $(NO_7)$	PM10	9.46	±	7.10	0.26	34.66	56	8.89	±	6.76	0.10	31.37	56
Nitrate (NO <sub>7</sub> )	PMar	4.83	±	5.77	0.17	25.23	56	4.78	±	5.05	0.21	18.34	56
Nitrate (NO <sub>7</sub> )	Undenude	d											
······································	PM2.5	11.59	±	7.67	0.14	31.65	51	1.61	±	2.05	0.02	12.84	52
Nitrate (NO <sub>3</sub> )	Denuded	10.05		6 76	0 59	26 74	50	6 62		5 77	1 13	30 EV	50
Nitric	<sup>rm</sup> 2.5	10.90	İ	0./0	0.00	30.74	50	0.52	I	5.77	1.15	30.34	JU
Acid (HNO <sub>3</sub> )	Gas	5.68	±	5.05	0.00	20.33	48	0.33	±	0.86	0.00	4.04	48

# Statistical Summary of Gas/Particle Ambient Concentrations for Samples Taken from the Fourth Quarter of 1988 Through the Third Quarter of 1989

#### Site Name: Azusa (Measurement Period: October 6, 1988 through September 25, 1989)

	·····						Concentrations	in µg/m <sup>3</sup>					
				Daytime ((	0601-18	00 PST)				Nighttime	(1801-06	00 PS1	r)
<u>Species</u>	Size	<u>Average</u>	e ±	Std. Dev.	<u>Min</u>	Max	Number of Samples	Average	±	Std. Dev.	<u>Min</u>	<u>Max</u>	Number of Samples
Particle Mass	PM2.5	33.48	t	19.50	8.46	96.46	5 56	25.57	±	17.52	3.23	88.72	2 54
Particle Mass	PM <sub>10</sub>	73.82	±	39.73	18.80	210.37	57	51.14	±	31.17	8.63	167.51	L 56
Sodium (Na <sup>+</sup> )	PM2.5	0.24	t	0.20	0.00	1.02	2 56	0.21	±	0.21	0.00	1.14	56
Sodium (Na <sup>+</sup> )	PM10	1.17	±	0.92	0.045	3.93	57	1.13	±	1.04	0.026	5.90	) 57
Magnesium (Mg <sup>++</sup> )	PM2.5	0.041	±	0.026	0.0054	4 0.14	56	0.031	±	0.035	0.00	0.22	2 56
Magnesium (Mg <sup>++</sup> )	PM <sub>10</sub>	0.23	±	0.14	0.041	0.61	57	0.18	±	0.15	0.0037	0.76	5 57
Potassium (K <sup>+</sup> )	PM2.5	0.066	±	0.052	0.00	0.25	5 56	0.08	±	0.15	0.00	1.13	56
Potassium (K <sup>+</sup> )	PM10	0.21	±	0.23	0.040	1.76	57	0.17	±	0.16	0.038	1.21	57
Calcium (Ca <sup>++</sup> )	PM2.5	0.11	±	0.073	0.00	0.35	5 56	0.052	±	0.038	0.00	0.19	56
Calcium (Ca <sup>++</sup> )	PM <sub>10</sub>	0.92	±	0.53	0.055	2.16	5 57	0.40	±	0.25	0.00	1.27	57
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM2.5	2.88	±	2.47	0.23	11.92	53	2.76	±	2.48	0.097	14.99	55
Ammonium (NH <sub>4</sub> <sup>+</sup> )	PM10	3.36	±	2.93	0.41	11.49	55	3.60	±	3.93	0.081	24.09	55
Chloride (Cl <sup>'</sup> )	PM2.5	0.041	±	0.075	0.00	0.49	52	0.079	±	0.14	0.00	0.69	53
Chloride (Cl <sup>-</sup> )	PM <sub>10</sub>	0.17	±	0.31	0.00	1.94	53	0.50	±	0.77	0.00	4.44	53
Sulfate (SO <sup>7</sup> )	PM2 5	4.20	±	3.48	0.43	17.80	54	3.74	±	3.18	0.25	14.45	5 55
Sulfate (SO₄)	PM10	5.45	±	4.44	0.62	21.59	55	4.87	±	4.83	0.34	23.94	55
Sulfur	10												
Dioxide (SO <sub>2</sub> )	Gas	4.77	±	3.19	0.33	16.86	52	1.78	±	1.26	0.00	4.88	52
Nitrogen													
Dioxide (NO <sub>2</sub> )	Gas	66.26	±	55.12	1.40	370.00	57	70.44	±	46.72	2.60	254.98	3 55
Ammonia (NHz)	Gas	9.37	±	5.00	0.36	22.59	58	5.26	±	3.00	0.25	13.96	5 57
Nitrate (NOz)	PM <sub>10</sub>	8.66	±	7.33	0.79	30.72	55	8.79	±	8.54	0.00	51.23	3 55
Nitrate $(NO_z)$	PM2 5	4.77	±	5.78	0.22	22.41	54	5.18	±	5.49	0.44	31.28	55
Nitrate (NOz)	Undenuded												
Nitrate (NO <sub>2</sub> )	PM <b>2.5</b> Denuded	13.74	±	10.64	0.0037	7 54.48	51	1.82	±	1.44	0.00	7.34	53
·	PM2 5	13.32	±	7.38	1.89	40.20	52	7.12	±	5.94	1.02	30.55	5 51
Nitric	2.5												
Acid (HNO <sub>3</sub> )	Gas	5.54	±	6.99	0.00	37.28	3 47	0.50	±	1.42	0.00	9.00	) 49

set, and the maximum values in Table 7-2 do not necessarily correspond to the same sample. The amount by which a  $PM_{10}$  concentration exceeds the  $PM_{2.5}$  concentration for a species provides some insight into the potential origins of those species.

For geologically related materials such as magnesium, potassium, and calcium, more than 50% of the concentration is in the size range between 2.5 and 10  $\mu$ m (coarse particles). Exceptions to this generalization can be seen for potassium on nighttime samples from Gasquet, Yosemite, and Sequoia and on daytime and nighttime samples taken in Sacramento and Bakersfield, where the PM<sub>2.5</sub> potassium is as high as 80% of the PM<sub>10</sub>. Each of these areas is known to be affected by very small particles from campfires, forest fires, residential wood combustion, or agricultural burning, especially during winter months. Vegetative burning is a major source of water-soluble PM<sub>2.5</sub> potassium. At sites near the Pacific Coast, such as Gasquet, Fremont, Santa Barbara, and Long Beach, the PM<sub>10</sub> sodium and chlorine averages are two to four times the corresponding PM<sub>2.5</sub> values. This observation is consistent with particle size measurements of sea salt, which show it to be in the coarse particle size range.

From 60 to 100% of the  $PM_{10}$  sulfate, nitrate, and ammonium particles are found in the  $PM_{2.5}$  size fraction. The majority of these particles are expected to come from chemical reactions of  $SO_2$ ,  $NO_x$ , and  $NH_3$ , and these reactions produce fine rather than coarse particles. At Santa Barbara, the nitrate  $PM_{2.5}/PM_{10}$  ratio is 0.58, which is consistent with the hypothesis of gaseous nitric acid reacting with coarse particle sodium chloride in sea salt. At Bakersfield, the  $PM_{2.5}$ particulate nitrate is double the  $PM_{10}$  nitrate, which implies a substantial dissociation of ammonium nitrate on the  $PM_{10}$  Teflon filter. At most of the other sites, the average  $PM_{10}$  nitrate measured on a Teflon filter appears to be much less volatile than the  $PM_{2.5}$  nitrate measured on a Teflon filter.

#### 7.3.2 Daytime/Nighttime

The daytime average concentrations are similar to the nighttime averages for all of the particulate species. The gaseous species, however, show substantial variability between daytime and nighttime samples. The most notable of these is nitric acid, which decreases by a factor of 10 from day to night. Nitric acid is an end-product of daytime photochemical reactions, and its deposition and reactivity rates are large.

The daytime average sulfur dioxide concentration is larger than the nighttime average at most sites, and it is more than twice the nighttime average at Fremont, Santa Barbara, Long Beach, Los Angeles, and Azusa. This may be related to transport from  $SO_2$  emitters or larger  $SO_2$  emission rates during daytime hours in the vicinity of these sites. Ammonia concentrations are also higher during daytime than at night. Ammonia emissions from many sources are larger at higher temperatures.

Average nitrogen dioxide concentrations are higher at night, by almost a factor of two, at Gasquet and Bakersfield, but they are nearly equal at Fremont, Long Beach, Los Angeles, and Azusa. There is no obvious explanation for this observation.

#### 7.3.3 Differences Among Sampling Sites

The largest differences in the averages are observed among the different sampling sites. Average and maximum concentrations of most species at Gasquet, Yosemite, and Sequoia are much lower than those found at the urban sites.  $NO_2$  was not found at Yosemite or Sequoia, while Gasquet averaged 2 to 4  $\mu$ g/m<sup>3</sup> of  $NO_2$ . This is consistent with the location of Gasquet near a major state highway, while the Yosemite and Sequoia sites are quite a distance from heavily travelled roadways. Sulfate, nitrate, and nitric acid averages are highest at Sequoia, which is known to experience a greater amount of pollutant transport from the San Joaquin Valley than does Yosemite. The concentrations for these species at Gasquet are several times less than those found at the Sierra Nevada sites.

The coastal sites of Fremont, Santa Barbara, and Long Beach show sodium concentrations which are two to three times higher than sodium measured at inland sites such as Bakersfield and Sacramento. Particulate nitrate and nitric acid are at their highest average concentrations at Bakersfield, Los Angeles, and Azusa. The geologically related species of magnesium, potassium, and calcium are similar among most sites, except for the fine particle potassium which was noted above as possibly originating from vegetative burning.

A better picture of inter-site similarities and differences is given by Figures 7-5 and 7-6. Figure 7-5 shows the summertime averages of reactive species for the daytime and nighttime samples, while Figure 7-6 shows similar results for wintertime averages.

These figures show that  $SO_2$  is highest at Bakersfield during the summer, with Long Beach and Azusa exhibiting the highest levels during winter. The daytime and nighttime distributions of  $SO_2$  are fairly constant across the South Coast Air Basin during summertime, but a west-to-east gradient develops at night during the winter when the onshore transport patterns are not as dominant as they are during the summertime. These observations are consistent with known emissions in these areas. Bakersfield is affected by oil-extraction activities during which heavy crude oil containing large amounts of sulfur is burned. The Long Beach site is near oil refineries, oil- or gas-burning power plants, and ship traffic.

The sulfate concentrations roughly follow the  $SO_2$  concentrations, but the differences among sites are not as great as those for  $SO_2$ . The South Coast Air Basin sites have the highest sulfate levels during summertime, both day and night, while Bakersfield has the highest sulfate during the wintertime. Summertime sulfate at Santa Barbara is of the same magnitude as that measured at Bakersfield, but greater than the sulfate found at Sacramento and Fremont. This difference may be caused by offshore oil exploration and ship traffic located several miles off the Pacific Coast. The higher sulfate during daytime with respect to nighttime might correspond to the onshore winds which transport pollutants emitted over the ocean to the sampling site.

Nitric acid concentrations are significant only during the summer on daytime samples, and only at urban sites (Bakersfield, Long Beach, Los Angeles, and Azusa).



Comparison of sites Summer 1989 nighttime averages



Figure 7-5. Comparison of June, July, and August Average Concentrations at Different Sampling Locations.



Comparison of sites Winter 1988-89 nighttime averages



Figure 7-6. Comparison of December, January, and February Average Concentrations at Different Sampling Locations. (Sufficient data were not available from Santa Barbara and Gasquet for this period.)

Particulate nitrate is highest at Azusa during summer daylight hours and shows a steady increase in concentration across the South Coast Air Basin (from Long Beach to Los Angeles to Azusa). At night, the average summertime nitrate levels in the South Coast Air Basin drops to about half the daytime values, and the west-to-east gradient becomes less pronounced. Average summertime nitrate levels at the other urban sites are less than half those found in the South Coast Air Basin, with Bakersfield having slightly higher average nitrate than Fremont, Sacramento, and Santa Barbara.

The particulate nitrate distribution is markedly different in the wintertime, when nitrate levels are more than twice their summer averages at Fremont, Sacramento, and Bakersfield. Bakersfield has the largest particulate nitrate concentration during winter, and the west-to-east gradient in the South Coast Air Basin disappears. The cooler temperatures during wintertime favor particulate ammonium nitrate over gaseous nitric acid. Figures 7-5 and 7-6 show that there is sufficient ammonia gas present to allow neutralization of the nitric acid. The high wintertime nitrate at Bakersfield may also be enhanced by aqueous-phase reactions of nitric acid in persistent tule fogs, which are common occurrences in the San Joaquin Valley during winter months.

Figures 7-5 and 7-6 show that there is always excess ammonia at the urban sampling sites, with especially high levels at Sacramento and Bakersfield during the summer. These high ammonia concentrations are consistent with expectations of substantial emissions from agricultural operations in the San Joaquin and Sacramento Valleys.

# 7.4 Correlations

Table 7-3 shows time series correlation coefficients among the measured variables for three selected sites: Sacramento, Sequoia, and Azusa. These coefficients show which concentrations change in the same way over time. Coefficients which exceed 0.75 show a fairly strong covariation, coefficients between 0.5 and 0.75 show a moderate covariation, and coefficients which are less than 0.50 are not considered to be physically significant (though they may be statistically significant). High correlation coefficients are observed when pairs of variables originate from the same source, are equally affected by transport and dispersion, or undergo related chemical transformations.

In most cases, the  $PM_{2.5}$  and  $PM_{10}$  measurements of the same species are moderately to highly correlated. This is reasonable because, as noted above,  $PM_{2.5}$  is a major fraction of  $PM_{10}$  for many species.

At Sacramento and Azusa, ammonium is very strongly correlated with nitrate, which is consistent with particulate nitrate being in the form of nitric acid. Nitrate correlations with sodium are not significant. This correlation would be higher if significant quantities of nitrate were present as sodium nitrate. Sulfate is moderately correlated with ammonium, consistent with its presumed compounds of ammonium sulfate and ammonium bisulfate.

#### Table 7-3

## Correlation Coefficients Among Gas/Particle Concentrations at Sequoia, Sacramento, and Azusa

Site Name: Sacramento

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28

<u>Variable<sup>a</sup></u>

FMass TMass FNa<sup>+</sup> TNa<sup>+</sup> FMg<sup>++</sup> TMg<sup>++</sup> FK<sup>+</sup> TK<sup>+</sup> FCa<sup>++</sup> TCa<sup>++</sup> FNH<sub>4</sub><sup>+</sup> TNH<sub>4</sub><sup>+</sup> FC1<sup>-</sup> TC1<sup>-</sup> FS0<sup>-</sup><sub>4</sub> TS0<sup>-</sup><sub>4</sub> SO<sub>2</sub>(g) NO<sub>2</sub>(g) NH<sub>3</sub>(g) TNO<sub>3</sub><sup>-</sup> FNO<sub>3</sub><sup>-</sup> NO<sub>3</sub><sup>-</sup> BU<sup>b</sup> PNO<sub>3</sub><sup>-</sup> C HNO<sub>3</sub>(g)

FMass 1.00 0.95 1.00 TMass FNa<sup>†</sup> -0.20 -0.11 1.00 TNa<sup>+</sup> -0.24 -0.140.92 1.00 FMg<sup>++</sup> 0.86 -0.11-0.02 0.94 1.00 TMg<sup>++</sup> -0.14-0.02 0.91 0.97 0.90 1.00 FK<sup>+</sup> 0.74 -0.02 -0.08 1.00 0.72 0.03 0.01 TK<sup>+</sup> 0.11 0.20 0.22 0.88 1.00 0.65 0.74 0.17 FCa<sup>++</sup> -0.03 0.37 0.21 0.29 0.02 0.02 0.03 0.53 1.00 TCa<sup>++</sup> 0.14 0.31 0.38 0.30 0.48 0.47 0.25 0.39 1.00 0.51 FNH4 0.90 0.85 -0.26 -0.28 -0.25 -0.23 0.57 0.49 -0.20 -0.08 1.00 TNH 0.86 -0.24 -0.28 -0.24 -0.25 0.55 0.52 -0.18 -0.14 0.97 1.00 0.86 0.14 FC1 0.07 0.15 -0.00 -0.02 0.00 0.04 0.20 0.29 -0.12 0.07 0.05 1.00 TC1 -0.12 -0.07 0.52 0.60 0.46 0.60 0.14 0.34 -0.06 0.05 -0.11 -0.19 0.10 1.00 FS04 0.19 0.56 0.55 0.19 0.20 0.24 0.55 0.40 0.05 0.29 0.59 0.52 -0.170.14 1.00 TSO2 0.56 0.24 0.25 0.25 0.27 0.42 0.41 0.02 0.21 0.62 0.61 0.03 0.09 0.95 1.00 0.54 S0<sub>2</sub>(g) 0.27 0.23 0.39 0.30 0.07 0.09 0.43 0.56 -0.16 -0.20 -0.13 0.07 0.28 0.21 -0.01 0.06 1.00 0.66 -0.08 -0.09 -0.06 -0.01 0.52 -0.08 0.22 N02(g) 0.62 0.49 0.49 0.48 0.09 -0.01 0.30 0.22 0.06 1.00 0.02 0.09 0.02 -0.05 -0.06 0.23 -0.17 -0.19 -0.18 -0.07 0.01-0.03 0.35 -0.07 1.00 NH<sub>3</sub>(g) -0.06 -0.03 0.01 0.27 0.95 0.98 -0.22 1.00 TNO3 0.84 0.85 -0.17 -0.19 -0.18 -0.17 0.56 0.56 -0.18 -0.14 0.21 -0.12 0.46 0.57 -0.21 0.52 0.84 -0.25 -0.27 -0.24 -0.24 0.53 0.49 -0.21 -0.15 0.98 0.95 0.08 -0.10 0.47 0.52 -0.23 0.49 -0.190.96 1.00 FNO<sub>3</sub> 0.89 N0380<sup>b</sup> 0.18 0.25 0.08 -0.05 0.09 0.00 0.27 0.21 0.31 0.43 0.12 0.15 0.09 -0.16 0.34 0.19 0.45 0.06 0.21 0.12 0.03 1.00 PNO3 -0.25 0.52 0.50 0.95 0.97 0.16 -0.14 0.44 0.51 -0.15 0.54 0.97 0.94 0.84 0.84 -0.24 -0.28 -0.24 -0.15 -0.09 -0.140.23 1.00 0.25 0.15 0.06 0.21 0.14 0.24 0.20 0.25 0.34 0.12 0.09 0.18 0.06 0.29 0.16 0.41 0.01 0.23 0.07 0.09 0.51 0.08 1.00 HNO<sub>2</sub>(g) 0.23

## Correlation Coefficients Among Gas/Particle Concentrations at Sequoia, Sacramento, and Azusa

Site Name: Sequoia

1.00

1.00

<u>Variable</u><sup>a</sup>

FMass TMass FNa<sup>+</sup> TNa<sup>+</sup> FMg<sup>++</sup> TMg<sup>++</sup> FK<sup>+</sup> TK<sup>+</sup> FCa<sup>++</sup> TCa<sup>++</sup> FNH<sup>+</sup><sub>4</sub> TNH<sup>+</sup><sub>4</sub> FC1<sup>-</sup> TC1<sup>-</sup> FS0<sup>+</sup><sub>4</sub> TS0<sup>+</sup><sub>4</sub> SO<sub>2</sub>(g) NO<sub>2</sub>(g) NH<sub>3</sub>(g) TNO<sup>+</sup><sub>3</sub> FNO<sup>+</sup><sub>3</sub> NO<sup>+</sup><sub>3</sub>BU<sup>b</sup> PNO<sup>+</sup><sub>3</sub><sup>-</sup> HNO<sub>3</sub>(g)

TMass 0.96

FMass

0.26	0.30	1.00																					
0.13	0.24	0.51	1.00																				
0.29	0.40	0.68	0.65	1.00																			
0.18	0.31	0.42	0.82	0.64	1.00																		
0.46	0.55	0.33	0.29	0.41	0.32	1.00																	
0.15	0.19	0.12	0.19	0.18	0.42	0.37	1.00																
0.11	0.15	0.23	0.28	0.33	0.22	0.30	0.14	1.00															
0.27	0.41	0.33	0.42	0.52	0.67	0.43	0.40	0.31	1.00														
0.22	0.26	0.20	0.14	0.20	0.18	0.23	0.03	0.06	0.05	1.00													
0.18	0.26	0.20	0.45	0.30	0.48	0.26	0.11	0.17	0.22	0.80	1.00												
0.01	0.00	0.16	-0.10	-0.07	-0.08	-0.02	0.08	0.20	-0.05	0.02	-0.04	1.00											
0.03	0.03	0.11	0.41	0.42	0.28	-0.01	0.02	0.08	0.11	-0.06	0.03	0.07	1.00										
0.33	0.38	0.32	0.29	0.44	0.38	0.23	0.14	-0.04	0.23	0.72	0.59	-0.11	0.05	1.00									
0.31	0.40	0.41	0.50	0.56	0.63	0.42	0.23	0.18	0.38	0.66	0.74	0.04	0.12	0.78	1.00								
0.24	0.36	0.46	0.38	0.51	0.49	0.33	0.21	0.03	0.43	0.33	0.35	0.09	-0.02	0.40	0.44	1.00							
0.68	0.67	0.02	-0.04	0.09	0.03	0.56	0.24	0.07	0.19	0.08	0.02	0.01	0.02	0.13	0.16	-0.00	1.00						
0.40	0.51	0.25	0.22	0.33	0.29	0.54	0.25	0.08	0.31	0.29	0.36	0.04	0.06	0.32	0.53	0.46	0.45	1.00					
0.26	0.35	0.27	0.67	0.39	0.62	0.35	0.21	0.24	0.29	0.36	0.63	-0.07	0.27	0.25	0.48	0.32	0.09	0.23	1.00				
0.29	0.29	-0.01	0.03	-0.01	-0.00	0.36	0.17	0.07	-0.03	0.49	0.54	-0.01	-0.01	0.12	0.15	0.01	0.42	0.34	0.48	1.00			
0.12	0.22	0.39	0.23	0.41	0.31	0.22	0.07	0.02	0.25	0.47	0.42	0.10	0.12	0.52	0.57	0.47	0.02	0.52	0.19	0.04	1.00		
0.17	0.21	0.23	0.20	0.18	0.17	0.18	0.02	0.18	0.17	0.49	0.53	-0.00	0.06	0.23	0.26	0.08	0.03	0.13	0.43	0.64	0.19	1.00	
0.13	0.18	0.20	0.05	0.20	0.12	0.10	0.06	-0.06	0.12	0.23	0.12	0.04	0.05	0.34	0.34	0.32	0.04	0.36	-0.00	-0.03	0.82	-0.11	1.00
	0.26 0.13 0.29 0.18 0.46 0.15 0.11 0.27 0.22 0.18 0.01 0.03 0.33 0.31 0.24 0.68 0.40 0.26 0.29 0.12 0.17 0.13	0.26 0.30   0.13 0.24   0.29 0.40   0.18 0.31   0.46 0.55   0.15 0.19   0.11 0.15   0.27 0.41   0.22 0.26   0.18 0.26   0.01 0.00   0.03 0.33   0.33 0.38   0.31 0.40   0.24 0.36   0.68 0.67   0.40 0.51   0.26 0.35   0.29 0.29   0.12 0.22   0.17 0.21   0.13 0.18	0.26   0.30   1.00     0.13   0.24   0.51     0.29   0.40   0.68     0.18   0.31   0.42     0.46   0.55   0.33     0.15   0.19   0.12     0.11   0.15   0.23     0.27   0.41   0.33     0.22   0.26   0.20     0.18   0.26   0.20     0.18   0.26   0.20     0.18   0.26   0.20     0.18   0.26   0.20     0.18   0.26   0.20     0.18   0.26   0.20     0.11   0.00   0.16     0.03   0.03   0.11     0.33   0.38   0.32     0.31   0.40   0.41     0.24   0.36   0.46     0.68   0.67   0.02     0.40   0.51   0.25     0.26   0.35   0.27     0.29   -0.01   0.12	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.18 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.18 0.26 0.20 0.45 0.30 0.48 0.26 0.11 0.17 0.22 0.80 1.00   0.03 0.30 0.11 0.41 0.42 0.28 -0.01 0.02 0.08 0.11 -0.06 0.33 0.72 0.59 -0.	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.18 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.01 0.00 0.16 -0.07 -0.08 -0.22 0.08 0.21 -0.04 1.00   0.33 0.34 0.32 0.29 0.44 0.38 0.23 0.14 -0.04 0.23 0.72 0.59 -0.11 0.05   0.31	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.33 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.18 0.26 0.20 0.45 0.30 0.48 0.26 0.11 0.17 0.22 0.80 1.00   0.01 0.00 0.16 -0.10 -0.07 -0.08 -0.02 0.08 0.21 -0.04 1.00   0.33 0.33 0.31 0.44 0	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.33 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 1.00   0.18 0.26 0.20 0.44 0.28 0.01 0.17 0.22 0.80 1.00   0.33 0.33 0.41 0.42 0.28 -0.01 0.02 0.08 0.11 -0.06 0.03 0.07 1.00   0.33 0.33 0.32 0.29 0.44 0.38 0.23	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.33 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.22 0.30 1.06 0.05 1.00   0.30 0.16 -0.10 -0.07 -0.08 -0.20 0.08 0.20 -0.04 1.00   0.33 0.38 0.32 0.29 0.44 0.38 0.23 0.11 -0.06 0.03 0.07 1.00   0.33 0.34 0.44 0.38 0.23	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.11 0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.33 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 1.07 0.22 0.60 1.00 0.01 0.00 0.16 -0.10 -0.02 0.08 0.20 -0.80 1.00 0.02 0.08 0.21 0.05 0.02 0.04 1.00   0.30 0.11 0.41 0.42 0.28 0.01 0.02 0.08 0.11 -0.06 0.33	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.33 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.44 0.20 0.18 0.23 0.06 0.05 1.00   0.18 0.26 0.20 0.44 0.20 0.18 0.22 0.08 0.21 0.05 1.00   0.33 0.34 0.44 0.28 -0.11 0.17 0.22 0.80 1.00 0.02 0.81 1.00   0.33 0.34 0.44 0.28 0.11 0.10<	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.11 0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.11 0.15 0.23 0.28 0.67 0.43 0.40 0.31 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.22 0.66 0.10 1.00   0.18 0.26 0.20 0.44 0.38 0.22 0.08 1.00 0.05 1.00   0.33 0.33 0.32 0.29 0.44 0.28 -0.01 0.02 -0.08 0.11 -0.16 0.3 0.07 1.00   0.33 0.33 0.32 0.29	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.28 0.20 0.14 0.20 0.18 0.22 0.30 0.14 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.28 0.20 0.44 0.20 0.18 0.23 0.05 1.00 0.00 0.00 0.01 0.00 0.02 0.03 0.07 1.00 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.00 0.01 0.00 0.00 0.01 0.00 0.01 0.00	0.26 0.30 1.00   0.13 0.24 0.51 1.00   0.29 0.40 0.68 0.65 1.00   0.18 0.31 0.42 0.82 0.64 1.00   0.46 0.55 0.33 0.29 0.41 0.32 1.00   0.15 0.19 0.12 0.19 0.18 0.42 0.37 1.00   0.27 0.41 0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.22 0.30 0.14 1.00 0.17 0.22 0.80 0.44 0.40 0.31 1.00   0.22 0.26 0.20 0.14 0.20 0.18 0.23 0.03 0.06 0.05 1.00   0.33 0.42 0.52 0.67 0.43 0.40 0.31 1.00 0.00 0.02 0.04 1.00   0.33 0.34 0.32 0.34 0.20 0.05 0.22 0.04 1.00 0.00 0.01<								

#### Correlation Coefficients Among Gas/Particle Concentrations at Sequoia, Sacramento, and Azusa

<u>Variable<sup>a</sup></u>

Site Name: Azusa

TMass FNa<sup>+</sup> TNa<sup>+</sup> FMg<sup>++</sup> TMg<sup>++</sup>  $TK^{+}$  FCa<sup>++</sup> TCa<sup>++</sup> FNH<sub>4</sub><sup>+</sup> TNH<sub>4</sub><sup>+</sup> FC1<sup>-</sup> TC1<sup>-</sup> FS0<sup>-</sup><sub>4</sub> TS0<sup>-</sup><sub>4</sub> SO<sub>2</sub>(g) NO<sub>2</sub>(g) NH<sub>3</sub>(g) TNO<sub>3</sub> FNO<sub>3</sub><sup>-</sup> NOZBU<sup>b</sup> PNOZ<sup>C</sup> HNOz(g) FK<sup>+</sup> FMass 1.00 FMass 0.88 1.00 TMass FNa<sup>+</sup> 0.08 0.20 1.00 TNa<sup>+</sup> -0.01 0.78 0.21 1.00 FMg<sup>++</sup> 0.14 0.25 0.79 0.58 1.00 TMg<sup>++</sup> FK<sup>+</sup> 0.18 0.44 0.76 0.86 0.70 1.00 0.14 0.05 0.59 0.24 1.00 0.10 0.24 тк\* 0.21 0.35 0.34 0.33 0.55 0.45 0.55 1.00 FCa<sup>++</sup> 0.25 0.29 0.02 0.33 0.50 0.18 0.16 0.24 1.00 TCa<sup>++</sup> 0.49 0.73 0.30 0.24 0.43 0.53 0.14 0.38 0.59 1.00 FNH4 0.81 0.62 -0.07 -0.09 -0.01 -0.01 -0.06 1.00 -0.10 0.01 0.06 TNH4 0.75 -0.01 -0.04 -0.01 -0.10 0.03 0.90 0.63 -0.11 -0.04 -0.16 1.00 FC1 -0.07 -0.12 -0.18 0.03 -0.12 -0.06 -0.09 -0.11 -0.06 0.03 0.10 0.03 1.00 TC1 -0.13 0.39 0.49 0.37 0.05 0.04 -0.00 0.13 1.00 -0.04 0.30 0.01 -0.13 -0.07 FS04 0.63 0.56 0.24 0.22 0.17 0.38 0.06 0.10 -0.03 0.18 0.74 0.57 0.10 -0.10 1.00 TSO4 0.18 0.25 0.07 -0.03 0.18 0.64 0.62 0.10 0.30 0.03 0.69 0.76 -0.06 -0.03 0.83 1.00 (g)رSO 0.29 0.27 0.34 0.40 0.38 0.35 0.57 -0.06 -0.11 0.14 0.18 0.32 0.50 0.02 0.07 0.14 1.00 0.25 N02(g) 0.54 0.55 0.11 0.06 0.10 0.17 0.17 0.09 0.40 0.31 0.34 0.00 0.04 0.17 0.22 0.14 1.00 0.52 0.19 0.23 0.19 0.39 0.10 0.09 0.26 0.60 0.07 0.16 -0.10 0.00 0.18 0.30 0.28 0.28 1.00  $NH_3(g)$ 0.35 1.00 TNO 0.68 0.61 -0.04 0.06 -0.09 0.07 -0.00 0.03 -0.06 0.11 0.78 0.88 0.02 -0.00 0.34 0.50 0.15 0.43 0.20 0.47 -0.26 -0.29 -0.24 -0.23 -0.02 -0.04 -0.07 -0.01 0.82 0.79 0.11 -0.11 0.27 0.29 0.02 0.35 -0.03 0.85 1.00 FNO 0.67 NO3BU<sup>b</sup> 0.54 0.29 0.25 0.01 -0.11 0.41 0.32 0.46 0.06 0.24 0.36 0.66 0.15 0.03 -0.10 -0.26 0.42 0.32 0.46 0.18 0.55 1.00 PNOZ 0.73 -0.02 -0.05 0.01 0.11 0.48 0.64 -0.05 -0.26 0.34 0.45 0.32 0.46 0.55 0.52 0.77 0.04 0.10 0.24 0.63 0.67 0.64 1.00 0.23 0.16 0.18 0.23 0.43 0.20 0.01 -0.00 -0.19 0.44 0.23 0.02 0.26 -0.04 -0.04 0.84 0.19 HNO<sub>3</sub>(g) 0.28 0.36 0.29 0.37 0.04 0.40 1.00

 $^{a}$  An "F" prefix designates PM<sub>2.5</sub>fraction and a "T" prefix designates PM<sub>10</sub> fraction.

<sup>b</sup> NO<sub>3</sub>BU = Nitrate measured on Nylon Backup filter in non-denuded airstream.

<sup>c</sup>  $PNO_3^- = PM_{2,5}particulate nitrate (sum of FNO_3^- and NO_3^-BU).$ 

#### 8.0 SUMMARY AND RECOMMENDATIONS

#### 8.1 Summary

A dry deposition monitoring component of the California Acid Deposition Monitoring Program has been implemented to allow the estimation of fluxes of reactive species at representative locations throughout the State. Sampling-site installation began in May, 1988 and was completed in April, 1989. The resulting data base contains nearly one million hourly average values for ozone, wind speed, wind direction, atmospheric stability, temperature, dew point, time of wetness, and solar radiation. It also contains over 30,000 12-hour average values for daytime and nighttime measurements of sulfur dioxide, ammonia, nitrogen dioxide, nitric acid, mass, chloride, nitrate, sulfate, ammonium, sodium, magnesium, potassium, and calcium concentrations. The data base is fully documented, includes data validation flags, and is available on IBM-PC compatible floppy disks in dBase III+ formats.

Collocated measurements taken with the gas/particle samplers showed high precision for most of the species measured. Lower quantifiable limits were adequate to quantify most species at urban sites on over 90% of the samples. The lower concentrations encountered at non-urban sites were quantified on 60 to 90% of the samples for most species. Maintenance and performance tests of the gas/particle sampling system showed that calibrations were stable for more than one year of every-sixth-day operation.

The continuous monitoring systems for ozone and meteorological variables performed well with the exception of the dew point sensor. The lithium chloride sensor installed at most sites generally reports dew point temperatures which are several degrees lower than the real dew point. This is a consistent problem at several sites.

Standard operating procedures and computer software were created to document the network operations and to facilitate data processing. These were revised in collaboration with ARB staff. Network operations have been fully transferred to ARB staff.

# 8.2 Recommendations

An evaluation of the first  $1\frac{1}{2}$  years of monitoring yields the following recommendations:

- An annual inspection and maintenance visit should be made to each site. Sampling inlets should be cleaned and flow rates should be recalibrated on these visits. These visits are in addition to emergency repair visits.
- A more accurate dew point sensor should be identified and installed at each site. The sensor in current use has been found to be inaccurate.

- High laboratory throughput can be obtained using automated injection and data acquisition systems. The labor savings more than pay for the hardware and software expenses. The ARB laboratory should procure an ion chromatographic auto-injection system and interface it to its existing equipment.
- Several of the forms used for recording data and chain of custody can and should be simplified.
- The dry deposition data base should be integrated with the wet and occult deposition data bases. Data interpretation projects should be defined and sponsored to use these data for the estimation of deposition fluxes, improving understanding of pollutant transport and chemical transformation, and to identify the sources of pollutants.
- Communications with forest response researchers need to be established to determine the extent to which the current measurement program is applicable to the assessment of tree damage.

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