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The purpose of this study was to evaluate the separate and combined effects of ozone and acidic deposition on mixed conifer forests in the San Bernardino mountains of southern California. The primary objectives were to acquire a long-term data base of specified accuracy, precision and validity for atmospheric pollution concentration, local and stand meteorology, wet and dry deposition fluxes to forest canopies, and biological responses of forest vegetation and soils. Some data were used to parameterize and run simulations with the Big Leaf model. Furthermore, to document the procedures used in the project, complete descriptions of measurement techniques, research protocols and quality assurance objectives were compiled in a companion document to the final report. This multi-disciplinary study provides a data base describing many attributes of a California mixed conifer forest ecosystem exposed to a moderate level of gas and particle deposition compared to the highest possible levels in the western portions of the San Bernardino mountains. Acidic pollutants were not implicated in any short-term tree response, however, long-term effects are possible and should be investigated. The interaction of ozone and periodic droughts will continue to be the greatest threat to long-term health of these forests.

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EXECUTIVE SUMMARY

Evaluation of the possible long-term consequences of pollutant deposition to forest ecosystems requires an initial descriptive data base including as many attributes of the atmosphere, plants and soil as possible. This study addressed the need to evaluate the separate and combined effects of ozone and acidic deposition on the condition of pine and mixed conifer forests in the San Bernardino mountains of southern California. The hypothesis to be examined was whether ozone and acidic deposition have cumulative effects on a California mixed conifer forest ecosystem that together cause more perturbation to functional processes than either acting alone. The primary objectives of the project were to acquire a long-term data base of specified accuracy, precision and validity for atmospheric pollution concentration, local and stand meteorology, wet and dry deposition fluxes to forest canopies, and biological responses of forest vegetation and soils. Some of these data were used to parameterize and run simulations with the Big Leaf deposition model. Furthermore, to document the procedures used in the project, complete descriptions of measurement techniques, research protocols and quality assurance objectives for all aspects of the project were compiled in a companion document to the final report.

A forested area with moderate ozone damage in the vicinity of Barton Flats was selected for a study of the combined effects of ozone and acidic species on tree health and other ecosystem properties. Ozone damage to ponderosa (*Pinus ponderosa*) and Jeffrey (*P. jeffreyi*) pines was reported here in the late 1960's and useful background information was available. A complete air quality and meteorological monitoring station was established near the Forest Service Visitor Information Center at Barton Flats on State Highway 38, at an elevation of 1982 m. Within 1.6 km from the monitoring station three forest vegetation monitoring plots were established (plot #1 at 1982 m, plot #2 at 2171 m and plot #3 at 2207 m elevation). At each plot the initial state of vegetation and soils was determined in the autumn of 1991 and spring of 1992. Also in the spring of 1992, precipitation and throughfall collectors and needle litter collectors were installed at all plots. At plot #2 a 29 m climbable scaffold was erected to allow measurements to be made above and below the top of the forest canopy with meteorology and air quality monitoring systems and container-grown trees. Most measurements in the plots were carried out in spring, summer and fall from 1992 to 1994.

The meteorology and air chemistry monitoring and analyses were carried out by the Energy and Environmental Engineering Center of the Desert Research Institute (Section 2). The meteorology in the study area was characterized by sea breeze and upslope/downslope flow patterns during summer which resulted in consistent diurnal patterns. In winter the synoptic scale weather system caused greater day-to-day variability. Ozone was the air pollutant most often present at phytotoxic concentrations. Hourly ozone concentrations exceeded the National Air Quality Standard of 120 ppb on over 20 percent of the sampling days. Peak ozone concentrations exceeding 200 ppb usually coincided with periods of high daily maximum temperatures. Particles emitted and formed in the Los Angeles Basin were transported to the Barton Flats station during spring, summer and early fall. Dry deposition samples for $PM_{2.5}$ mass and ions (i.e., nitrate, sulfate, ammonium) were found above the lower quantifiable limits (LQLs) for more than 80 percent of the samples. Precursor gas (i.e.,sulfur dioxide, nitrogen dioxide, nitric acid, ammonia) concentrations were above LQLs in over 70 percent of the samples. The sum of ionic species versus $PM_{2.5}$ mass revealed that chloride, nitrate, sulfate and ammonium accounted for approximately 50 percent of $PM_{2.5}$ mass. The relationship of daytime average concentrations for all the particulate species to the nighttime averages were similar during all seasons. Season-to-season variations were significant for $PM_{2.5}$ mass, and ions, with the lowest values reported during winter and reaching maximum concentrations during summer.

Anions were above LQLs in over 70 percent of the wet deposition samples (i.e., chloride, nitrate, sulfate), whereas cations (i.e., ammonium, sodium, magnesium, calcium) were detected in over 60 percent of the cases. Potassium ions were detectable in less than 35 percent of the cases. Wet deposition was non-acidic, with pH normally exceeding 5.5. The lowest pH value measured was 4.2 during the summer of 1993 in a small volume precipitation event (less than 2.5 cm). Nitrate and sulfate ions were the most prominent species in wet deposition samples, accounting for 50 and 25 percent of the total measured ions, respectively.

Canopy meteorology was measured and compared as monthly averages in all seasons at 2 m and 15 m (below and above the forest canopy) at the Barton Flats monitoring station--and in the summer months at 2 m and 29 m at plot #2 (Section 3). Temperatures at 15 m were usually slightly higher than in shaded understory at 2 m. There was no difference between adjacent air and leaf temperature measurements at 2 m based on monthly averages. In summer months the daytime temperatures and relative humidity were virtually the same at 2 m and 29 m positions at plot #2. Night temperatures at 2 m were 5° C cooler and relative humidity about 10 percent higher than at 29 m. Daytime wind speeds at 29 m were 3 m s^{-1} and 0.9 m s^{-1} at 2 m. At night wind speed was 2 m s^{-1} at 29 m and 1 m s^{-1} at 2 m. Ozone concentrations in the lower canopy at 2 m were slightly (10-15 percent) lower than at 15 m during both day and night in early July and lower only at night in September and October. Daytime reductions may be explained by higher stomatal conductance and consequently higher rates of ozone uptake by foliage in early to mid summer, i.e., when soil moisture is still available. The concentrations of several gases (i.e., nitric acid, nitrous acid, ammonia, and sulfur dioxide), and particles containing nitrate, sulfate, and ammonium were not significantly different when sampled at 29 m, 23 m, 16 m, and 11 m. Concurrent ozone measurements at the monitoring site and plot #2 showed good agreement, although these locations were 1.6 km apart. However, when concentration-weighted ozone exposure indices (Sum 60) were computed and compared, differences between sites were more than for the comparison of 24 h averages.

The deposition fluxes of nitrate and ammonium in particles were dependent on position of branches in the canopy (Section 4). For example, during three summer seasons the deposition varied from about 30 μg m^{-2} h^{-1} at the bottom to about 200 μg m^{-2} h^{-1} at the top. Even though air concentrations of these ions were shown to be uniform through the canopy, deposition rates were higher at the canopy top due to the higher wind speed. Deposition fluxes were similar at all vegetation plots. By using two different estimates of leaf area index and by considering wet deposition data collected at plot 2 in the 1993 season, the total N deposition rate was in the range of 5 - 9 kg ha^{-1} yr^{-1}, or about half the amount of total N deposition predicted by the Big Leaf Model (Section 8).

Similarly for other ions (Section 5), the higher position within the canopy, the higher the dry deposition of potassium, calcium, magnesium and sodium. In general, the highest deposition fluxes were determined for California black oak (*Quercus kelloggii*). For the April 15 through October 15, the deposition flux was highest for calcium (3.7 kg ha^{-1}), followed by sodium (2.8 kg ha^{-1}), potassium (2.2 kg ha^{-1}) and magnesium (0.7 kg ha^{-1}). Dry deposition of potassium, calcium, magnesium were elevated and may be an important source of compensation for the negative effects of the excessive deposition of nitrogen at some sites in the western portion of the San Bernardino mountains, i.e., compensation for the reduced availability of these metals.

Wet deposition data for the National Atmospheric Deposition Program/National Trends Network station at Tanbark Flat (a lower elevation, higher pollution site closer to Los Angeles) was compared with Barton Flats from December 1991 to November 1993 (Section 6). Analyte deposition amounts

were slightly higher at Tanbark Flat, mainly because both sites were influenced by the high-volume winter storms that have near background burdens of acidic pollutants. Combined wet and dry deposition was monitored for one winter along another transect in the San Bernardino mountains where Camp Paivika is at the western end with Heart Bar at the eastern end, and Barton Flats in the middle. Winter and early springtime N and S inputs in wet deposition at Camp Paivika totaled 11.9 and 2.7 kg ha^{-1} yr^{-1}. N and S deposition at Barton Flats and Heart Bar were about 10 times lower for the same period. Current deposition rates at Camp Paivika are sufficient to raise concern about soil nitrogen saturation.

The system of "flip-top" rain and throughfall collectors, operated in the spring, summer and fall at plots 1, 2, and 3 showed that rainfall acidity ranged from pH 4.2 to 4.8 and throughfall acidity ranged from pH 4.0 to 4.6 (Section 7). Although annual throughfall deposition loads (kg ha^{-1}) were within the range of many forests exposed to air pollution, ionic concentrations in throughfall at Barton Flats, were high relative to forests in eastern North America and Europe. Concentrations of N in throughfall were especially high due to washoff of accumulated dry pollutants from mature canopies by low rain volummes. Internal leaching from foliage was a likely major source of K^+ and Ca^{2+} in throughfall. Throughfall concentrations were generally highest under white fir (*Abies concolor*), the species with the greatest foliage surface area, and lowest under black oak.

To characterize pollutant deposition to the forest canopy at Barton Flats, rates were determined by direct measurement (leaf washing and throughfall analyses) and inferential techniques (Big Leaf model). Simulations of atmospheric deposition from the Big Leaf model (Section 8) estimated that total N deposition via wet and dry processes was 14.5 kg ha^{-1} yr^{-1}. Dry deposition accounted for 85 percent of this total, and HNO_3 and NH_3 were the principal chemical species contributing to N input. In the case of S deposition, total inputs were 2 kg ha^{-1} yr^{-1}, and dry deposition accounted for 25 percent of the total. The deposition of O_3 was highly variable among species and over time (seasonal and diurnal time steps). Peak deposition rates for O_3 were predicted to occur at 4 or 5 pm on a daily basis and in June or July on a seasonal basis. Based on total N deposition, it appears that model predictions provided an upper bound for deposition estimates compared to measurements described in Section 4.

The soils at Barton Flats are "young" in terms of profile development. They are classified as coarse, mixed Typic Xerumbrepts. Based on their overall physical and chemical properties these soils are considered to be insensitive to pH related, short term phenomena (Al and Mn toxicity) associated with acid deposition (Section 9). The data collected for soil properties and tissue nutrient contents for ponderosa pine, white fir, and black oak (Section 10) were also used to parameterize a nutrient cycling model (NuCM) to be reported in the final report for California Air Resources Board Contract No. 92-335. In consideration of current levels of N uptake by trees, there is no indication that N supplies limit tree growth at Barton Flats. However, soil concentrations of P and K may become growth-limiting; excess N deposition may render these nutrients less available for uptake and force their conservation. Needle nutrient contents were poorly correlated with visual indicators of ozone damage.

Trees of all species in size classes $\geq$ 10 cm diameter-at-breast-height were labeled with numbered metal tags at vegetation plots 1, 2 and 3 (Section 11). A subset of approximately 40 ponderosa and/or Jeffrey pines at each plot provided a baseline set of data for following the effects of air pollution and other stresses on tree condition. For plots 1, 2, and 3 ponderosa and Jeffrey pines represent 26, 37, and 38 percent of the total number of stems, and 51, 49, and 69 percent of the basal area (m^2 stem

cross-sectional area ha^{-1}), respectively. The remaining species in each plot are mainly white fir and black oak. Overstory trees are mainly pines in larger diameter classes which are the product of earlier days when frequent fires constantly controlled the numbers of fire sensitive species like white fir. Between 1991 and 1994 the percent increase in basal area was less than 2 percent for pines, 6-11 percent for white fir and 3-6 percent for black oak. In the continued absence of fire these growth differences among species provide an approximate prediction of future stand composition; white fir and black oak may be more successful competitors and pines will no longer be the dominant species.

Ponderosa and/or Jeffrey pines at Barton Flats were already known to have needle injury from ozone and other leaf symptoms for which the cause(s) were not fully understood. In September of each year from 1991 to 1994 the Ozone Injury Index (OII) was determined for the subset of 40 ponderosa and/or Jeffrey pines in each plot. The OII ranges from 0 (no ozone injury) to 100 (the maximum ozone injury). The average OII for all trees in all 3 plots increased from 38 in 1991 to 49 in 1994. This indicated a significant increase of chronic ozone injury. Crown position class of individual trees influenced OII since dominant trees had lower index values (41 in 1994) than intermediate trees (52 in 1994). Along a 20 km ozone gradient in the San Bernardino mountains, values for the OII were 53 at Angelus Oaks (westernmost site), 49 at Barton Flats (10 km east), and 31 at Heart Bar (20 km east). Close-up inspection of individual needle whorls on five sample branches each year allowed for examining relationships between various ozone exposure indices and amount of chlorotic mottle symptoms on needles. One of the highest correlation coefficients was obtained with the sum of hours exceeding 80 ppb. The sum of all hourly values $\geq$ 60 ppb was also favorable especially when computed for the spring and early summer months when ozone flux to foliage was believed to be the highest. One needle symptom described as upper needle surface necrotic fleck or winter fleck was present on needles following their first full winter. Winter fleck was most prevalent in 1993 and least in 1994. An inspection of wet and dry deposition of N and S and extremes of temperature in winter and summer did not explain the difference between winter fleck severity in 1993 and 1994. Observations of 1700 ponderosa and/or Jeffrey pines in the central and southern Sierra Nevada suggests that winter fleck is more intense at sites with higher photochemical air pollution exposure. Without some controlled exposure experiments it will not be possible to learn if acidic deposition may be involved.

In summary, this multi-disciplinary study succeeded in providing a data base describing many attributes of a California mixed conifer forest ecosystem exposed to a moderate level of gas and particle deposition compared to the highest possible levels in the western portions of the San Bernardino mountains. Specifications have been provided for the accuracy, precision, and validity of measurements including detailed documentation of the techniques and protocols employed. Acidic pollutants were not implicated in any short-term tree response, however, long term effects are possible and should be investigated. The interaction of ozone and periodic droughts will continue to be the greatest threat to the long-term health of these forests.

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1.0 DESCRIPTION OF PROJECT AND LITERATURE REVIEW

P. Miller

1.1 Introduction

This is the report of a multidisciplinary study of the chronic effect of wet and dry deposited acidic compounds and ozone on components and processes of a California mixed conifer forest ecosystem in the San Bernardino National Forest. Work began in June 1991 and some tasks continued through the winter-spring of 1994.

1.1.1 Overview

An integrated study was planned which utilized the combined skills of scientists at the Forest Service, U.S. Department of Agriculture, Pacific Southwest Research Station, Riverside Fire Laboratory (PSW/RFL) and the Desert Research Institute, Energy and Environmental Engineering Center (DRI/EEEC) and the DRI Biological Sciences Center to examine dry and wet deposition of pollutants and their effects on forest vegetation in a region of the San Bernardino National Forest where moderate ozone effects have been observed for many years. Vegetation includes the ponderosa pine-white fir and Jeffrey pine-white fir types in the 5500 to 7500 ft elevational zone near Barton Flats in the Santa Ana River drainage, 24 miles east of the City of San Bernardino (Figure 1-1).

One reason for using this site is that forest vegetation here is analogous to six companion sites in the Sierra Nevada where ARB Project 92-346 (John Carroll, University of California, Davis) is measuring ozone and meteorological variables. Nearby each of these sites three forest vegetation plots were installed and the condition of pine trees were determined each year in accordance with an agreement between ARB and the USDA Forest Service, Region 5, Air Quality Management staff. Rating of tree condition each year was done with the same procedure for both Sierra and San Bernardino National Forest projects.

1.1.2 Project Objectives

1.1.2.1 Primary Objectives

1) Acquire a long-term data base of specified accuracy, precision, and validity for atmospheric pollution concentrations, wet and dry deposition fluxes to forest canopies, and meteorological variables.

2) Acquire a long-term data base of specified accuracy, precision and validity for responses of California mixed conifer forest vegetation and soils to atmospheric pollution concentrations, and environmental variables.

3) Establish measurement techniques, protocols and data analysis methods which can facilitate long-term and cost-effective evaluation of the effects of acidic species and associated oxidants on forest response at a variety of California locations.

The results obtained for both item 1 and item 2 are contained in this report. For item 3 a separate manual was prepared in two volumes. Volume 1 contains procedures used for measuring biological variables. Volume 2 describes all procedures associated with air chemistry and meteorology.

1.1.2.2 Description of Experimental Tasks

The research tasks and the assignment of responsibility to each investigator is listed in Table 1-1. Several additional tasks were proposed in the original proposal but were discarded in the process of negotiating the final objectives of the project. The project was designed with the purpose of investigating atmospheric deposition and forest responses in a ecosystem context. The collection of air quality and vegetation response data began in September 1991 and continued through November 1994. Figure 1-2 presents the research tasks in their proper location in a stylized forest ecosystem diagram.

1.2 Literature Review

1.2.1 Summary of NAPAP Results

Federal government agencies embarked on a 10-year project to investigate the effects of acid deposition on cultivated and natural ecosystems. The so-called National Acidic Precipitation Assessment Program did not find acidic deposition to be a significant factor contributing to current forest health problems in North America, with the possible exception of red spruce (*Picea rubens Sarg.*) dieback and mortality at high elevations in the Appalachians (NAPAP, 1989). In that case acidic cloudwater may reduce the resistance of red spruce to low temperatures and other natural stresses. None of the NAPAP-sponsored studies included situations where ozone was present at concentrations as high as those in California or where the long-term interaction of ozone injury with acidic deposition was tested.

In the absence of direct effects of wet acidic deposition on foliage and above-ground processes there is still the possibility that a gradual degradation of forest ecosystems may be developing through cumulative impacts on soils. Mechanisms for cumulative impact may include accelerated soil acidification (Reuss and Johnson, 1986), trace metal accumulation (Smith, 1981), and nitrogen saturation (Aber et al., 1989). The nitrogen saturation hypothesis is important to consider because nitrogen accumulation appears to be a highly probable result for southern California wildlands exposed to photochemical smog.

One admitted limitation of the NAPAP, Forest Response Program (FRP) was that forest level studies were short-term. A key recommendation for the future was to supplement deposition monitoring with experiments lasting longer than 5 years in an effort to determine if cumulative impacts may be mediated through the soil system (NAPAP, 1989).

Experiments studying seedling response to sulfur, nitrogen, and associated pollutants were another major product of the FRP (Peterson et al., 1989). As with field level studies the seedling experiments were short-term. The period of exposure to pollutants and growth in the following summer did not exceed 15 months in most cases. Experiments simulating exposures of western conifer species to summer ozone and winter acid fog were completed at Corvallis, OR (Hogsett et al., 1989). They obtained a mixture of results.

Effects of ozone or ozone followed by acid fog were observed to be stimulating to seedling growth as often as they diminished growth.

Other seedling exposures to simulated acid rain and ozone were carried out with ponderosa pine for a three year period at Whitaker Forest, an experimental site in the southern Sierra Nevada. This experiment was part of the Electric Power Research Institute research program entitled: Response of Plants to Integrated Stress (ROPIS). The experimental design included acid rain (pH 3.5, 4.4, 5.3), ozone (CF, NF, NF150, AA), two levels of dry deposition (90% and 60% filtration), and two levels of soil moisture availability (adequate and drought stressed). After 3 consecutive years of exposure the preliminary results suggest no effect from acid rain treatments, a much greater effect of ozone on adequately watered seedlings compared to those drought-stressed, and an interaction between 60% particle filtration and ozone resulting in more ozone injury (Temple et al., 1992).

1.2.2 Atmospheric Deposition and Forest Response

1.2.2.1 Wet and Dry Deposition of Nitrogen

Oxides of nitrogen occur in the atmosphere in various forms including nitric oxide (NO), nitrogen dioxide (NO_2) and nitric acid vapor (HNO_3). Ambient concentrations of these oxides reflect a balance between natural or anthropogenic emissions, atmospheric chemical cycling with ozone, and deposition to landscape surfaces (Finlayson-Pitts and Pitts, 1986). Dry deposition fluxes of N compounds and associated ions were determined in the South Coast Air Basin by three monitoring sites at Los Angeles, Long Beach and Azusa. Measurements have shown typical levels of total nitrate in the 5-47 $\mu g/m^3$ range (Ashbaugh et al., 1989). These stations are part of the California Dry Acid Deposition Monitoring Network (CADMP) (Ashbaugh et al., 1989).

A detailed study of the gaseous and particulate species of sulfur and nitrogen was done in a rural area in the Kern River Canyon east of Bakersfield, and two urban areas including Martinez and San Jose (John et al., 1984). The oxides of nitrogen were present at higher concentrations than sulfur oxides at all sites.

The southern California database for wet deposition suggests that winter rainfall pH ranges from 4.6 in the vicinity of point sources of pollution along the coast to 5.8 at a distance of 150 km to the northeast (Zeldin and Ellis, 1984). Normal rain is considered to be pH 5.6. The highest sulfate concentrations in rain are found in the Los Angeles-Lynwood-Long Beach area, while the highest nitrate concentrations are observed at inland locations such as San Bernardino, Riverside and Tanbark Flat. Acid fogs with pH values ranging between 1.7 and 5.8 have been measured in the Los Angeles basin during periods of low inversion heights, weak transport winds, and weak offshore surface gradients (Waldman et al., 1985).

It is generally predicted that dry deposition is more important than wet deposition for removing airborne pollutants from anthropogenic sources (Marenco and Montan, 1976). Dry deposition is always cleansing the lower atmosphere at ground level while wet deposition is less frequent, particularly in California's summer dry climate. It was estimated that more than 90 percent of the ambient load of acidic compounds deposited in the Basin is deposited through dry deposition mechanisms (Marenco and Montan, 1976).

At Tanbark Flat in the San Gabriel mountains very low concentrations of nitric oxide were recorded. However, concentrations of nitrogen dioxide at this location were high with peak values (96 -297 $\mu g/m^3$) co-occurring with the afternoon ozone peak concentration (Bytnerowicz et al., 1987).

HNO_3 vapor is produced by reactions of NO_2 with airborne hydroxyl radicals (Finlayson-Pitts and Pitts, 1986; Atkinson, 1989). Concentrations of this gas in the southern California mountains are exceptionally high, with the 12-hr daytime averages reaching 40 μgm^3 (John et al., 1984, 1985; Bytnerowicz et al., 1987). It can be assumed that because of diurnal cycles of photochemical smog formation, the afternoon peak concentrations of HNO_3 may be several times higher than the above-mentioned 12 hr average value.

1.2.2.2 Plant Responses to Nitrogen Deposition

Zinke (1980) reported the results of foliage analyses of big cone Douglas-fir (*Pseudotsuga macrocarpa* [Vasey] Mayr) across gradients of decreasing chronic pollutant exposure in the Basin. Foliage nitrogen concentration was highest in the most polluted portions of two out of three transects. Nitrate concentrations, assumed to have originated from canopy and soil surfaces, were found to be one to three orders of magnitude greater in streamwater in the San Gabriel Mountains than the nitrate concentrations in streamwater from the nearby Santa Monica and Palomar Mountains (Riggan et al., 1985).

Nitric oxide is not readily absorbed either by leaf tissues (Hill, 1971), or by soil or cement surfaces (Judeikis and Wren, 1978). Nitrogen dioxide is more water soluble and is readily absorbed by actively transpiring leaves. Hill (1971) estimated that alfalfa in the South Coast Air Basin may absorb as much as 0.28 kg N $ha^{-1}day^{-1}$ as nitrogen based on an assumed hourly concentration of 6.0 pphm nitrogen dioxide. Dry deposition of nitrogen dioxide to Scots pine (*Pinus sylvestris L.*) was shown to increase linearly with increasing concentration in both laboratory and field experiments. In Mediterranean climates the uptake of nitrogen dioxide may be limited mainly to the spring-early summer period when soil moisture is still available. Little is known about the uptake of nitric acid although it is present in fairly high concentrations.

Very little is known about the effects of HNO_3 vapor on plants. It is believed that the cuticular layer and the substomatal cavities of the leaf are particularly susceptible to injury by HNO_3 (Taylor et al., 1988). It has been demonstrated that exposure of plants to gaseous air pollutants and acidic precipitation may damage the structure of the wax layer of cuticles (Turunen and Huttunen, 1990), and similar effects can be expected from the exposure to HNO_3. Transport of HNO_3 through stomatal cavities and cuticular channels has been demonstrated, but very little is known about the penetration of HNO_3 into the leaf interior (Taylor et al., 1988; Marshall and Cadle, 1989).

Elevated concentrations of nitrate and changes in the activity of nitrate reductase have been observed following exposure to HNO_3 (Aber et al., 1989; Norby et al., 1989). It is known that nocturnal concentrations of nitrate reductase are low in foliage of most of the woody plant species (Kramer and Kozlowski, 1979). However, synthesis of this enzyme has been observed to be stimulated by an increase of the substrate, i.e., nitrate, in some plant species. Therefore, the extent of metabolic disturbance due to uptake of HNO_3 would most likely depend upon the degree to which nitrate reductase synthesis has been stimulated.

Daily peak concentrations of O_3 and HNO_3 are coincident in the southern California mountains (Bytnerowicz et al., 1987). Interactions between these two pollutants may be of special importance due to differences in the mechanisms by which injury occurs. HNO_3 is deposited primarily to cuticles and stomatal cavities and may potentially alter the function of stomata. One possible effect of a change in stomatal control may be increased conductance leading to more ozone uptake and damage to mesophyll cells. Therefore, plants exposed to elevated concentrations of HNO_3 may be predisposed to the phytotoxic effects of other air pollutants through changes in stomatal conductance or changes in the integrity of the cuticle leading to water loss from leaves.

Another aspect of HNO_3 deposition to forest communities is its role as a source of nitrogen. Compared to other pollutants, HNO_3 has a very high deposition velocity in the range of 1 to 5 cm s^{-1} (Dasch, 1988). It is readily taken up by plant canopies, mainly due to high surface deposition. Thus it may be expected that a high proportion of the total N deposited from the atmosphere in the southern California mountains is in the form of HNO_3. Nitrogen compounds are deposited to all surfaces including vegetation, litter, and soil.

1.2.2.3 Nitrogen Effects on Litter Decomposition, and Saturation of Ecosystem Pools

The nitrogen content of ponderosa pine litter was positively correlated with litter decomposition rates (Fenn and Dunn, 1989). The same was true of litter decomposition rates of sugar pine and incense cedar; also, ponderosa pine foliage exhibiting severe ozone damage at high pollution plots abscised 2-4 years earlier than foliage from low pollution plots. Retranslocation of N and P prior to needle abscission was not inhibited in the high pollution plots. Higher N levels in litter at the high pollution plots did not appear to be due to reduced retranslocation of N from senescing foliage (Fenn, 1991). Earlier studies of litter decomposition rates at study plots located along the pollution gradient in the San Bernardino mountains showed more rapid decomposition rates at the western plots even when litter bags of Jeffrey pine needles from the eastern plots were exposed in the western plots (Bruhn, 1980). Levels of NO_3^- and NH_4^+ washed from foliage and litter of ponderosa and Jeffrey pines at ten sites across an O_3 gradient in the San Bernardino mountains were highly correlated ($r=0.73$ to 0.82) with average hourly ozone concentrations. Deposition of sulfur also followed the same pattern (Fenn and Bytnerowicz, 1993).

Nitrogen availability in the litter layer is affected indirectly by the rate of ozone-induced litter fall, as well as the nitrogen content of needle tissue. The amount of litter fall was greatest from trees with moderate amounts of crown injury (Arkley and Glauser, 1980), as compared to severely injured and uninjured trees. Therefore, the total amount of nitrogen varies with litter depth and can be expected to be quite variable over the landscape depending on amounts of crown injury from tree to tree. From ozone injured trees the litter has a higher proportion of needles from younger whorls inherently higher in nitrogen content (and lower in Ca content). This undoubtedly contributes to the increased nitrogen content of litter at plots in the western portions of the San Bernardino mountains (Fenn and Dunn, 1989). The greater abundance of nitrogen in needle tissues of ponderosa pines at plots with severe crown injury may partly explain, along with the higher soil moisture-holding capacity, the ability of trees with fewer annual whorls (lower ozone injury index) to improve in stem growth in recent years (Miller et al., 1989).

Hypotheses have been offered to implicate nitrogen overloading or nitrogen saturation of forest ecosystems as a stress on these systems (Aber et al., 1989). Nihlgard (1985) describes the "ammonium hypothesis" as an

additional explanation of forest dieback in Europe. In the Netherlands a foliage yellowing of Scots pine was associated with higher levels of total nitrogen and imbalances of Mg, P, and K with respect to N (van Dijk and Roelofs, 1988). There is sufficient evidence to raise concern regarding nitrogen saturation in forest ecosystems (Aber et al.1995).

1.3 Forest Conditions in the San Bernardino National Forest

The following sections describe some important physical features of the study area.

1.3.1 Geographic Description and Soils

The San Bernardino Mountains are part of the Transverse Range Province that extends from west to east across parts of Santa Barbara, Ventura, Los Angeles, San Bernardino, and Riverside counties, California (Bailey and Jahns, 1954). The major geologic materials include gneisses, schists, plutonic rocks, sediments and recent alluvium. The most prominent material exposed is a light colored quartz monzonite of the Mesozoic age called Cactus granite (Bailey and Jahns, 1954).

The soils in the mixed conifer forests adjacent to the proposed monitoring site are coarse, mixed Typic Xerumbrepts. They are characterized by high base saturation, evidence of clay movement (an argillic horizon) and soil organic matter decreasing rapidly from the surface.

1.3.2 Meteorology and Air Quality

Life processes in the San Bernardino mountains are adapted to the summer-dry Mediterranean climate typical of southern California. More than 90 percent of the precipitation comes in the form of rain or snow between October and April as a result of large scale storms which originate in the Gulf of Alaska. The small amount of summer precipitation results from thundershower activity in August, concentrated mainly in the eastern one-third of the mountain area. During spring and early summer months the western half of the mountain area intercepts some moisture from the deep coastal fog which shrouds slopes and ridgetops below about 1800 m elevation.

1.3.3 Long Term Precipitation Record

One of the longest and most complete precipitation records (Figure 1-3) is that obtained at Big Bear Dam (2077 m elevation). The long-term average is 93.34 cm, (October 1 to September 30). The longest dry period was the seven years from 1895 to 1901, and the second longest was from 1946 to 1950. Clearly, the entire period from 1946 to 1990 had precipitation amounts generally below the average of the entire length of record. More recently, 1978-1983 had higher than average winter precipitation and 1984-1987 had lower than average winter precipitation (Miller et al., 1989).

1.3.4 Nature and Extent of Air Pollution

The most important pollutant is ozone. Other pollutants are present, including, nitrogen dioxide, peroxyacetyl

nitrate, nitric acid, ethylene and sulfur dioxide. However, concentrations of these pollutants are always much lower than ozone and specific symptoms of leaf injury have not been observed that could be traced to the individual or combined action of these pollutants. Other pollutants known to be present in the photochemical mixture include fine particulates, notably, ammonium nitrate (Bytnerowicz et al., 1987). Pollutant monitoring in the San Bernardino mountains has focused principally on ozone.

The possible effects of acidic wet deposition have not been monitored in the San Bernardino mountains. The pH of winter precipitation at 33 California sites between July 1984 and June 1986 was between 5.10 and 5.60 for 27 sites, and 4.71 to 5.02 for the 6 remaining sites which were all in urban locations in southern California (Air Resources Board, 1986). The rainfall pH in the San Bernardino mountains is probably in the 5.10 to 5.60 range, particularly because ammonia from dairy farms located between the urban source and the San Bernardino mountains tends to neutralize acids.

The situation is different for fogs that occur during the cool, moist, days (typical in late spring and occasionally in the fall). Waldman et al. (1985) found that fogs were sometimes as low as pH 1.69 in the South Coast air basin. However, specific injury symptoms on forest vegetation have not been observed that could be related to fog exposure.

The gradient of decreasing ozone concentration across the San Bernardino mountains from west to east was indicated by plotting the regression coefficients or the slopes of regressions of all other stations against the Sky Forest station (Figure 1-4). Sky Forest (SF, Figure 1-6) was chosen as a reference site because it had the longest and most complete record. The resulting scatter plots allow an estimate of the dissimilarity of ozone concentrations with distance from west to east. Another representation of these same data, in the form of 24 hr averages for the May through September period, showed that ozone injury to pines was barely detectable where the average ozone concentration was 50-60 ppb, beginning at about 30-45 km along the total 50 km length of the mountain area. Maximum amounts of tree injury were observed in the first 30 km of the transect. The highest level of injury was associated with averages of 100-120 ppb (Miller et al., 1982).

A comparison of the diurnal changes of ozone concentrations at Barton Flats (1891 m) with a basin station at Redlands (402m) indicate differences in heights of peak concentrations and times of peaks (Figure 1-5) consistent with the west to east transport of polluted air (Miller et al., 1986).

1.3.5 Vegetation Cover and Current Condition

San Bernardino mountain vegetation is a complex of closed forest, woodland, and shrub formations. The closed forest types cover large areas at elevations above 1225 m. The ponderosa pine (*Pinus ponderosa*) / Jeffrey pine (*P. jeffreyi*) series has an overstory composed of either species (sometimes both species mix along contact zones), the understory is herbaceous or shrubby. The mixed conifer series includes sugar pine (*P. lambertiana*), white fir (*Abies concolor*), ponderosa pine or Jeffrey pine, incense cedar (*Calocedrus decurrens*) and California black oak (*Quercus kelloggii*). The overstory is multistoried in dense stands and the understory growth is generally limited by excessive litter accumulation.

The forest vegetation in the vicinity of the proposed Barton Flats monitoring site is largely the

ponderosa/Jeffrey Pine type with about equal amounts of white fir and black oak.

1.3.5.1 Recent Trends in Crown Condition and Stem Growth

The principal source of data for evaluating changes in crown condition and stem growth is the group of 18 plots established for the multidisciplinary study carried out between 1973 and 1978 (Miller and Elderman, 1977; Taylor, 1980). These plots were located in the conifer forest along parallel west to east transects (Figure 1-6) corresponding to the gradient of decreasing ozone exposure (Figure 1-4). Observations and measurements were made annually between 1973 and 1978 (Taylor, 1980) and at 4-5 year intervals since 1978.

Ponderosa and Jeffrey pines in each plot served as indicators of change over time. Each plot contained a minimum of 50 ponderosa and/or Jeffrey pines in a 30 m width and a length which varied according to stand density. All stems $\geq$ 9.9 cm dbh (diameter at breast height) of all species were measured and crown condition was described (Miller and Elderman, 1977). At each observation the crown condition of individual trees was determined by close up or binocular examination of crowns to determine on average the number of annual needle whorls retained, the level of ozone symptom expression on needles of each whorl, relative needle length, and relative amount of branch mortality in the lower crown. These elements were combined to form an injury index (Miller et al., 1989).

Ozone injury as compared for 1974, 1978, and 1988 for all trees included in 15 plots to address the question of crown condition trends in the general region. For this comparison all plots were included independent of the ozone exposure variable. Trees were divided into three dbh classes (10-29.9, 30.0-59.9 and $\geq$ 60 cm) to help gain insight to the possible relationship of tree size to changes in crown injury. There were statistically significant improvements in the injury index of trees in all size classes between 1978 and 1988, but not between 1974 and 1978, except for Jeffrey pines $\geq$ 60 cm dbh (Miller et al., 1989). The latter were located at plots in the region of lowest ozone exposure. The improved crown condition in recent years appears to be related to the general decline of both average and peak ozone concentrations at a representative station, Lake Gregory.

1.4 Related Research

Mid-way through this project it became evident that the inclusion of some additional tasks could be helpful. Another proposal was prepared and submitted to the Air Resources Board for the purpose of:

1) Extending the dry deposition monitoring into an additional summer.

2) Applying a nutrient cycling model (NuCM) to the task of integrating the leaf-litter-soil data sets becoming available.

3) Measuring the seasonal course of stomatal conductance on ponderosa and Jeffrey pines of different size classes to provide a physiological basis for flux of pollutants to foliage.

4) Implementing a 2-week intensive monitoring period during July of 1993 in which dry deposition measurements were continuous. The results these tasks will be presented in a separate report.

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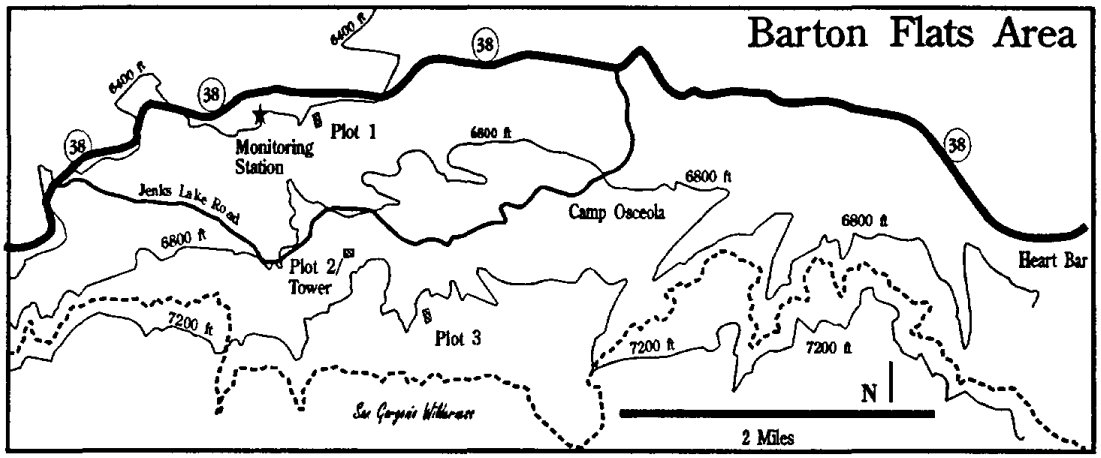
Table 1-1. Project tasks and assignments of co-investigators.

Task	Description	Institution	Investigators
1	Equipment Procurement	DRI	Chow, Watson, Frazier
2	Preparation of Site	PSW	Miller, Gomez, Jones
3	Installation of Air Monitoring Equipment	DRI/PSW	Frazier, Jones
4	Operation and Maintenance of Monitoring Site	PSW/DRI	Jones, Frazier
5	Selection of Forest Plots	PSW	Miller, Poth
6	Describe Vegetation and Soils at Plots	PSW	Miller, Poth, Glaubig
7	Assess Dry Deposition to Pine Foliage	PSW	Bytnerowicz, Glaubig
8	Through-fall Collection and Analysis	PSW	Fenn, Glaubig, Gomez
9	Foliage Nutrient Assessment	PSW	Poth, Glaubig
10	Branch Physiology	PSW	(Task not funded)
11	Annual Assessment of Foliar Condition and Leaf Litter Fall	PSW	Miller, Schilling, Jones, Gomez
12	Analyze Relationships	PSW/DRI	All investigators
13	Documentation and Technology Transfer	PSW/DRI	All investigators
14	Parameterize and Test Deposition Model	DRI	Taylor
15	Examine other Pollutants	DRI	(Task de-emphasized)
16	Relate Effects to Emission Sources	DRI	(Task de-emphasized)
17	Submit Reports	PSW/DRI	Miller, All

Figure 1-1. Map of the study area.



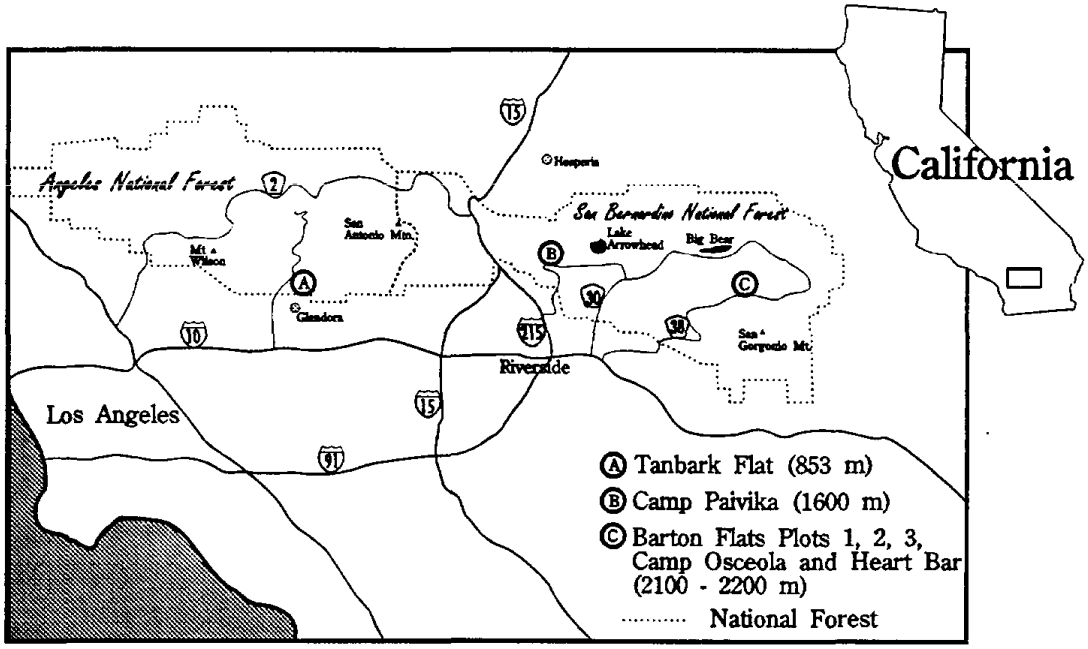


Figure 1-2. Diagramatic representation of research tasks.

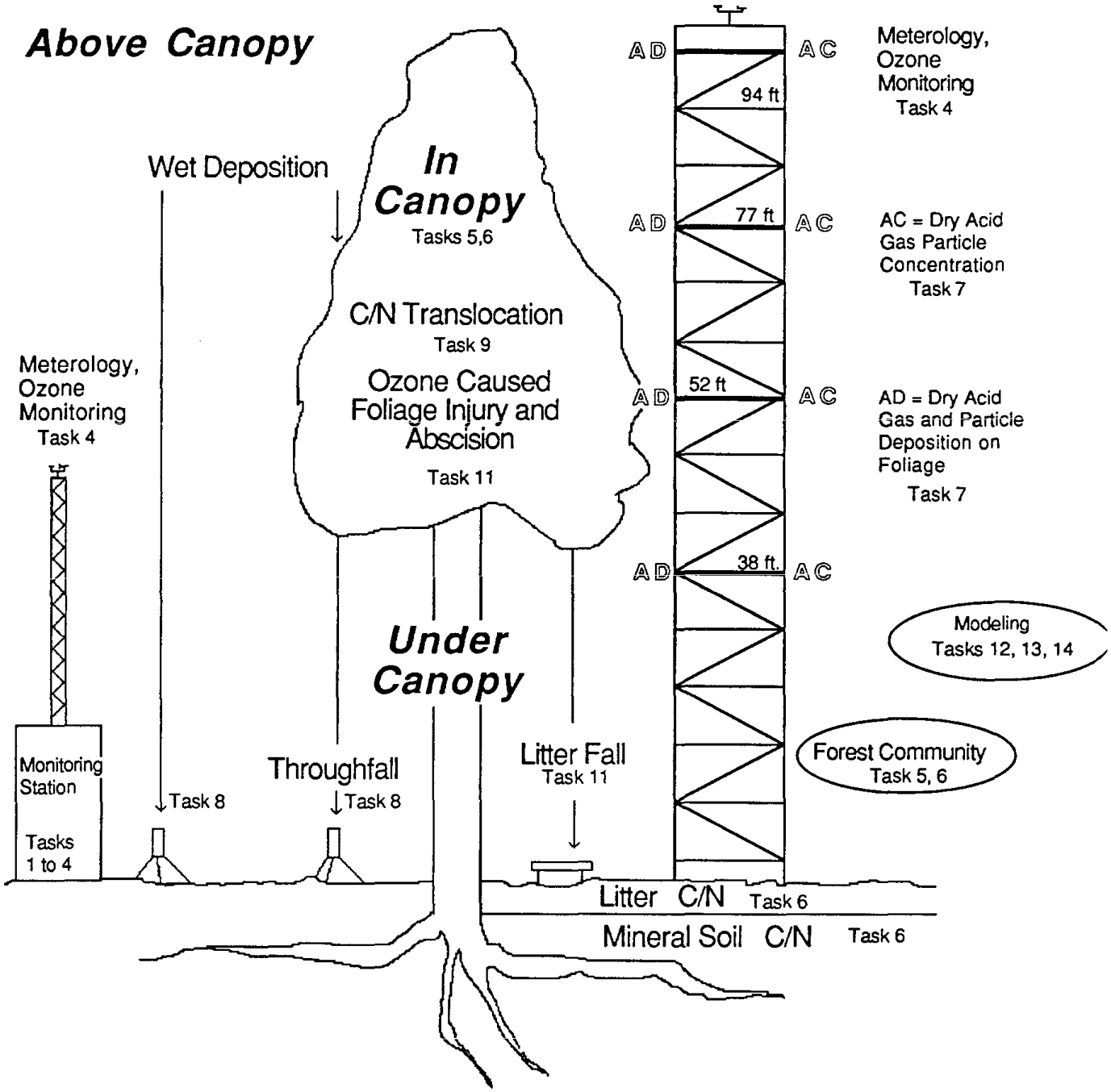


Figure 1-3. Long-term precipitation at Big Bear Dam, a site 8 km northwest of Barton Flats.

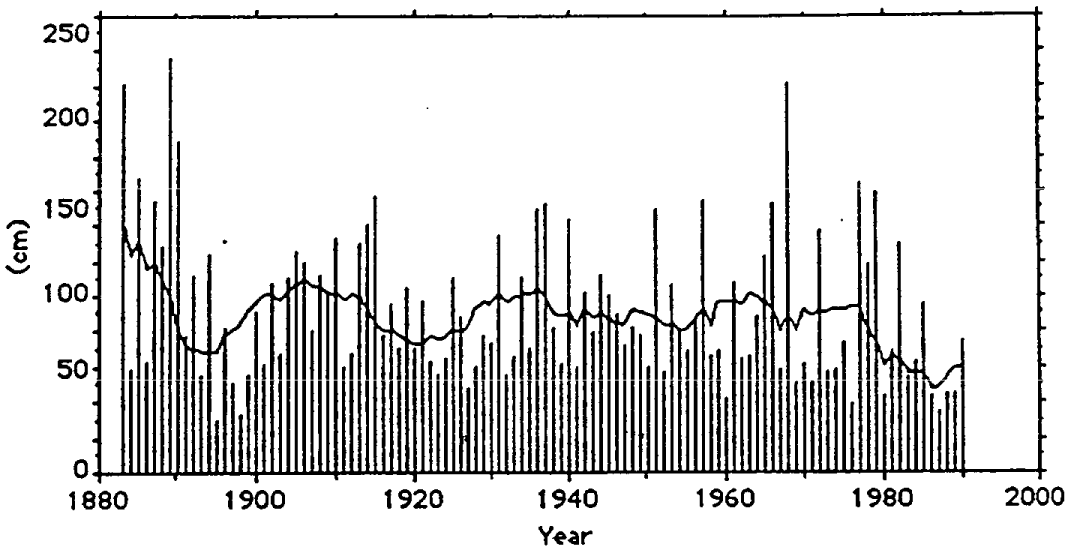


Figure 1-4. Regression coefficients (top) and slopes (bottom) from matching hourly average ozone concentrations at Sky Forest with similar data from 8 other stations in the San Bernardino Mountains indicating the west to east decreasing ozone concentration gradient (Miller et al., 1986).

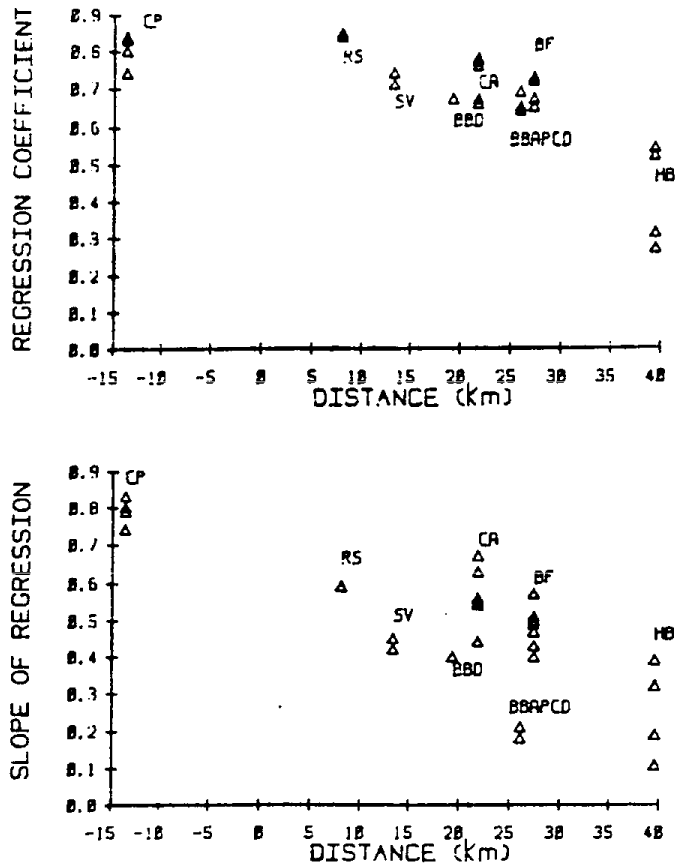


Figure 1-5. July-August, 1974-1978, average hourly ozone concentrations at adjacent basin and mountain stations, namely, Redlands (402 m) and Barton Flats (1891) m (Miller et al., 1986).

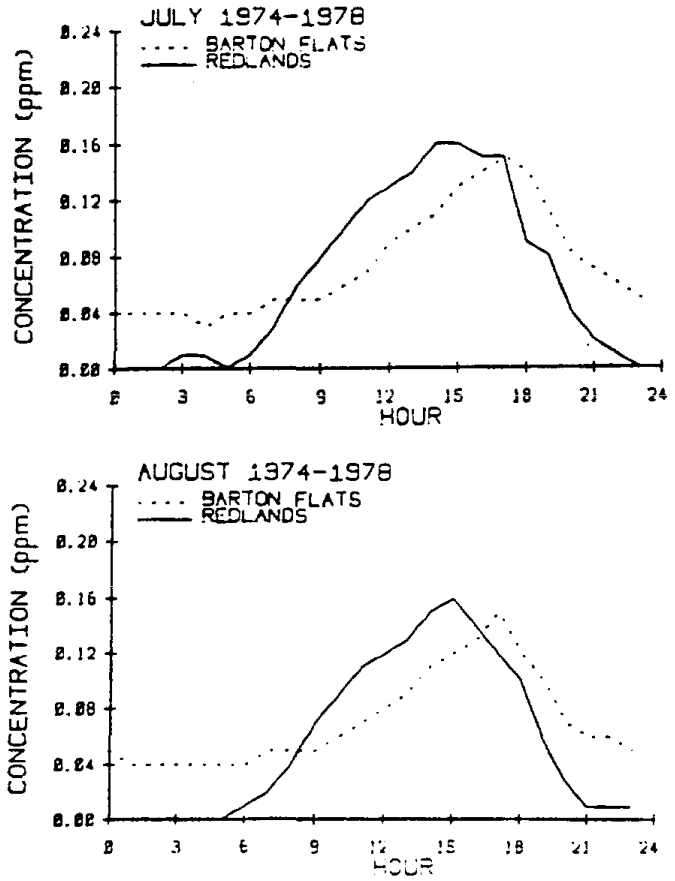
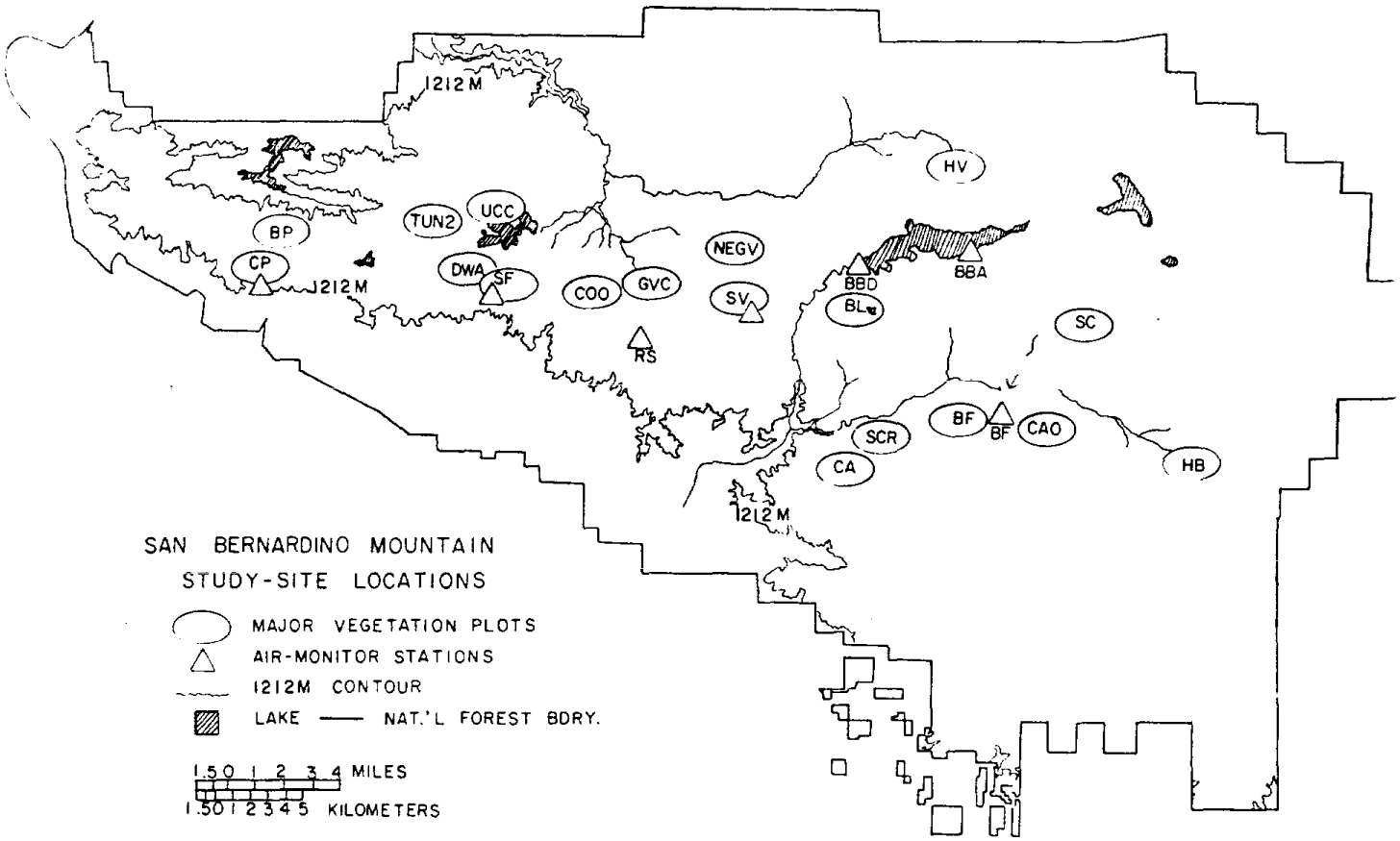


Figure 1-6. Locations of 18 forest plots in the San Bernardino Mountains used for assessing trends of ozone damage (Miller et al., 1982).



2.0 CHARACTERIZATION OF THE AEROMETRIC DATA AT THE BARTON FLATS STATION

2.1 Introduction

In order to assess the relationship between acidic species concentrations and forest effects, a series of ambient measurements were made to accomplish the following objectives to:

- Acquire a data base of specified accuracy, precision, and validity for the determination of dry and wet deposition of reactive atmospheric species in forests.
- Determine forest exposures to reactive atmospheric species over multi-year, seasonal, and daily time periods.
- Identify relationships between atmospheric concentrations and meteorological conditions that affect transport and deposition.

The following subsections document the ambient monitoring network and laboratory operations; summarize the air quality and meteorological data bases; specify the analytical accuracy, precision, and validity; examine the characteristics of chemical gaseous components and wind flow patterns; and establish relationships between ambient concentrations and meteorological conditions.

2.2 Aerometric Measurement Methods and Data Bases

Four types of aerometric measurements were acquired at the Barton Flats station between 10/30/91 and 09/30/93 and between 06/01/94 and 08/31/94. They are:

- Dry deposition measurement of reactive species in gaseous and particulate phases;
- Wet deposition measurement of pH, conductivity, and ionic species;
- Ultraviolet absorption measurement of ozone (O_3); and
- Meteorological measurements.

Table 2-1 summarizes the measurement parameters, averaging time, sampling duration and frequency, and measurement methods. Field and laboratory operations are described in the following subsections. Detailed standard operating procedures applied to this study have been completed in *Volume 2, Research Protocols* of this report and summarized in Table 2-2.

2.2.1 Field Measurements

2.2.1.1 Dry Deposition Measurements

Daytime (0600 to 1800 PST) and nighttime (1800 to next day 0600 PST) measurements were taken on U.S. Environmental Protection Agency (EPA) every-sixth-day sampling schedule between 11/02/91 and 09/28/93 and between 06/01/94 and 08/30/94 for: 1) sulfur dioxide (SO_2), ammonia (NH_3), nitrogen dioxide (NO_2), and nitric acid (HNO_3) gases on absorbing substrates; and 2) $PM_{2.5}$ mass, ammonium (NH_4^+), sulfate ($SO_4^=$), nitrate (NO_3^-) and chloride (Cl^-) on filter substrates. These filter substrate-based measurements were taken with a dry deposition sampling system.

In addition to the routine measurements daily, three-times-per-day, intensive sampling was conducted between 07/18/93 and 07/31/93 for the morning (0600 to 1200 PST), afternoon (1200 to 1800 PST), and

nighttime (1800 to next day 0600 PST) periods to assess the diurnal variations of reactive species during summer.

The dry deposition sampling system (Chow et al., 1993) was equipped with an acid-washed PFA (perfluoralkoxy) sampling surface with PFA Teflon-coated Bendix-Sensidyne Model 240 cyclone. Particles and gases were drawn through the Teflon-coated $PM_{2.5}$ inlet at a flow rate of 113 L/min into a conical plenum, where the open-faced filter packs were located.

These filter packs were connected to a vacuum manifold through differential pressure regulators. Vacuum pumps drew air through these filters when activated by the timer. The timer also switched the flow, via solenoid valves, between two identical sets of filter packs to allow for daytime and nighttime sampling of 12-hour duration without operator intervention. A total of 62 L/min was drawn through four filter packs simultaneously. In routine operation, air was drawn through the filter pack for NO_2 sampling at a flow rate of 2 L/min, and through the remaining three filter packs at a flow rate of 20 L/min apiece. The remaining flow (51 L/min) required to maintain the inlet cutpoint of 2.5 μm was drawn through an additional port in the sampling plenum. Four additional ports were provided for field blanks which were used to evaluate filter loadings during passive sampling periods and during filter handling.

For the intensive sampling period (i.e., 07/18/93 to 07/31/93), all samples except the filter pack from NO_2 sampling (remains at 2 L/min) were drawn at a flow rate of 30 L/min apiece to achieve the adequate loadings for 6- and 12-hour sampling durations.

Four separate filter packs were used for each 6- or 12-hour sample. Figure 2-1 illustrates the sample flow paths and identifies the analyses performed on each substrate.

The filter packs are labeled with a bar code prefix and color coded to assure that the proper filter pack is placed in the proper port. The bar code prefixes identify the following four configurations:

- A TK prefix designates a filter pack containing a potassium-carbonate-impregnated cellulose-fiber filter on the bottom grid, preceded by a citric acid-impregnated cellulose-fiber filter on a removable grid, and preceded by a Teflon-membrane filter on a removable grid. The filter pack sampled particulate, ammonia, and sulfur dioxide through the $PM_{2.5}$ inlet at a flow rate of 20 L/min.
- A GT prefix designates a filter pack containing a triethanolamine (TEA) impregnated cellulose-fiber filter on the bottom grid, preceded by a Teflon-coated glass-fiber filter on a removable grid. The GT filter pack sampled nitrogen dioxide through the $PM_{2.5}$ inlet at a flow rate of 2 L/min. The Teflon-coated glass-fiber filter removed nitrate particulate matter and was discarded following sampling.
- A QN prefix designates a filter pack containing a nylon-membrane filter on the bottom grid which is preceded by a quartz-fiber filter on a removable grid. The QN filter pack sampled $PM_{2.5}$ particles and gaseous nitric acid through a non-denuded $PM_{2.5}$ inlet at a flow rate of 20 L/min.
- A DN prefix designates a filter pack containing a nylon-membrane filter on the bottom grid. The airstream reaching this filter passes through an anodized annular denuder to remove gaseous nitric acid prior to reaching the filter pack. The DN filter pack sampled total particulate nitrate through a denuded $PM_{2.5}$ inlet at a flow rate of 20 L/min. The difference between the QN nitrate and the DN nitrate yields nitric acid (HNO_3) concentrations by denuder difference.

2.2.1.2 Wet Deposition Measurements

Wet deposition samples, averaged weekly, were taken at the Barton Flats station with the Aerochem Metrics precipitation collector for the sampling period between 11/05/91 and 09/28/93 and between 05/31/94 and 08/30/94. Wet deposition samples were analyzed for pH and conductivity both immediately at the field site and in the laboratory, and for Cl^-, NO_3^-, $SO_4^=$, NH_4^+, and Na^+ (soluble sodium), Mg^{++} (soluble magnesium), K^+ (soluble potassium), and Ca^{++} (soluble calcium) in the laboratory.

The modified Aerochem Metrics precipitation sampler consists of a pair of plastic buckets, one of which is covered during dry periods and the other is covered during wet periods. A water-sensitive conducting cell which was heated to melt snow moved the lid from one bucket to the other when it was wetted by rain or snow and when it dried after precipitation. The buckets were changed every Tuesday at 0900 PST for comparability with other wet deposition samples acquired in California.

If no rain occurred over the sampling week, the wet-side bucket was rinsed in 100 ml DDW and measured for pH, conductivity, and ionic species. This practice was only applied for the first year of the monitoring program to evaluate the background concentrations. If rain occurred, the bucket was weighed or measured in a graduated cylinder (depending on volume), then 5 ml (or less, if there was insufficient quantity) was transferred to a clean sample vial for pH and conductivity measurements in the field. The remaining precipitation sample was then transferred to a clean, labeled polystyrene bottle for shipment to the laboratory. The dry-side bucket was cleaned monthly in the field. The wet-side bucket was washed in DDW, dried in the laboratory, and returned to the sampling system. A Belfort Universal Recording rain gauge was collocated with the Aerochem Metrics sampler to obtain hour-to-hour changes in precipitation as well as total precipitation throughout each event.

2.2.1.3 Continuous Ozone Measurement

Ozone (O_3) concentrations, averaged hourly, were obtained from the Dasibi Model 1008AH Ozone Analyzer, which measures O_3 with ultraviolet (UV) absorption spectrophotometry. This instrument measures the amount of ultraviolet (UV) radiation absorbed by molecular ozone in a sample of ambient air. Maximum 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.

2.2.1.4 Meteorological Measurements

Hourly averaged wind speed, wind direction, atmospheric stability, temperature, relative humidity, solar radiation, and leaf wetness were obtained with Campbell Scientific and Met-One meteorological instruments and Campbell 21X data acquisition system.

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 switch closure signal whose frequency is proportional to wind speed. The data acquisition system converts the frequency to wind speed.

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 zero degree. Meteorological wind direction is defined as the direction from which the wind is coming. The 0-360° signal from the potentiometer is read by the data acquisition system as a continuously varying resistance and converted to angle.

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

Ambient temperature is measured by the electrical resistance of a thermistor housed in an aspirated radiation shield. Electrical resistance of the thermistor varies directly with temperature and read by the data acquisition system. Relative humidity is determined by the electrical resistance of a humidity sensor. The datalogger converts resistance to relative humidity using a fifth order polynomial. Dew point is calculated from ambient temperature and relative humidity values, using an equation reported by Robinson (1993):

$$DP = ((RH/100)^{1/8} \times (201.8 + 1.62 \times T) - 201.8 + 0.18 \times T)/1.8$$

where DP = dew point (°C)

RH = relative humidity (%)

T = ambient temperature (°C).

The sensor used to measure total direct and indirect solar radiation in the hemisphere above the horizon is a silicon photodiode (pyranometer) that generates an electrical current in the presence of sunlight. The generated solar radiation current is translated into units of energy flux (watts/m^2) and recorded by the data acquisition system.

Leaf wetness is measured using a printed circuit board with closely-spaced copper traces. As water bridges the circuit traces, resistance across the sensor decreases, leading to current flow through the sensor. The data acquisition system records current output from the sensor as a wet sensor condition. Data is processed by the data acquisition system to indicate the fraction of each hour that the sensor was wet.

2.2.2 Laboratory Measurements

Figure 2-2 shows the filter processing and chemical analysis activities for these gas/aerosol filter pack samples. Analogous procedures were carried out for the wet deposition samples.

2.2.2.1 Substrate Preparation

The substrates used for this study are as follows:

- Gelman (Ann Arbor, MI) polymethylpentane support ring, 2.0 μm pore size, 47 mm-diameter PTFE Teflon-membrane filters (#R2PI047) for $PM_{2.5}$ particle mass measurement;
- Schleicher and Schuell (Keene, NH) 1.2 μm pore size, Grade 66, 47 mm-diameter nylon-membrane filters (#00440) for volatilized particulate nitrate as well as total nitrate;

- Pallflex (Puttnam, CT) 47 mm-diameter Teflon-coated glass fiber filters (#TX40HI20) for removing particles;
- Pallflex (Puttnam, CT) 47 mm-diameter quartz-fiber filters (#2500 QAT-UP) for chloride, nitrate, sulfate, and ammonium measurements;
- Whatman No. 41 (Hillsboro, OR) 47 mm-diameter cellulose-fiber filters (#1441047) impregnated with citric acid for ammonia measurements and with potassium carbonate for sulfur dioxide measurements;
- Whatman #31 ET Chrome (Hillsboro, OR) 47 mm-diameter chromatography paper impregnated with triethanolamine (TEA) for nitrogen dioxide measurements.

Sample pretreatment for the dry deposition measurements includes the following:

- Washing Nylon-Membrane Filters. Nylon-membrane filters absorb nitric acid over time. Blank nylon filters were soaked for four hours in 0.015 M sodium carbonate (Na_2CO_3), then rinsed in DDW for 10 minutes, soaked overnight in DDW, rinsed three times in DDW, then dried in a vacuum oven at 60°C for 5 to 10 minutes. Extraction efficiency tests have shown that the sodium carbonate ion chromatographic eluent is needed to remove nitrates from the active sites of the nylon-membrane filter. Sets of washed nylon-membrane filters with nitrate levels exceeding 1 μg/filter were rejected. Pre-washed nylon-membrane filters were sealed and refrigerated prior to preparation for field sampling.
- Equilibrating Teflon-Membrane Filters. On several occasions, batches of Gelman ringed Teflon-membrane filters have exhibited significant (up to 100 μg/filter over a few days) weight loss after removal from manufacturer's packaging. As the time from manufacture increases, this variability decreases. Since Gelman, Inc. has minimized its long-term inventory of these filters and has manufactured them on an as-ordered basis, this variability has been observed with greater frequency. A one-month storage period of separated filters in a controlled environment followed by one week of equilibrium in the weighing environment were applied to these filters, and this appears to have reduced the variability to acceptable limits (within $\pm$ 15 μg/filter) for re-weights of 47 mm filters.
- Impregnating Cellulose-Fiber Filters. Small stacks of cellulose-fiber filters were placed into the impregnating solution contained in a Teflon jar. The jar and its contents were shaken to distribute the solution throughout the filters. The filter stacks were then placed in a Hirsch funnel attached to a vacuum flask and excess solution was drawn from them. The wet filter stacks were transferred to a container for vacuum drying. Impregnated filters were placed in a plastic Zip-loc bag and identified with the manufacturer's lot number. The Zip-loc bags were then placed in an air-tight container and refrigerated until use. The solutions for impregnating the filter substrate consist of:

- 15% potassium carbonate (K_2CO_3) and 5% glycerol solution (balance being water for sulfur dioxide sampling.
- 25% citric acid and 5% glycerol (balance being water) for ammonia sampling.
- 25% triethanolamine (TEA), 4% ethylene glycol, 25% acetone, and 46% water for nitrogen dioxide sampling.

2.2.2.2 Filter Pack Assembly and Disassembly

Filters were inspected visually at the time of filter pack assembly. Filter pack identification codes were assigned when the packs were assembled and labels bearing these codes were affixed to each filter pack.

The inlets and outlets of the filter packs were capped after assembly to prevent contamination prior to sampling. Eight filter packs were loaded into a carrying case (for day and night sampling) for shipment to the field site. Additional carrying cases were needed for dynamic blanks. An inventory log sheet was included with each set of filter packs.

After field sampling and receipt at the laboratory, filter packs were unloaded and the filters were placed in separate Petri dishes. Each filter was inspected visually and any anomalies were recorded on the accompanying field log sheets. The Petri dishes were assigned laboratory identification codes with duplicate bar code labels affixed to the dishes. These codes and the identification code for the filter pack were entered into a filter pack disassembly data system using optical bar code readers. The dishes were stored in a freezer prior to chemical analysis.

2.2.2.3 Gravimetric Analysis

Unexposed and exposed Teflon-membrane filters were equilibrated at 20 $\pm$ 5 °C and 30 $\pm$ 5% relative humidity for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electromicrobalance with $\pm$ 0.001 mg sensitivity. The charge on each filter was neutralized by a polonium source for 30 seconds prior to being placed on the balance pan.

The balance was calibrated with 20 mg Class M weight and the tare was set prior to weighing each batch of filters. After every 10 filters were weighed, the calibration and tare were re-checked. If the results of these performance tests deviated from specifications by more than $\pm$ 5 μg, the balance was recalibrated and the previous 10 samples were re-weighed. At least 30% of the weights were checked by an independent technician and samples re-weighed if these check-weights did not agree with the original weights within $\pm$ 15 μg. Pre- and post-weights, check weights, and re-weights (if required) were recorded on data sheets as well as being entered into a data base via RS232 connection.

2.2.2.4 Sample Sectioning, Extraction, and Archiving

Quartz-fiber filters were cut in half using a precision jig. One half was returned to the Petri dishes and the other half was placed in a Falcon (#2045) 16 x 150 mm polystyrene extraction vial. Whole nylon-membrane and impregnated cellulose-fiber filters were also placed in vials. One of the duplicate bar code labels attached to each Petri dish was removed and attached to the corresponding extraction vial.

The extraction vials were capped, sonicated for 60 minutes, and shaken for 60 minutes. Samples were stored in the refrigerator overnight prior to analysis to assure that all soluble species had been extracted from the filters and all filter fragments had precipitated to the bottom of the extraction vials.

2.2.2.5 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate

Approximately 5 ml of the quartz-fiber, nylon-membrane, and potassium carbonate-impregnated cellulose-fiber filter extracts and 5 ml of the precipitation samples were submitted to ion chromatographic analysis of

chloride, nitrate, and sulfate on a Dionex 2020 system operating at a flow rate of 1.5 ml/min provided by a nominal 1,000 psi pressure.

The anion analysis system contains an anion separator column (AS4A column Cat. No. 38019) with a strong basic anion exchange resin, and an anion micro-membrane suppressor column (250 x 6 mm ID) with a strong acid ion exchange resin. The anion eluent consists of 0.0045 M $NaHCO_3$ and 0.0018 M Na_2CO_3 prepared in DDW. This DDW is verified to have a conductivity of less than 10^{-7} ohm^{-1} cm^{-1} prior to preparation of the eluent.

Standard solutions of NaCl, KNO_3, and $(NH_4)_2SO_4$ were prepared with reagent grade salts which were dehydrated in a desiccator several hours prior to weighing. These anhydrous salts were weighed to the nearest 0.010 mg on a regularly calibrated analytical balance under controlled temperature (- 20 °C) and relative humidity ($\pm$40%) conditions. These salts were diluted in precise volumes of DDW. A standard solution was prepared monthly and stored in a refrigerator.

Calibration solutions were prepared daily by diluting the standard solution to concentrations covering the range of concentrations expected in the filter extracts. The calibration concentrations prepared were at baseline, 10%, 50%, 75%, and 100% of instrument full-scale setting. These transfer standards are traceable to NBS weights and volumes via the mass and volume measurements from which the standardized values were derived.

Calibration was performed before the sample run. The ions were identified by matching the retention times of each peak in the unknown sample with each peak in the chromatogram of the standard.

A DDW blank and a performance test standard were alternated every tenth specimen as quality control checks on baseline and calibration, respectively. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations on the baseline level or 5%), all of the samples between that standard and the previous performance test standard were reanalyzed. The Dionex IC is capable of measuring ions with 5 to 10 ppb detection limits for 0.5 ml sample volumes.

2.2.2.6 Automated Colorimetric Analysis for Nitrite and Ammonium

A Technicon TRAACS 800 System was used to measure ammonium on quartz-fiber and citric acid impregnated cellulose-fiber filter extracts for ammonium analysis and TEA-impregnated cellulose-fiber filter extracts for nitrite analysis.

Approximately 5 ml of filter extracts were submitted for ammonium and nitrite measurements and 5 ml of the precipitation samples were submitted for ammonium measurements.

Ammonium is reacted with phenol and alkaline sodium hypochlorite to produce indophenol, a blue dye. The reaction is catalyzed by the addition of sodium nitroprusside. The absorbance of the solution is measured at 630 nm.

Nitrate is reduced by hydrazine to nitrite, which reacts with sulfanilamide in an acidic solution to form a diazonium compound. This compound then couples with N-1 Naphthyl-ethylenediamine dihydrochloride to form a reddish-purple azo dye, which is measured colorimetrically at 520 nm.

Extraction vials are placed directly into the Technicon automatic sampler, which can accommodate 120 vials.

The sampler does not have to sample the vials sequentially. Instead, it is capable of accessing any vial at any time. Therefore, a single set of standards can be placed in the sampler for one run, and the standards can be reanalyzed at any time during the run. Similarly, any other analysis of any filter extract can be repeated without the necessity of loading the extract into more than one vial.

2.2.2.7 Atomic Absorption Analysis for Soluble Sodium, Magnesium, Potassium, and Calcium Ions

A Perkin Elmer Model 2380 Double Beam Atomic Absorption Spectrophotometer (AAS) was used to analyze soluble sodium (Na^+), magnesium (Mg^{++}), potassium (K^+), and calcium (Ca^{++}) ions in the precipitation samples. A standard calibration curve was established for each element before performing sample analysis. For instance, the stock solution of sodium (Na^+) was prepared by dissolving 2.542 g of dehydrated sodium chloride (analytical reagent grade) in a liter of DDW. The dilutions of the stock solution to be used as calibration standards were prepared daily prior to sample analysis. An oxidizing flame with air and acetylene was required with a sodium hollow cathode tube to measure the sodium absorption at 586 nm. Ionization was suppressed by addition of cesium (Cs) (final concentration 1,000 mg/ml) to samples and standard solutions. Similarly, magnesium, potassium, and calcium ions were analyzed by atomic emission at 279.1 nm, 766.5 nm, and 317.0 nm, respectively, in an air-acetylene flame.

Matrix effects by other components of samples and ions in solution can reduce the tendency to atomize. Standards with compositions similar to those being analyzed were used to minimize these biases. The precision of AAS is on the order of 1 to 2% (Smith, 1983).

2.2.2.8 pH and Conductivity Analysis

The pH and conductivity measurements were taken on the weekly precipitation samples (both in the field and in the laboratory) to measure the hydrogen ion concentration and electrical conductivity, respectively.

The pH meter uses the difference in electrical potential occurring between the sample solution and the electrode solution to measure the hydrogen ion concentrations (H^+). The pH meter consists of a pair of electrodes connected to a meter capable of measuring small voltages, on the order of millivolts. A voltage, which varies with the pH, is measured when the electrodes are placed in a solution. This is then converted into pH units in which the meter is calibrated. Acidic solutions have a pH less than 7.00, basic solutions have a pH greater than 7.00, and neutral solutions have a pH of 7.00. pH measurement is temperature dependent, therefore it is important that all solutions used in pH measurement be at the same temperature. VWR buffer solutions with a pH of 4.0, 7.0, and 10.0 were used in this study to calibrate the pH meter.

Conductivity is the measure of an aqueous solution's ability to conduct electricity. It depends on the concentration of ions present in the solution, their mobilities and valences, and the temperature at which the measurement is made. Conductance is determined by measuring the ratio of electrical current through a cell immersed in the aqueous sample to the applied voltage. The standard unit of electrical conductance is the siemens (or the mho), which is the inverse of electrical resistance in ohms (R). Conductivity is determined by multiplying the measured solution conductance by the cell constant K. American Chemical Society (ACS) reagent grade potassium chloride (KCl) was used to prepare 0.0005 M KCl working standard solution for instrument calibration.

2.2.3 Data Base and Data Validation

One of the objectives of this study is to acquire a data base of ambient $PM_{2.5}$ and gas concentrations, wet deposition measurements, and meteorological measurement data with specified precision, accuracy, and validity. Numerous air quality studies have been conducted over the past decade, but the data obtained are often not available or are of limited usefulness because the data bases lack documentation with regard to sampling and analysis methods, quality control/quality assurance procedures, accuracy specifications, precision calculations, and data validity. Lioy *et al.* (1980), Chow and Watson (1989), and Watson and Chow (1992) summarize the requirements, limitations, and current availability of ambient data bases in the United States. The dry deposition, wet deposition, and meteorological data bases for this study was designed to meet these requirements. The data base files have the following attributes:

- They contain the ambient dry deposition, wet deposition, and meteorological observables needed to assess acidic species deposition;
- They are available in a well-documented computerized form accessible by personal computers;
- Measurement methods, location, and schedules are documented;
- Quality control and quality audits are documented;
- Precision and accuracy estimates are reported; and
- Validation flags and comments are included.

Two different types of data base files result from the measurement program. They are: 1) data files, and 2) documentation files. Data files contain sample identification, measurement results, validation flags, and comments for each collected sample. Documentation files provide the information necessary to interpret and use results contained in the data files. Documentation files include a project description file, a database structure documentation file for each data base file, and validation flag definition files.

Data base files are organized according to measurement type and include the following three categories:

- $PM_{2.5}$ ambient aerosol mass and ionic species concentrations and ambient gaseous species concentrations (dry deposition);
- Wet deposition ionic species concentrations, conductivity and pH, as well as precipitation amounts; and
- Meteorological parameters and ambient ozone concentration.

This sub-section introduces the features, structures, and contents of the aerometric data base. The approach which was used to obtain the final data base is illustrated in Figure 2-3. Detailed data processing and data validation procedures are documented in the standard operating procedures entitled "Dry Deposition Field, Mass, and Chemical Data Processing and Data Validation" and "Meteorological and Continuous Gaseous Data Processing and Validation." These procedures are included in *Volume 2, Research Protocols* of this report. The data described in this sub-section are available for downloading by file transfer protocol (ftp) via Internet for convenient distribution to data base users.

2.2.3.1 Data Base Structures and Features

FoxPro for Windows 2.5 (Fox Software, Inc., 1991), a relational data base management system which is

commercially available for implementation on microcomputers, was used to document and compile the measurements. It can accommodate 256 fields of up to 4,000 characters per record and up to one billion records per file. This system can be implemented on most IBM PC-compatible desk-top computers. The data base files can also be read directly into a variety of popular statistical, plotting, data base, and spreadsheet programs without having to use any specific conversion software.

The structure of each data base file was established by first defining the fields for data to be stored. One of five field types, namely character, date, numerical, logical, or memo, can be assigned to each observable. Sampling sites and particle size fractions are defined as "Character" fields, sampling date is defined as a "Date" field, and measured data are defined as "Numeric" fields. "Logical" fields are used to represent a "yes" or "no" value applied to a variable, and "Memo" fields are designed to accommodate large blocks of textual information and can be used to document the data validation processes.

FoxPro data base files use the Xbase standard ".DBF" file format, and can be read by other Xbase programs. The ".DBF" files contain data for all field types except memo fields. For data base files that have one or more memo fields, FoxPro stores the memo field data in a separate file with the same root name as the ".DBF" file, but with an ".FPT" extension. FoxPro cannot read the ".DBF" file unless the ".FPT" file is present on the same disk. Memo file structures are not standardized among the various Xbase languages, but FoxPro can translate its memo files to other Xbase versions.

Data contained in different FoxPro files can be linked by indexing on and relating to common attributes in each file. Sampling date, sampling period, and filter pack IDs are the common fields among various data files which are used to relate data in one file to the corresponding data in another file.

To assemble the final data files, information was merged from many data sets derived from field monitoring and laboratory analyses by relating information on the common fields cited above. Detailed explanations and programming techniques for manipulation of this data base in FoxPro are presented by Christensen et al. (1989).

2.2.3.2 Data Base Documentation Files

Project documentation files for this study are listed in Table 2-3 and are described below:

- File README.DOC is a Microsoft Word 6.0 file that presents a brief overview of the scope of the project and the study objectives. It also describes the sampling location and provides the measurement periods for the dry deposition, wet deposition, and meteorological measurements. In addition, this file lists all the data base documentation and data files with brief descriptions of the data contained in each file. README.TXT is an ASCII text version of the file.
- File FOFLDNAM.DBF provides the field names, their definitions, data type and format and measurement units that are utilized in the data base files. The structure of this file is shown in Table A2-1 of Appendix 2 of this report.
- The data base structures and their definitions for both dry and wet deposition measurements are contained in the data documentation files DRYSTRU.TXT and WETSTRU.TXT, respectively. Data base structure for the meteorological and ozone data is documented in METSTRU.TXT. Structures for supplementary meteorological files are contained in files SCMTSTRU.TXT and

SCSTSTRU.TXT for meteorological data and site information acquired in California's South Coast Basin, respectively. These files duplicate some of the information in FOFLDNAM.DBF, but allow an easy way to print the file structure definitions. The content of these files is also included as Tables A2-2 through A2-6 in Appendix 2 of this report. The data base structure documentation files are updated when changes are made in the data base. Users should review the current documentation on the set of disks containing the data base since this documentation may differ from the tables presented in Appendix 2.

- Field sampling validation flag definitions are provided in ASCII text file FLDFLAG.TXT, and analysis validation flag definitions are provided in file CHMFLAG.TXT. Meteorological/ozone validation flags are defined in file METFLAG.TXT. Flag definitions are also provided as Tables A2-7, A2-8 and A2-9, respectively, in Appendix 2.

2.2.3.3 Data Base Description

The aerometric data base for this study consists of one .DBF file for each of three measurement systems used at the Barton Flats station (i.e., dry deposition, wet deposition and meteorology/ozone), two .DBF files for supplemental South Coast meteorological data, plus a number of documentation files. Table 2-3 summarizes both the validated data files and the documentation files that constitute the dry and wet deposition and meteorological data base. File structures and field name definitions for each data base file are detailed in Tables A2-2 through A2-6 in Appendix 2 of this report. These tables also state the number of records, most recent file modification date, missing value code, and data precisions for the ambient data. File structures and field name definitions are also provided in Xbase format in file FOFLDNAM.DBF.

Flag fields and a comment field are included as part of the data base structure and are used to document sample validity. Flags are entered to document sampling problems or sample properties that may affect analysis results. If one of the pre-defined flags does not fully describe a particular sample, explanatory comments are added to the comment field. There is one field flag field for each of four filter pack types, and one analysis flag for each laboratory measurement method. Field flags are assigned during sample login and unloading based on field data sheet entries and filter pack appearance. Analysis flags are assigned during sample sectioning, extraction, and analysis procedures.

2.2.3.3.1 Dry Deposition Data Base

The dry deposition data base is contained in file FOCON.DBF and its associated memo file FOCON.FPT. Each observable is identified by a separate field in the file. Field names are derived from simple naming conventions to allow one to understand their meaning without constant reference to the definition table. Filter pack ID fields are four characters, with the first two characters indicating the filter pack type (i.e., "TK" = Teflon-membrane/citric acid impregnated/K_2CO_3 impregnated, "GT" = Teflon-coated glass-fiber/triethanolamine impregnated, "QN" = quartz-fiber/nylon-membrane, and "DN" = denuded nylon-membrane). The last two characters are "ID." Field flag field names are five characters, with the first two indicating filter pack type and the last three "FLG." Sample volume field names use the same filter pack type codes followed by "VOC" for volume or "VOU" for volume uncertainty. Field names for mass or chemical concentrations are four or five characters derived from the following pattern: The first two characters represent the measurement species (i.e., "MS" = mass, "CL" = Cl^-, "N3" = NO_3^-, "S4" = $SO_4^=$, "N4" = NH_4^+, "NH" = NH_3, "SO" = SO_2, and "NO" = NO_2). The third character designates

the analysis method (i.e., "G" = gravimetry, "I" for = chromatography and "C" = automated colorimetry). For species measured on backup filters or denuded filters, the fourth character is "B" or "D", respectively. The last character is "C" for concentration fields or "U" for concentration uncertainty fields. Analysis flag field names are the same as concentration field names except that the last character is "F" and the first two characters for the anion analysis flag (which applies to measurement of Cl^-, NO_3^- and $SO_4^=$) is "AN."

File FOCON.DBF contains the $PM_{2.5}$ mass and chemical concentrations and gaseous species concentrations and their propagated uncertainties as measured on samples collected with the dry deposition sampling system. Daytime (0600 to 1800 PST) and nighttime (1800 to next day 0600 PST) 12-hour samples were collected from 11/02/91 to 09/28/93 and from 06/01/94 to 08/30/94 on the U.S. EPA every-sixth-day sampling schedule. The file also contains data for the intensive sampling period which consisted of three samples (i.e., 0600 to 1200 PST, 1200 to 1800 PST, and 1800 to next day 0600 PST) collected daily from 07/18/93 through 07/31/93. The data base structure of this file is described in Table A2-2 of Appendix 2 of this report.

$PM_{2.5}$ mass and chemical analyses for chloride (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), and ammonium (NH_4^+) were performed on each valid sample. In addition, NO_3^- acquired on a backup nylon-membrane filter and on a nylon-membrane filter behind a nitric acid (HNO_3) denuder was measured to determine nitric acid concentration; NH_4^+ collected on a citric acid-impregnated filter was measured to determine gaseous ammonia (NH_3) concentration; $SO_4^=$ collected on a potassium carbonate-impregnated filter was measured to determine gaseous sulfur dioxide (SO_2) concentration; and nitrite (NO_2^-) collected on a triethanolamine-impregnated filter was measured to determine gaseous nitrogen dioxide (NO_2) concentration.

2.2.3.3.2 **Wet Deposition Data Base**

The wet deposition data base is contained in file FOWET.DBF and its associated memo file FOWET.FPT. Field name conventions are similar to the dry deposition data base, with the addition of more chemical species codes (i.e., "NA" = Na^+, "MG" = Mg^{++}, "KP" = K^+ and "CA" = Ca^{++}) and an additional analysis method code ("A" = atomic absorption spectrophotometry).

File FOWET.DBF and its associated memo file FOWET.FPT contain the wet deposition sample data for samples collected from 11/05/91 through 09/28/93 and from 05/31/94 through 08/30/94. Daily and weekly precipitation amounts collected with a Belfort rain gauge are also included in this file. The data base structure of this file is described in Table A2-3 of Appendix 2 of this report.

Samples for which no precipitation occurred were treated as "rinse blanks" by adding DDW to the empty collection bucket. Some of the rinse blank samples were analyzed to obtain background or blank concentration data. Chemical analyses for chloride (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), ammonium (NH_4^+), sodium (Na^+), magnesium (Mg^{++}), potassium (K^+), and calcium (Ca^{++}) were performed on each valid sample. In addition, pH and conductivity measurements were performed on each sample in the field after collection, and later in the laboratory.

2.2.3.3.3 **Meteorological Parameter and Ozone Data Base**

Files FOMET.DBF and FOMET.FPT contain hourly-averaged meteorological and ozone data based on readings taken every two seconds. Data were collected from 10/30/91 to 11/30/94. The data base structure

of the meteorological/ozone data is illustrated in Table A2-4 of Appendix 2 of this report.

The hourly meteorological data base files contain the following parameters: 1) scalar wind speed, 2) vector wind speed, 3) scalar wind direction, 4) vector wind direction, 5) sigma theta (atmospheric stability), 6) maximum wind speed, 7) minimum wind speed, 8) temperature, 9) relative humidity, 10) leaf wetness, 11) solar radiation, and 12) ozone concentration. The data produced by the Campbell datalogger includes the year (field YRCC) and Julian day (i.e., day of the year, field JDAT), and time at the end of the hourly average observation period (field HEC). Data in these fields was used to create DATE (date in MM/DD/YY format) and HR (time in hours at beginning of averaging period) fields. In addition, a "fractional date" field (FDAT) which is the "Julian day + HR/24" was added to facilitate time series plotting.

2.2.3.3.4 Supplemental Meteorological Data Base

Meteorological data were acquired from the South Coast Air Quality Management District for 33 sites in California's South Coast Basin. These data are reported in file SCMET.DBF, which includes hourly average measurements of vector wind speed, vector wind direction, temperature, and relative humidity for 11/01/91 through 10/31/93. Not all parameters are available at all of the sites or for all dates. Field STATION in this file specifies the South Coast Air Quality Management District site number. File SCSITES.DBF provides the site name and location for each field STATION. The data base structure of SCMET.DBF and SCSITES.DBF are given in Tables A2-5 and A2-6 in Appendix 2 of this report.

The supplemental South Coast meteorological data was not validated or flagged using the procedure employed for the Barton Flats data. However, the data were checked for reasonableness, and it was discovered that at random time intervals anomalous high wind speed values occurred at all sites during the same day and hour. These values result from a problem in the data downloading procedure, and occur once every one or two weeks (Miller, 1994). These invalid data were all identified and changed to the missing data value code.

2.3 Results

2.3.1 Analytical Specifications for the Dry and Wet Deposition Data Base

Every measurement consists of four attributes: 1) a value; 2) a precision; 3) an accuracy; and 4) a validity (Hidy *et al.*, 1985; Watson *et al.*, 1989). The measurement methods described in Section 2.2.2 are used to obtain the value. Performance testing via regular submission of standards, blank analysis, and replicate analysis are used to estimate precision. These precisions are reported within the data bases described in Section 2.2.3 so that they can be propagated through air quality models and used to evaluate how well different values compare with one another. The submission and evaluation of independent standards through quality audits are used to estimate accuracy. Validity applies both to the measurement method and to each measurement taken with that method. The validity of each measurement is indicated by appropriate flagging within the data base, while the validity of the methods has been evaluated in this study by a number of tests.

The precision, accuracy, and validity of the dry and wet deposition measurements are defined as follows:

- **A measurement** is an observation at a specific time and place which possesses four attributes: 1) value-the center of the measurement interval; 2) precision-the width of the measurement interval; 3) accuracy-the difference between measured and reference values; and 4) validity-the

compliance with assumptions made in the measurement method.

- **A measurement method** is the combination of equipment, reagents, and procedures which provide the value of a measurement. The full description of the measurement method requires substantial documentation. For example, two methods may use the same sampling systems and the same analysis systems. These are not identical methods, however, if one performs acceptance testing on filter media and the other does not. Seemingly minor differences between methods can result in major differences between measurement values.

- **Measurement method validity** is the identification of measurement method assumptions, the quantification of effects of deviations from those assumptions, the ascertainment that deviations are within reasonable tolerances for the specific application, and the creation of procedures to quantify and minimize those deviations during a specific application.

- **Sample validation** is accomplished by procedures which identify deviations from measurement assumptions and the assignment of flags to individual measurements for potential deviations from assumptions.

- **The comparability and equivalence** of sampling and analysis methods are established by the comparison of values and precisions for the same measurement obtained by different measurement methods. Interlaboratory and intralaboratory comparisons are usually made to establish this comparability. Simultaneous measurements of the same observable are considered equivalent when more than 90% of the values differ by no more than the sum of two one-sigma precision intervals for each measurement.

- **Completeness** measures how many environmental measurements with specified values, precisions, accuracy's, and validities were obtained out of the total number attainable. It measures the practicality of applying the selected measurement processes throughout the measurement period. Data bases which have excellent precision, accuracy, and validity may be of little utility if they contain so many missing values that data interpretation is impossible.

A total of 51 periods of weekly wet deposition samples and a total of 146 daytime and nighttime dry deposition sample pairs and 14 sets of morning, afternoon, and nighttime dry deposition sample sets were acquired from the field campaign. Samples were submitted for comprehensive chemical analyses which resulted in nearly 4,000 data points as documented in Section 2.2.3.

- A data base with numerous data points such as that in this study requires detailed documentation of precision, accuracy, and validity of the measurements. This section addresses the procedures followed to define these quantities and presents the results of those procedures.

2.3.1.1 Precision

Dry and wet deposition measurement precisions reported in the data bases are propagated from precisions of the volumetric measurements, the chemical composition measurements, and the field blank variability using the methods of Bevington (1969). The following equations are used to calculate the precision associated with filter-based measurements:

$$C_i = (M_i - B_i)/V \qquad (2\text{-}1)$$

$$V = F \times t \qquad (2\text{-}2)$$

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij} \quad for\ B_i > \sigma_{Bi} \qquad (2\text{-}3)$$

$$B_i = 0 \quad for\ B_i \le \sigma_{Bi} \qquad (2\text{-}4)$$

$$\sigma_{Bi} = STD_{Bi} = [\frac{1}{n}\sum_{j=1}^{n}(B_{ij} - B_i)^2]^{0.5} \qquad (2\text{-}5)$$

$$\sigma_{B_i} = SIG_{B_i} = [\frac{1}{n}\sum_{j=1}^{n}(\sigma_{Bij})^2]^{0.5} \quad for\ STD_{Bj} \le SIG_{Bi} \qquad (2\text{-}6)$$

$$\sigma_{C_i} = [\frac{(\sigma_{Mi}^2 + \sigma_{Bi}^2)}{V^2} + \frac{\sigma_V{}^2 (M_i - B_i)^2}{V^4}]^{0.5} \qquad (2\text{-}7)$$

$$D_{Mij} = \frac{|M_{ijf} - M_{ijr}|}{0.5(M_{ijf} + M_{ijr})} \qquad (2\text{-}8)$$

$$D_{Mi} = \frac{1}{n}\sum_{j=1}^{n} D_{Mij} \qquad (2\text{-}9)$$

$$\sigma_{M_i} = M_i \times D_{Mi} \qquad (2\text{-}10)$$

$$\sigma_{RMS_i} = (\frac{1}{n}\sum_{j=1}^{n}\sigma_{C_i}^2)^{0.5} \qquad (2\text{-}11)$$

$$\sigma_V/V = 0.05 \qquad (2\text{-}12)$$

where:

B_i	=	average amount of species i on field blanks
B_{ij}	=	the amount of species i found on field blank j
C_i	=	the ambient concentration of species i
D_{Mij}	=	the absolute difference between the original and replicate analysis of species i on sample j
D_{Mi}	=	the average fractional difference between original and replicate analyses for n pairs of samples
F	=	flow rate throughout sampling period
M_i	=	amount of species i on the substrate
M_{ijf}	=	amount of species i on sample j from original analysis
M_{ijr}	=	amount of species i on sample j from replicate analysis
n	=	total number of samples in the sum
SIG_{Bi}	=	the root mean square error (RMSE), the square root of the averaged sum of the squared of s_{Bij}.
STD_{Bi}	=	standard deviation of the blank
σ_{Bi}	=	blank precision for species i
σ_{Bij}	=	precision of the species i found on field blank j
σ_{Ci}	=	propagated precision for the concentration of species i
σ_{Mi}	=	precision of amount of species i on the substrate
σ_{RMS_i}	=	root mean square precision for species i
σ_V	=	precision of sample volume
t	=	sample duration
V	=	volume of air sampled

Dynamic field blanks for the dry deposition measurements were periodically placed in each sampling system without air being drawn through them to estimate the magnitude of passive deposition for the period of time which filter packs remained in a sampler (typically 5 days). Approximately three dry deposition blanks were obtained at the Barton Flats station per calendar quarter. No significant quarter-to-quarter differences in field blank concentrations were found for any species. The average field blank concentrations were calculated at the end of each quarter for each species on each substrate (i.e., Teflon-membrane, nylon-membrane, quartz-fiber, impregnated cellulose-fiber filters).

Blank precisions (s_{Bi}) are defined as the larger value of either the standard deviation of the blank measurements, STD_{Bi}, or the square root of the averaged squared uncertainties of the blank concentrations, SIG_{Bi}. If the average blank for a species was less than its precision, the blank was set to zero (as shown in Equation 2-4). Dynamic field blank concentrations are given in Table 2-4 for dry deposition samples in μg/filter.

As shown in Table 2-4, the standard deviation of the field blank is often a factor of two or greater than its

corresponding root mean square error (RMSE) for most of the ionic species. It is speculated that large standard deviations result from large variability in passive deposition relative to analytical precision, and from the small number of the data set (four to five field blanks). Examining the individual field blank values shows that these values are well within the range of the standard deviation of the average blank concentrations found in other non-urban areas (Watson *et al.*, 1991).

As discussed in Section 2.2.1.2, wet deposition samples for which no precipitation occurred were treated as "rinse blanks" by adding DDW to the empty collection bucket. Table 2-4 shows that these rinsed blanks were generally very low.

Table 2-5 summarizes the analytical speciations for the 12-hour dry deposition measurements and for the weekly wet deposition measurements. The minimum detectable limit, the root mean squared (RMS) precision, and lower quantifiable limits (LQL) are given. The LQL is defined as a concentration corresponding to two times the precision of the dynamic field blank. The LQLs in Table 2-5 were derived assuming sample volumes of 1.44 m^3 for nitrogen dioxide samples and 14.4 m^3 for all the other 12-hour substrate samples. Actual volumes varied from sample to sample, typically within $\pm$ 5% of the pre-set volume. The LQLs should always be equal to or larger than the analytical MDLs because they include the standard deviation of the field blank and flow rate precision (Watson *et al.*, 1989). This is the case for the chemical compounds noted in Table 2-5. This table indicates that the RMS precisions are lower than the LQLs but comparable in magnitude to the LQLs for most species.

The number of reported (non-void, non-missing) concentrations for each species and the number of reported concentrations greater than the LQLs are also summarized in Table 2-5. For the dry deposition measurement, $PM_{2.5}$ mass, sulfate, nitrate, and ammonium were detected on over 90% of the cases. $PM_{2.5}$ chloride concentrations were generally low, especially during winter, and only detected on 15% of the cases. Precursor gases for sulfur dioxide, nitrogen dioxide, nitric acid, and ammonia were detected on over 70% of the cases.

With respect to the wet deposition measurement, chloride, nitrate, sulfate, and ammonium were detected in over 70% of the cases; whereas soluble sodium, magnesium, and calcium ions were detected in over 60% of the cases. Soluble potassium ion concentrations were generally low, and were detected in less than 35% of the cases.

2.3.1.2 Quality Assurance

Five performance audits of field operations were performed as part of the quality assurance. Both system and performance audits were performed during field measurements. Auditors acquired and reviewed the standard operating procedures and examined all phases of measurement activities to assure that procedures were being followed and that operators were properly trained. All procedures reviewed by the auditor were acceptable and proved to be adequate for the study.

For the dry deposition sampling system, flow rates were checked monthly against the independently-calibrated rotameter. The results of these checks are given in Table 2-6a. Overall, the differences between the "setpoint" and "test" flow rates were within $\pm$ 5% of each other. In only a few cases did the percent deviation exceed $\pm$ 10%, but this is still within the tolerance of flow rate variations.

The total inlet flow rates were compared to the sum of the individual flow rates, and these are compared with the actual setpoint flows in Table 2-6a. In most cases, the total flow rates were 4% to 8% lower than the sum of the individual flows, but no leaks were found. The total flow rates were lower than the sum of the individual flow rates because of the flow restriction of the total flow rate measurement adapter.

New setpoints for the sampler magnehelics were determined during each re-calibration on a biannual basis. Flow rates are at their specified levels when these setpoints are achieved. The variations among the flow rates were found to be within ± 5% between each calibration.

The ozone monitor was audited with DRI's transfer standard. As shown in Table 2-6b, the percent deviations were generally within ± 5% except for the audit checks performed on 05/15/92. Malfunction of the ozone monitor was discovered after maintenance on this day, and was replaced with a new Dasibi 1008AH monitor on 05/16/92.

With respect to meteorological monitoring, synchronous motors with different rotation rates were attached to the wind speed sensors and the sensor outputs were compared to the manufacturers' expected values; wind direction was checked by aiming the vane at targets having known bearings; temperature was checked with an aspirated thermometer (placed as close to the sensor as possible); relative humidity was checked with a psychrometer; and the solar radiation sensor was checked by placing an Eppley Model PSP Pyranometer as close to the sensors as possible. The test results except temperature and relative humidity on 5/24/94 are all within manufacturer specifications and are summarized in Table 2-6c. The temperature and relative humidity sensor was replaced as a result of the audit, and data were flagged as suspect or invalid for the dates shown in the table.

Interlaboratory comparisons of filter samples as well as U.S. EPA spiked filters were submitted for ion chromatographic analysis. Analysis of audit standards was within approximately ±10% of the standard value for most species. It was concluded that the measurements acquired from these analyses were valid, accurate, and precise to the extent which can be determined by audit.

2.3.1.3 Dry and Wet Deposition Data Validation

Data acquired from this study was submitted to four data validation levels:

- Level 0 sample validation designates data as they come off the instrument. This process ascertains that the field or laboratory instrument is functioning properly.
- Level I sample validation: 1) flags samples when significant deviations from measurement assumptions have occurred; 2) verifies computer file entries against data sheets; 3) eliminates values for measurements which are known to be invalid because of instrument malfunctions; 4) replaces data from a backup data acquisition system in the event of failure of the primary system; and 5) adjusts values for quantifiable calibration or interference biases.
- Level II sample validation takes place after data from various measurement methods have been assembled in the master data base, and it is the first data analysis task. Level II applies consistency tests to the assembled data based on known physical relationships between variables.
- Level III sample validation is part of the data interpretation process. The first assumption upon

finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as: 1) extreme values; 2) values which would otherwise normally track the values of other variables in a time series; and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern.

Level I validation flags and comments are included with each data record in the data base. Level II validation tests and results are described in the following subsections.

Level II tests evaluated the chemical data for internal consistency. In this study, Level II data validation was made for: 1) sum of ionic species versus $PM_{2.5}$ mass; 2) $PM_{2.5}$ particulate nitrate versus nitric acid denuded nitrate; and 3) cation and anion balance. Correlations and linear regression statistics were computed and scatter plots prepared to examine the data. Suspect data were flagged and data validation summaries were documented in the "memo" field of the data base as described in Section 2.3.1.1.

2.3.1.3.1 Sum of Ionic Species Versus $PM_{2.5}$ Mass

$PM_{2.5}$ mass and ions (i.e., Cl^-, NO_3^-, $SO_4^=$, NH_4^+) were acquired on the dry deposition samples. The sum of these ionic concentrations for $PM_{2.5}$ should be less than or equal to the corresponding gravimetrically measured mass concentrations. This sum includes chemicals quantified on the quartz-fiber filters from the "QN" filter pack (double stage quartz-fiber/nylon-membrane filters), which is compared to the $PM_{2.5}$ mass concentrations measured on the Teflon-membrane filter from the "TK" filter pack (triple stage Teflon-membrane/citric acid-impregnated/potassium carbonate-impregnated filters). Figure 2-4 displays scatter plots of the $PM_{2.5}$ sum of ionic species versus mass at the Barton Flats station for the daytime and nighttime samples acquired every sixth day between 11/02/91 and 09/28/93 and between 06/01/94 and 08/30/94. Regression statistics with mass as the independent variable (X) and sum of ionic species as the dependent variable (Y) are calculated. As intercepts are low compared to the measured concentrations, the slope closely represents the ratio of Y over X.

Figure 2-4 shows that the sum of ionic species are always less than the corresponding $PM_{2.5}$ mass within the measurement uncertainties. A reasonably good relationship is found between the sum of ionic species and $PM_{2.5}$ mass with correlation coefficients exceeding 0.80 for the entire sampling period, though data are more scattered at higher $PM_{2.5}$ concentrations. This figure also shows that Cl^-, NO_3^-, $SO_4^=$, and NH_4^+ were the major components of $PM_{2.5}$ mass, which accounts for approximately 50% of the $PM_{2.5}$ mass in this study.

2.3.1.3.2 Volatilization of Particulate Nitrate

As shown in Figure 2-1, the quartz-fiber filter from the "QN" filter pack (double stage quartz-fiber/nylon-membrane filters) measures $PM_{2.5}$ non-volatilized nitrate, while the nylon-membrane filter from the "DN" filter pack (single stage nylon-membrane filter preceded by nitric acid denuders) measures $PM_{2.5}$ total particulate nitrate (non-volatilized and volatilized particulate nitrate). The nitric acid-denuded total particulate nitrate should be greater than or equal to the non-volatilized particulate nitrate, depending on the extent of volatilization.

Figure 2-5 illustrates the scatter plots of $PM_{2.5}$ particulate nitrate versus nitric acid-denuded total particulate

nitrate for each season. As discussed in Watson *et al.* (1994), secondary ammonium nitrate is not a stable compound. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. Figure 2-5 shows that the dissociation of particulate nitrate from the front quartz-fiber filters was more prevalent in the summertime when temperatures were higher. The regression statistics yielded a slope of 0.14 $\pm$ 0.022 for the summer and 0.85 $\pm$ 0.049 for the fall, with negligible intercepts. On average, approximately 85% of the particulate nitrate from the quartz-fiber filters volatilized during the summer. This volatilization decreased to approximately 50% of particulate nitrate for the winter and spring periods, and to 15% of particulate nitrate during the fall when temperatures were lower. The variations in volatilization were greater during the summer ($r = 0.48$) as compared to winter ($r = 0.93$). Volatilized nitrate is not part of the measured $PM_{2.5}$ mass, so this loss does not show up in the sum of ionic species comparisons.

2.3.1.3.3 **Anion and Cation Balance**

Ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), and potassium chloride (KCl) are the potential compounds present in the San Bernardino Mountains area.

The equivalent amount of anions and cations are expected if the correct species are identified and measured accurately. In the wet deposition samples, all the anions (Cl^-, NO_3^-, $SO_4^=$) were acquired by ion chromatographic (IC) analysis; ammonium (NH_4^+) was obtained by automated colorimetric (AC) analysis; soluble sodium (Na^+), magnesium (Mg^{++}), potassium (K^+), and calcium (Ca^{++}) ions were obtained by atomic absorption spectrophotometric (AAS) analysis; whereas hydrogen ion (H^+) was obtained by pH meter.

Figure 2-6 illustrates that these ionic measurements were highly correlated ($r = 0.98$), with most of the data points falling within one standard deviation of the regression line. Nearly all of the anions could be balanced with the cations on a microequivalence basis, with a slope of 1.04 and a low (3.37 μeq/l) intercept. This anion and cation balance provides confidence, in that the ionic measurements made by IC, AC, and AAS for the wet deposition samples were in good agreement among each other.

Ammonium is the only cation acquired in the dry deposition samples. To verify the validity of the ionic species measurements, ammonium is calculated based on the stoichiometric ratios of the different compounds and is compared to the actual measurement.

It is assumed that all of the particulate nitrate is in the form of ammonium nitrate and sulfate is either ammonium sulfate (i.e., calculated ammonium = 0.38 x sulfate + 0.29 x nitrate) or ammonium bisulfate (i.e., calculated ammonium = 0.192 x sulfate + 0.29 x nitrate). Measured ammonium concentrations should equal those calculated from ammonium nitrate and ammonium sulfate or ammonium bisulfate on a molar-to-molar basis. These comparisons assume that nitrate lost by volatilization of ammonium nitrate from the front quartz-fiber filter depletes both particulate nitrate and ammonium.

Figure 2-7 illustrates the scatter plot of calculated versus measured $PM_{2.5}$ ammonium for the entire study period. This figure shows that the majority of ammonium sulfate points are on the one-to-one line. This suggests that most of the sulfates are neutralized and ammonium sulfate is the dominant compound at the site.

Regression statistics resulted in excellent correlation ($r > 0.98$) between the calculated and measured ammonium with negligible intercept and a slope of 0.96 $\pm$ 0.008 for ammonium sulfate and 0.82 $\pm$ 0.01 for

ammonium bisulfate.

Scatter plots of calculated versus measured ammonium were created for each season. An upward shift of the calculated ammonium was found in winter (i.e., December, January, and February) samples, with a mixture of the ammonium bisulfate and ammonium sulfate points on the one-to-one line, as shown in Figure 2-8. The slope increased to 1.15 $\pm$ 0.04 for ammonium sulfate and 0.91 $\pm$ 0.03 for ammonium bisulfate. This suggested that $PM_{2.5}$ aerosol is more acidic (i.e., sulfate is present as bisulfate or sulfuric acid) during winter, and/or that $PM_{2.5}$ nitrate is associated with cations other than ammonium, such as sodium. Sea salt aerosol reacts with nitric acid to produce coarse particle sodium nitrate. Since nitric acid concentrations are generally low during winter, it is unlikely to find significant sodium nitrate in the $PM_{2.5}$ size fraction. It is possible that less ammonia is available during the wintertime to fully neutralize the available sulfate in the atmosphere.

The anion/cation balance supports the accuracy and precision of the nitrate, sulfate, and ammonium measurements on the quartz-fiber filters. The anion and cation balance would not be so consistent if these analyses were invalid. This ion balance also demonstrates that most of the nitrate and sulfate present in the $PM_{2.5}$ occurs as ammonium nitrate and ammonium sulfate. The decision not to measure hydrogen ions is justified, since the potentially acidic particles appear to be entirely neutralized by available ammonia during a majority of the time.

2.3.2 Meteorological and Ozone Data Validation

Meteorological and ozone data were processed and validated according to the procedure "Meteorological and Continuous Gaseous Data Processing and Validation" included in *Volume 2, Research Protocols* of this report. The general flow of data processing operations is shown in Figure 2-9.

Meteorological and continuous gaseous analyzer readings were collected and processed at the Barton Flats station by a Campbell data acquisition system, periodically transmitted to a laboratory computer, and saved as both ASCII and FoxPro .DBF files. Individual FoxPro .DBF files accumulated over the course of the monitoring program were combined into one file before processing. Duplicate or missing data records were identified by program FINDMISS and corrected so that a continuous data base of hourly readings was constructed.

A file of validation test values for minimum value, maximum value and rate of change for each measurement sensor was created. These validation values were based on parameters that are reasonable for the Barton Flats station. These validation values were applied to the meteorological/ozone data set by program METVAL to identify data that were either physically impossible (i.e. wind direction > 360°), or so unusual as to suggest a possible sensor malfunction (i.e., temperature > 40 °C). The program also tested for vector wind speeds greater than scalar wind speeds, for leaf wetness values greater than zero while relative humidity was less than 50%, and for missing data. Each data record that failed any validation test was tagged by applying the appropriate flag (as shown in Table A2-9 of Appendix 2 of this report) to the TESTFLAGS field of the data base. Flagged records were listed with program FLAGCT.

A descriptive analysis of the meteorological and ozone data was prepared by plotting the data with program TSGRAPH (Time Series GRAPH). This program displays a time series plot of one or more parameters along with a spreadsheet-like table of data values. Individual values in the data base can be located by placing a

cursor over a point on the time series plot, and data can be corrected and flags entered while viewing the plot. The data analysis summarized the patterns associated with each measurement parameter and the relationships between parameters.

After all parameters were summarized, data were plotted again, using both long and short time scale ranges to scan the data for inconsistencies with the patterns and relationships established earlier. Ancillary records such as site visit logs, telephone conversation records relating to ozone or meteorological measurements, and site audit records were examined as well. Data that were flagged by the METVAL program were examined in detail. Validation flags as listed in Table A2-9 of Appendix 2 were applied based on the combined information from the TESTFLAGS, comparison of plotted data with the data patterns and relationship summaries, and ancillary data. Comments were added to a memo field to supplement the information provided by validation flags where needed. As the final step of processing and validation, data that were not otherwise flagged, were flagged as valid data by running program FLAGVALD.

2.3.2.1 Pair Comparisons on Collocated Ozone Measurements

A solar-powered Dasibi Model 1008AH ozone monitor was located at the "Plot 2" site (Figure 1-7) for 33 days between 07/16/93 and 09/24/93 and for 7 days between 08/15/94 and 08/21/94. The same instrument was located at the "Heart Bar" site (see Figure 1-7) between 08/30/94 and 09/05/94 and between 09/12/94 and 09/20/94. These data were compared with the concurrent ozone measurements at the Barton Flats station. Figure 2-10 displays the scatter plot of these hourly ozone measurements. The correlation coefficients are high ($r > 0.87$) at both locations. A large intercept (11.4 ppb) was found at the "plot" site with a slope of 0.86. This slope was increased to 1.00 as the regression analysis was done by forcing the regression line through zero (i.e., set intercept equal zero). A similar slope ($a = 0.85$) was found with ozone data acquired at the "Heart Bar" site. This implied that ozone measurements collected at the Barton Flats station were consistently 15% higher than those acquired at the "Heart Bar" site.

Even though the two ozone monitors were not exactly "collocated" at the same location, their pair comparisons indicated that hourly ozone measurements were fairly consistent with reasonably good agreement within the study region.

2.4 Discussion

2.4.1 Characteristics of Chemical Components

The most rudimentary form of descriptive data analysis consists of examination of spatial and temporal distributions of atmospheric constituents and relative amounts of certain chemical species. When coupled with a conceptual understanding of the emissions sources, meteorology, and chemical transformation mechanisms, this receptor-oriented analysis provides qualitative and even semi-quantitative evidence of relationships between source emissions and receptor concentrations. The following sub-sections examine correlations, summary statistics, as well as temporal distribution of dry and wet deposition measurements.

2.4.1.1 Correlations Among the Dry and Wet Deposition Measurements

Correlations of the aerometric measurements are often used to examine the relationship among the air quality variables. Coefficients which exceed 0.80 show a fairly strong covariation, coefficient between 0.50 and 0.80

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. Table 2-7 presents the correlation matrices for the dry and wet deposition samples. Ozone, temperature, and relative humidity data were also included in the dry deposition sample data set for comparison.

High correlation coefficients ($r > 0.80$) were found between $PM_{2.5}$ mass and ions (i.e., sulfate, ammonium, $PM_{2.5}$ total particulate nitrate), and between ammonium and nitrate compounds (i.e., $PM_{2.5}$ non-volatile nitrate, total particulate nitrate). Ozone was only moderately correlated with temperature ($r = 0.73$) and nitric acid ($r = 0.67$). The precursor gases of nitric acid, sulfur dioxide, and ammonia showed little ($r < 0.5$) or no correlations with their secondary products of nitrate, sulfate, and ammonium, respectively. Nitrogen dioxide also reported low correlations ($r < 0.5$) with nitric acid or ozone, the photochemical end product.

Besides ozone, temperature was also moderately ($r > 0.6$) correlated with nitric acid, sulfur dioxide, and ammonia, which is consistent with the theory of thermal equilibrium. Relative humidity was generally negatively correlated with $PM_{2.5}$ mass and reactive gases with low ($r < 0.5$) correlation coefficients.

Excellent correlations ($r > 0.90$) were found for chloride versus sodium ions and nitrate versus sulfate. High correlations ($r > 0.80$) were also discovered for chloride versus magnesium ions, nitrate versus ammonium, nitrate versus calcium ions, and sulfate versus calcium ions. Many of these correlation pairs can directly relate to their chemical forms in the atmosphere such as ammonium nitrate and calcium sulfate.

Conductivity was found to be highly correlated ($r > 0.8$) with sulfate, nitrate, magnesium ion, and calcium ion concentrations; and moderately ($r > 0.6$) correlated with chloride, ammonium, and sodium ion concentrations. No association was found between pH and the ionic concentrations in these precipitation samples. No significant correlation was found between precipitation amount and other wet deposition parameters. However, correlation coefficients between -0.2 and -0.4 for precipitation amounts and all ions suggests the possibility of an inverse relationship.

2.4.1.2 Statistical Summary of Chemical Concentrations of Dry and Wet Deposition Samples

Table 2-8 presents averages, standard deviations, and maximum concentrations for 12-hour daytime and nighttime dry deposition samples acquired for the following four seasons:

- Winter: includes December of 1991, January, February, and December of 1992, and January and February of 1993;
- Spring: includes March, April, and May of 1992 and 1993;
- Summer: includes June, July, and August of 1992 and 1993; and
- Fall: includes November of 1991, September, October, and November of 1992, and September of 1993.

Table 2-8 shows that the daytime average concentrations were similar to the nighttime averages for all the particulate species at all seasons. The largest differences in these averages are observed among the different seasons. Average $PM_{2.5}$ mass concentrations varied from 1.62 ± 1.77 $\mu g/m^3$ (at daytime during winter) to

9.73 ± 3.48 $\mu g/m^3$ (at daytime during summer) with a maximum 12-hour $PM_{2.5}$ mass concentration of 27.5 ± 1.65 $\mu g/m^3$ during the daytime period on 10/21/92. Maximum $PM_{2.5}$ non-volatilized nitrate (14.1 ± 6.7 $\mu g/m^3$), $PM_{2.5}$ total (i.e., non-volatilized plus volatilized) particulate nitrate (13.85 ± 0.80 $\mu g/m^3$), sulfate (3.53 ± 0.27 $\mu g/m^3$), and ammonium (5.42 ± 0.32 $\mu g/m^3$) concentrations were also observed on the same sample.

The sum of the ionic species (i.e., chloride, nitrate, sulfate, and ammonium) to mass ratio on the samples acquired during the daytime of 10/21/92 was 0.84, which is 35% higher than the typical ratio of 0.50 reported in Section 2.3.1.3.1 for most samples acquired during the study. It is interesting to note that the precursor gases during this sampling period for ammonia (1.71 ± 0.08 $\mu g/m^3$), sulfur dioxide (0.62 ± 0.09 $\mu g/m^3$), and nitric acid (1.25 ± 1.06 $\mu g/m^3$) concentrations are comparable to or below their corresponding seasonal average for the fall period. Nitrogen dioxide concentrations (6.32 ± 1.12 $\mu g/m^3$) on the same sampling period were twice the seasonal average.

Examining the hourly meteorological and ozone data on 10/21/92 reveals that winds were generally low (< 3 m/sec) with predominant westerly to northwesterly wind flow during the daytime. Temperature was low (< 12 °C) during the daytime with high relative humidities (80%) developed in the afternoon, as shown in Figure 2-11. As expected, photochemical reaction on this day was minimal, with low ozone (< 60 ppb) concentrations and low (< 300 watts/m^2) solar radiation. This is consistent with the finding of Russell *et al.* (1983), that most of the nitrate will be in the particle phase as ammonium nitrate at temperatures lower than 15 °C and these nitrate particles will be in the gas phase as nitric acid (HNO_3) at temperatures greater than 30 °C. It is apparent that low dispersion, low temperature, and high relative humidity environs on 10/21/92 favor the reaction and formation of the secondary aerosol.

The average ratio of $PM_{2.5}$ non-volatilized nitrate to total particulate nitrate was lowest (0.25) during daytime in the summer and highest (0.76) during nighttime in the fall. Average $PM_{2.5}$ non-volatilized nitrate concentrations varied by more than one order of magnitude among different sampling periods and seasons, ranging from 0.19 ± 0.33 $\mu g/m^3$ (at nighttime during winter) to 2.30 ± 3.47 $\mu g/m^3$ (at daytime during fall). Average $PM_{2.5}$ total particulate nitrate varied in the same magnitude, ranging from 0.43 ± 0.69 $\mu g/m^3$ (at nighttime during winter) to 3.87 ± 2.4 $\mu g/m^3$ (at daytime during fall). As discussed in Section 2.3.1.3.2, the dissociation of nitrate from the front quartz-fiber filters was enhanced during summer when temperatures were higher. This volatilization was less prevalent during the fall and winter as temperatures were lower.

Maximum gaseous concentrations all occurred during daytime, with maximum nitrogen dioxide concentration (10.21 ± 1.19 $\mu g/m^3$) reported on 10/27/92; maximum nitric acid concentrations (4.33 ± 0.73 $\mu g/m^3$) reported on 07/30/93; maximum sulfur dioxide concentration (1.76 ± 0.14 $\mu g/m^3$) reported on 08/05/93; and maximum ammonia concentration (7.04 ± 0.32 $\mu g/m^3$) reported on 09/10/93.

Reactive gaseous species, however, experience substantial variability between daytime and nighttime samples. The most noticeable of these is nitric acid, with average concentrations ranging from 0.07 ± 0.07 $\mu g/m^3$ (at nighttime during winter) to 2.46 ± 1.09 $\mu g/m^3$ (at daytime during summer). These average nitric acid concentrations decreased by a factor of two from daytime to nighttime during winter, and by a factor of seven to eight from daytime to nighttime during the other seasons. Nitric acid is an end-product of daytime photochemical reactions, and its deposition and reactivitiy rates are large.

Average sulfur dioxide concentrations were low, ranging from 0.19 ± 0.26 $\mu g/m^3$ (at nighttime during

winter) to 0.82 ± 0.41 $\mu g/m^3$ (at daytime during winter). The daytime average sulfur dioxide concentrations was 1.5 to 2.2 times the nighttime averages at the Barton Flats station. This may be related to transport from the sulfur dioxide emitters or larger sulfur dioxide emission rates during daytime hours in the vicinity of the San Bernardino Mountains.

Average ammonia concentrations varied by a factor of 25, ranging from 0.16 ±0.16 $\mu g/m^3$ (at nighttime during winter) to 3.92 ± 1.60 $\mu g/m^3$ (at daytime during summer). Daytime average ammonia concentrations were also more than twice the nighttime average concentrations, which is directly related to the source emissions and meteorology. Average nitrogen dioxide concentrations were highest during the summer, with equivalent daytime and nighttime concentrations averaging 3.10 ± 1.07 $\mu g/m^3$ during daytime and 3.19 ± 1.46 $\mu g/m^3$ during nighttime. These concentrations were variable during the other seasons, and it was 20% to 80% higher during the daytime as compared to the nighttime averages.

Intensive monitoring was conducted daily between 07/18/93 and 07/31/93 at three times per day to assess the diurnal variations of particulate matter and reactive gaseous species. Table 2-9 summarizes the averages; standard deviations; maximum and minimum concentrations for the morning (0600 to 1200 PST), afternoon (1200 to 1800 PST), and nighttime (1800 to next day 0600 PST) periods, and time weighted average of morning and afternoon samples.

The breakdown of daytime sampling intervals into the morning and afternoon periods provided more insight into the concentration variations. Table 2-9 shows that maximum mass, ions, and reactive species concentrations all occurred during the afternoon periods. In contrast, the lowest concentrations for the intensive monitoring period all occurred during the morning period, with the exception of $PM_{2.5}$ chloride and gaseous ammonia, sulfur dioxide, and nitric acid concentrations. This could be the reason that similar average daytime and nighttime concentrations were found in Table 2-8 for all the particulate species. It also implies that $PM_{2.5}$ mass and ions varies significantly during the daytime and much of the information was not attainable by acquiring an integrated 12-hour sample.

Average daytime and nighttime concentrations during the intensive sampling period (from 07/18/93 to 07/31/93 on a daily sampling schedule) are comparable to the summer average (acquired during June, July, and August of 1992 and 1993 on an every-sixth-day sampling schedule) presented in Table 2-8. Note that three out of the 14 intensive sampling days fell on the every-sixth-day sampling schedule and it is included in the calculations for both data sets. This similarity suggested that day-to-day or year-to-year variations in particle and gaseous concentrations were not significant during these sampling periods. Therefore, emissions and meteorology during the intensive sampling period were representative of the summer of 1992 and 1993.

Maximum afternoon concentrations for mass, ions, and gaseous species during the intensive sampling period were lower than those observed for routine monitoring periods on an every-sixth-day sampling schedule between 11/02/91 and 09/28/93, with the exception of nitric acid and ammonia. Maximum nitric acid concentration (6.73 ±0.53 $\mu g/m^3$) occurred during the afternoon of 07/27/93, whereas maximum ammonia concentration (8.96 ± 0.41 $\mu g/m^3$) occurred during the afternoon of 07/30/93. This is also the day (07/30/93) that maximum 12-hour nitric acid concentrations were found on the every-sixth-day sampling schedule between 11/02/91 and 09/28/93.

Table 2-10 presents the statistical summary of the averages, standard deviations, maximum, and minimum concentrations for data acquired during the summer of 1994 between 06/01/94 and 08/31/94. Average and

maximum daytime and nighttime concentrations during the summer of 1994 were comparable to those of the previous summers of 1992 and 1993 on all species except for the daytime nitric acid concentrations. Maximum nitric acid concentrations of 12.2 $\pm$ 0.60 $\mu g/m^3$ were found during the daytime on 06/13/94. This is a factor of three higher than the maximum nitric acid concentrations of 4.33 $\pm$ 0.44 $\mu g/m^3$ (07/30/93) found during the previous two summers. As a result, the average nitric acid concentrations (4.5 $\pm$ 2.4 $\mu g/m^3$) during the summer of 1994 nearly doubled the summer averages of 1992 and 1993 (2.46 $\pm$ 1.09 $\mu g/m^3$) reported in Table 2-8.

2.4.1.3 Temporal Variations of $PM_{2.5}$ Non-Volatilized Nitrate, $PM_{2.5}$ Volatilized Nitrate, and Gaseous Nitric Acid

As discussed earlier, three types of nitrate compounds were measured in this study. They are: 1) $PM_{2.5}$ non-volatilized nitrate (i.e., measured on quartz-fiber filters); 2) $PM_{2.5}$ total particulate nitrate (i.e., measured on nylon-membrane filters preceded by nitric acid denuders); and 3) gaseous nitric acid (i.e., calculated by the denuder differences between the nondenuded [QN filter pack] and denuded [DN filter pack] sampling ports).

Figure 2-12 depicts how these types of nitrate vary from sample to sample and from season to season. The bottom bar represents the $PM_{2.5}$ non-volatilized nitrate, the middle bar represents the volatilized $PM_{2.5}$ nitrate, and the height of all bars represents the sum of gaseous nitric acid and $PM_{2.5}$ total particulate nitrate. Note that most samples contain non-volatilized particulate nitrate, but their proportions vary with sampling days, time of day, and sampling season. $PM_{2.5}$ non-volatilized nitrate concentrations were much higher during the daytime in the fall than in the other seasons. These $PM_{2.5}$ non-volatilized nitrate concentrations were also pronounced during the nighttime in the fall and during the daytime and nighttime in the spring as compared to those of other seasons.

$PM_{2.5}$ non-volatilized nitrate is much lower in the summer, especially during daytime, and they were present as either volatilized nitrate or as nitric acid It is apparent that nitrate compounds tended more toward the volatilized nitrate and nitric acid phases during the daytime and toward the particulate phase during the nighttime. This is consistent with changes in equilibrium which correspond to diurnal changes in temperature (Russell et al., 1983). All three types of nitrate compounds reported lowest concentrations during the winter, especially at nighttime.

Figure 2-13 presents the nitrate variations during the summer of 1994. As compared to Figure 2-12, the proportion of the three types of nitrate compounds are similar among the three summers with slightly elevated nitrate concentrations observed during 1994.

2.4.1.4 Temporal Variations of $PM_{2.5}$ Non-Volatilized Ammonium, $PM_{2.5}$ Volatilized Ammonium, and Gaseous Ammonia

Similar to nitrate compounds, three types of ammonium were acquired in this study. They are: 1) $PM_{2.5}$ non-volatilized ammonium (i.e., measured on quartz-fiber filters); 2) $PM_{2.5}$ total particulate ammonium (i.e., calculated from $PM_{2.5}$ total particulate nitrate based on the stoichiometric ratio, assuming that all particulate nitrate is in the form of ammonium nitrate. This is justified due to the one-to-one relationship found in ion balance presented in Section 2.3.1.3.3. Hence, calculated ammonium = 0.29 x nitrate); and 3) gaseous

ammonia (i.e., measured by the citric acid impregnated cellulose-fiber filter on the "TK" filter pack).

Figure 2-14 illustrates temporal variations of three types of ammonium compounds. Analogous patterns were discovered for $PM_{2.5}$ non-volatilized ammonium, $PM_{2.5}$ volatilized ammonium, and gaseous ammonia. It is apparent from this figure that $PM_{2.5}$ non-volatilized ammonium reached its maximum during the daytime in the fall. Figure 2-14 also shows the presence of excessive quantities of ammonia during all seasons. Gaseous ammonia concentrations were lowest during winter and reached their maximum during the daytime in summer and fall. These excessive ammonia levels also explain the fact that most sulfates are neutralized at the Barton Flats station and are present mostly in the form of ammonium sulfate rather than ammonium bisulfate.

Figure 2-15 shows that similar characteristics were found for the ammonium variations during the summer of 1994. Compared to Figure 2-14, the proportions of three types of ammonium compounds are similar among the three summers with the presence of excessive ammonia concentrations.

2.4.1.5 Diurnal Variations of Particulate Nitrate, Nitric Acid, Particulate Ammonium, and Ammonia

Variations of gaseous and particulate phases of nitrate and ammonium compounds were examined for the morning, afternoon, and nighttime samples. Figure 2-16 shows that nitrate and ammonium compounds were a factor of two or more higher during the afternoon periods as compared to the other sampling periods. The most distinguishing features were found for $PM_{2.5}$ volatilized nitrate and ammonium concentrations which were a factor of two to ten times higher during the afternoon periods. Nitric acid concentrations were similar between the morning and afternoon samples, and a factor of seven to ten higher than the nighttime samples. Similar phenomena were found for ammonia with more pronounced concentrations during the afternoon periods.

2.4.1.6 Seasonal Variations of Wet Deposition Measurements for Precipitation Amount, pH, Conductivity, and Ions

Averages, standard deviations, maximum, and minimum concentrations of the wet deposition measurements between 11/05/91 and 09/21/93 and between 05/31/94 and 08/23/94 were examined for their seasonal variations. Table 2-11 showed that approximately 50% of the precipitation events occurred during the winter, with less than 20% of them occurring during the summer.

Precipitation amounts were even more heavily weighted to the winter months. Eighty percent of the total precipitation measured during the study occurred during winter. Out of a total precipitation of 58.58 inches measured during the study, 46.60 inches fell during the winter season (December of 1991, January, February and December of 1992, and January and February of 1993). Total spring season (March, April and May of 1992 and 1993) precipitation was 5.89 inches. Total summer season (June, July and August of 1992, 1993 and 1994) precipitation was 4.94 inches. The driest season was fall (November of 1991, September, October and November of 1992, and September of 1993), receiving only 1.16 inches of precipitation. The winter of 1992/1993 received the most precipitation of any single season during the study, 34.50 inches.

Both the field (on-site) and laboratory measurements of pH and conductivity are reported in Table 2-11 for comparison. Variation of pH measurements were low, typically within $\pm$ 5%. Conductivity measurements in the laboratory were consistently around 10% lower than those reported in the field. The properties of the

precipitation samples may have been altered during shipping and storage. Since the wet deposition bucket usually stayed in the field for a week, the conductance measured on-site should be considered as a lower bound of the true measurement. On-site data are used for the following discussions.

No apparent variations were found on the seasonal averaged pH values. Precipitation in the San Bernardino Mountains was not acidic, with average pH values ranging from 5.0 $\pm$ 0.52 during summer to 6.50 $\pm$ 1.02 during winter. The lowest pH value measured was 4.2 during the week of 07/27/93 and 08/02/93, with less than one inch of precipitation.

Conductivity in the solutions varied by a factor of four from season to season and ranged from 5.4 $\pm$ 6.6 μS/cm during the winter to 21.2 $\pm$18.9 μS/cm during the summer, which followed the same trend as those of the ionic concentrations. Average ionic concentrations were very low during winter, with maximum concentrations occurring during spring or summer.

Only two precipitation events during the summer of 1994 yielded adequate quantities for chemical analyses. These data are also listed in Table 2-11 for comparison. It is interesting to note that except for sulfate, the ionic concentrations during the summer of 1994 were a factor of two higher than those reported from 1992 and 1993 precipitation.

Overall average concentrations in Table 2-11 revealed that nitrate, by far, was the most significant species in the wet deposition samples, with an average of 1.93 $\pm$2.58 μg/ml and accounting for approximately 50% of the all ionic species being measured. Average sulfate concentrations (0.82 $\pm$ 1.04 μg/ml), accounting for 25% of the total measured ions, were only half of those observed for nitrate. Average chloride, ammonium, soluble sodium, and soluble calcium ion concentrations were similar, in the range of 0.2 to 0.5 μg/ml. Average soluble magnesium and potassium ion concentrations experienced the lowest level, in the range of 0.04 to 0.05 μg/ml.

2.4.2 Characteristics of Ozone Concentrations

High ozone concentrations were found frequently at the Barton Flats station. Hourly ozone concentrations exceeded the National Ambient Air Quality Standard (NAAQS) of 120 ppb on 235 days (22% of all sampling days) during the study period between 11/02/91 and 09/30/94. These exceedances occurred from late April through early October each year, between 1300 and 1800 PST.

Peak ozone concentrations often occurred in the late afternoon and lasted two to three hours. Maximum hourly ozone concentrations exceeded 200 ppb on 07/18/92 (220 ppb at 1700 PST), on 06/25/94 (204 ppb at 1700 PST), and on 06/30/94 (213 ppb at 1500 PST and 210 ppb at 1600 PST).

The ozone data, stratified by season, year, and time of day are shown in Figure 2-17. The top and bottom of the box for each hourly measurement represent the 75th and 25th percentile, respectively. Median concentrations are shown in the middle of the box. The top and bottom of the error bar represent the 90th and 10th percentile, respectively. Extremes and outliers are shown as circles which represent measurements above the top 90% and below the bottom 10% of the measurements. A statistical summary of ozone concentrations showing average, standard deviation, maximum and minimum concentrations and number of measurements by year, season, and time of day is provided in Table 2-12.

The daily average ozone concentration was highest during summer (63 - 70 ppb), next highest in spring and

fall, which had nearly equal concentrations (48 - 53 ppb), and lowest in winter (37 - 41 ppb). For high ozone concentrations to occur, strong sunlight and transport from areas with significant quantities of ozone precursors are required. Both of these conditions are met most often in summer. The high sun angle and consistent transport of ozone and precursors into the study area by the seabreeze and upslope winds in summer cause the high ozone levels to occur. During winter and spring, the sun angle and resulting solar radiation is less, and flow from polluted areas is not quite as consistent as in summer; thus ozone concentrations are generally less. Winter has more clouds and lower sun angles, resulting in less solar radiation. Winter also does not have consistent transport from polluted areas. These factors all contributed to winter having the lowest ozone concentrations. Year-to-year differences in average daily ozone concentrations for each season were small, especially when compared to differences between seasons.

For all yearly and seasonal averages, afternoon (1200 to 1800 PST) ozone concentrations were the highest, followed by daytime (0600 to 1800 PST), with nighttime (1800 to 0600 PST) being the lowest. This diurnal variation in ozone concentrations was season dependent. Afternoon ozone concentrations were higher than nighttime ozone concentrations by less than 10% during winter, by 40% to 60% during spring and fall, and by 80% to 90% during summer. Figure 2-17 shows that peak ozone concentrations occurred at about 14:00 PST in winter, 15:00 PST in fall, 16:00 PST in spring and 17:00 PST in summer. Afternoon ozone concentrations were highest because transport from polluted areas was greatest at this time and the sun angle was high. The overall daytime averages were somewhat lower because morning hours were averaged in. Morning had lower ozone concentrations than afternoon due to less transport from polluted areas and less time for the photochemical reactions to occur. Transport from polluted areas by the seabreeze and upslope flow peaked in the later afternoon (see sections 2.4.4 and 2.4.5).

2.4.3 Characteristics of Temperature, Relative Humidity and Solar Radiation

Daily average temperature, relative humidity, and solar radiation are shown in Table 2-13. Solar radiation is determined by sun angle and cloudiness. Sun angle is highest in summer, followed by spring, fall, and winter. Year-to-year variations in seasonal solar radiation were small and reflect small differences in average amounts of cloudiness. The seasonal temperature pattern followed the solar radiation pattern, except experienced a lag. Summer was the warmest, winter the coldest, but fall was warmer than spring even though solar radiation was less. This was because the Pacific Ocean reaches its minimum temperature in early spring, well after the minimum in solar radiation occurs. The Pacific Ocean reached its maximum temperature in early fall, well after the maximum in solar radiation. Temperatures in the study area were substantially affected by Pacific Ocean temperature because the air flow was usually from the ocean. This caused temperatures to be higher in fall than in spring.

2.4.4 Characteristics of Wind Flow Patterns

Wind flow patterns in the study area are affected by three main features: 1) the large scale (synoptic) positions of high and low pressure systems; 2) differential heating of inland areas versus coastal areas (sea breezes and land breezes); and 3) terrain-driven circulations (upslope and downslope flows). Local winds, and the transport of air pollutants in the study area are determined from the combined effects of these three factors.

Green et al. (1992a, 1992b) generated typical wind flow patterns for southern California for the main weather

patterns in summer and winter. Green et al. (1992a, 1992b) also looked at the effects of these wind fields upon the extinction coefficient, which was an indicator of transport of polluted air from the Los Angeles Basin. Flow patterns in the summer are dominated by the sea breeze and upslope/downslope flows. This results in a very consistent diurnal pattern. Because the ocean is cooler than inland areas nearly all hours of the day in summer, onshore flow (sea breeze) occurs most of the day, becoming strongest in the afternoon. The patterns explained by Green *et al.* (1992a, 1992b) are demonstrated here using data generated for this study. Figures 2-18 to 2-20 show the wind field for 0800 to 0900 PST, 1600 to 1700 PST, and 2200 to 2300 PST on 07/24/93, respectively. Light onshore flow occurs from 0800 to 0900 PST. As shown in Figure 2-19, a strong sea breeze/upslope flow pattern occurs by 1600 PST. Figure 2-20 shows that the onshore flow has become light at 2100 PST, and the Barton Flats Station shows a nighttime drainage (downslope) flow.

Only slight differences in wind patterns occur from day to day in the summer. When there is a synoptic scale high pressure system developed east of California (typically over the Great Basin), this high pressure diminishes the strength of the onshore flow, causes lower mixing depths and low dispersion. When there is a low pressure system to the east (also typically over the Great Basin), the onshore flow is stronger than normal. This pattern also has higher mixing depths and greater dispersion than the more typical summer pattern.

Winter, which shows much greater day-to-day variability than summer, has three main types of patterns. The most common pattern, the Santa Ana, results from high pressure to the northeast of the area and lower pressure near the coast. Dry winds bring air into the study area from the Mojave Desert. Under the second main winter pattern, synoptic scale pressure gradients are weak, and flows are governed by local conditions. Weak sea breeze/upslope flows occur during the day and weak downslope/offshore flows occur at night. During the third pattern, low pressure over the Great Basin or Four Corners area results in continuous onshore flow and flow over the mountains into the Mojave Desert.

The greater variability in winter compared to summer can be illustrated by examining plots of wind speed and wind direction at the Barton Flats Station for summer and winter. Figure 2-21 shows 0700 to 1900 PST and 1901 to next day 0700 PST wind roses for the Barton Flats Station for June to August, 1992. Essentially all the daytime winds show upslope flow (from the west to northwest)), the nighttime winds show downslope flow (from the southeast). Figure 2-22 shows that during winter, upslope and downslope flows are still dominant, but a significant amount of flow from the east occurs also. These easterly winds occur during the stronger Santa Ana conditions.

Time series plots for typical summer and winter periods are used to illustrate the differences or consistencies between summer and winter. Figure 2-23 shows a time series of wind speed and wind direction for June 1992, whereas Figure 2-24 displays a similar trend for December 1991. Note the very consistent diurnal cycle in wind speed and direction during June 1992. However December 1991 shows a much less consistent diurnal pattern; much of the variation is on a time scale of a few days. This indicates the greater importance of synoptic scale weather systems in winter than summer and the domination of the sea breeze pattern in the summer.

2.4.5 Relationships between Wind Flow Patterns and Pollutant Concentrations

During the summer, transport of pollutants by the sea breeze/upslope flows bring pollutants from the Los Angeles Basin into the surrounding mountain areas nearly every afternoon. This is demonstrated in Figure 2-

25, which shows the time series of ozone concentrations at the Barton Flats Station for June 1992. When a high pressure system is east of the region, the weaker sea breeze and enhanced stability cause high pollutant levels in the Los Angeles Basin. In the mountain areas, pollutant levels are lower than typical summer conditions until late in the day when the weaker than normal sea breeze/upslope flow bring in highly polluted air. This causes high peak ozone concentrations as discussed in Section 2.4.2. In the summer pattern with a low pressure east of the study area, good vertical mixing and higher wind speeds results in pollutant concentrations lower than for average summertime conditions.

During the winter, the Santa Ana conditions are associated with transport from the Mojave Desert and have low pollutant concentrations. For the winter pattern with a low pressure to the east of the study area, transport from the Los Angeles Basin during most hours of the day causes increased pollutant concentrations. As the weak pressure gradient winter pattern developed, concentrations were low for most hours of the day due to lack of significant transport. High pollutant concentrations often occurred for a few hours in the late afternoon as weak onshore/upslope flow transports emissions from the Los Angeles Basin.

To further explore the relationships among emissions, meteorology, and ambient concentrations, a few special days were selected and described as follows:

- ***10/21/92*** - This day had the passage of a weak surface front and a weak upper level low pressure over the area. About one-quarter inch of rainfall was recorded at Los Angeles International Airport. Under these conditions, transport of emissions from the Los Angeles Basin into the Barton Flats area would be expected for many hours of the day, with abundant moisture available for formation of secondary particulates. The highest $PM_{2.5}$ mass, particulate sulfate, nitrate, and ammonium concentrations were reported on this day.
- ***10/27/92*** - This day was meteorologically similar to 10/21/92. An upper level low pressure system covered the area. Very light precipitation was recorded at some locations in southern California. Again, transport of emissions from the Los Angeles Basin would be expected to impact Barton Flats many hours of the day. The highest nitrogen dioxide and high particulate nitrate concentrations were found on this day.
- ***07/27/93*** - This day had a high concentration of nitric acid in the afternoon and higher than usual ratio of nitric acid to volatilized particulate nitrate. A trough of low surface pressure was present over the western United States. A trace of precipitation was recorded at San Diego. There appeared to be a deep marine layer, resulting in greater than usual inland penetration of low clouds. This moisture would enhance formation of nitric acid, while the lower temperatures would minimize the volatilization of particulate nitrate.

2.5 Summary and Conclusions

An aerometric data base with specific accuracy, precision, and validity was acquired to determine the dry and wet deposition of reactive atmospheric species in forests. The results of this effort are as follows:

- Dry deposition samples for $PM_{2.5}$ mass and ions (i.e., nitrate, sulfate, ammonium) were found above the lower quantifiable limits (LQLs) for more than 80% of the samples. Precursor gas (i.e., sulfur dioxide, nitrogen dioxide, nitric acid, ammonia) concentrations were detectable in over 70% of the samples. $PM_{2.5}$ chloride concentrations were often below LQLs, especially for the winter periods.

- Significant fractions (approximately 85%) of $PM_{2.5}$ ammonium nitrate volatilized during the summer when temperatures were high. Less than 15% of ammonium nitrate typically volatilized during the fall when temperatures were low. Approximately 50% of $PM_{2.5}$ ammonium nitrate volatilized during the winter and spring seasons. Thermal equilibrium between gas and particle phases of $PM_{2.5}$ total particulate nitrate and ammonium corresponded to diurnal changes in temperature. $PM_{2.5}$ nitrate and ammonium concentrations showed more volatilization during the daytime and less volatilization during the nighttime.
- Anion/cation balances for the dry deposition samples supported the accuracy and precision of ion chromatographic (IC) measurements for nitrate and sulfate and of automated colorimetric (AC) measurements for ammonium. Measured ammonium was completely explained by the presence of ammonium sulfate and ammonium nitrate in the majority of cases. During winter, a mixture of ammonium bisulfate and ammonium sulfate as well as ammonium nitrate made up the measured ammonium.
- The sum of ionic species versus $PM_{2.5}$ mass revealed that chloride, nitrate, sulfate, and ammonium were the major components of $PM_{2.5}$ mass, accounting for approximately 50% of the $PM_{2.5}$ mass in this study.
- High correlation coefficients ($r > 0.80$) were found between $PM_{2.5}$ mass and ions (i.e., sulfate, ammonium, $PM_{2.5}$ total particulate nitrate) and between ammonium and nitrate compounds (i.e., $PM_{2.5}$ non-volatilized nitrate, total particulate nitrate). The precursor gases of nitric acid, sulfur dioxide, and ammonia showed little ($r < 0.5$) or no correlations with their secondary product of nitrate, sulfate, and ammonium, respectively.
- Daytime average concentrations for all the particulate species were similar to the nighttime averages at all seasons. Season-to-season variations were significant for $PM_{2.5}$ mass and ions, with the lowest values reported during winter and reaching maximum concentrations during summer.
- Reactive gaseous species experienced substantial variability between daytime and nighttime and among the four seasons. Elevated gaseous concentrations almost always occurred during the daytime, which is consistent with the higher source emission rates, photochemical reactions, and potential transport phenomena during the daytime.
- The separation of daytime sampling intervals into the morning and afternoon periods during the intensive monitoring program between 07/18/93 and 07/31/93 provided insight into the diurnal variations of particle and gaseous concentrations. In most cases, gas and particle concentrations were lowest during the morning (i.e., 0600 to 1200 PST) and highest during the afternoon (i.e., 1200 to 1800 PST). Similar distribution and concentration levels were found among the routine and intensive monitoring data acquired during the summers of 1992, 1993, and 1994.
- Wet deposition samples for anions (i.e., chloride, nitrate, sulfate) were detected in over 70% of the cases, whereas cations (i.e., ammonium, soluble sodium, soluble magnesium, soluble calcium) were detected in over 60% of the cases. Soluble potassium ions were detectable in less than 35% of the cases.
- Charge balance for the wet deposition samples provides confidence in that the ionic measurement made by ion chromatographic (i.e., chloride, nitrate, sulfate), automated colorimetric (i.e., ammonium), atomic absorption spectrophotometric (i.e., soluble sodium, magnesium, potassium, and

calcium), and pH (i.e., hydrogen ion) analyses were in good agreement with each other.

- Consistent pH measurements were acquired both at the field (on-site) and in the laboratory with a precision of $\pm$ 5%. Conductivity measurement in the laboratory were consistently 10% lower than the on-site field measurement, which implies the decrease of conductance on precipitation samples over time.
- Wet deposition is non-acidic, with pH normally exceeding 5.5. The lowest pH value measured was 4.2 during the summer of 1993 with less than one inch of precipitation. No apparent seasonal variations were found in the pH value.
- Correlations among the wet deposition ionic species were directly related to their chemical forms in the atmosphere. Conductivity measurements were also highly correlated with the ionic species, with low concentrations in winter and maximum concentrations in summer.
- Nitrate and sulfate ions were the most prominent species acquired in the wet deposition samples, accounting for 50% and 25% of the total measured ions, respectively.
- Concurrent hourly ozone measurements at the "Plot 2" and "Heart Bar" sites showed reasonably good agreement ($r > 0.87$) with the ozone measurements acquired at the Barton Flats station.
- Ozone was the most frequently observed reactive compound at the Barton Flats Station. Hourly ozone concentrations exceeded NAAQS of 120 ppb on over 20% of the sampling days. Peak ozone concentrations exceeding 200 ppb were found.
- The meteorology in the study area is characterized by: synoptic-scale high/low pressure systems, sea breeze/land breeze, and upslope/downslope flows. Sea breeze and upslope/downslope flows are the predominant wind flow patterns during summer which results in consistent diurnal patterns, whereas, the synoptic scale weather system often causes greater day-to-day variability during winter.
- Particles emitted and formed in the Los Angeles Basin were transported into the Barton Flats Station area during late spring, summer, and early fall. This transport corresponded to the afternoon upslope flows. Downslope flows occurred after sunset and returned some of the pollutants to the Barton Flats Station site.

2.6 References

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Table 2-1

Aerometric Measurements Acquired at the Barton Flats Station, CA

Measurement	Averaging Time	Duration and Sampling Frequency	Measurement Method/Instrument
I. Dry Deposition			
$PM_{2.5}$ Mass	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Gravimetric analysis with microbalance of Teflon filters (Cahn 31 Electro-microbalance)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	
$PM_{2.5}$ Cl^-, NO_3^-, and $SO_4^=$	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Ion chromatography on quartz-fiber filter extracts (Dionex 2020i Ion Chromatographic System)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	
$PM_{2.5}$ NH_4^+	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Automated colorimetry on quartz-fiber filter extracts (TRAACS 800 System)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	

Table 2-1 (continued)

Aerometric Measurements Acquired at the Barton Flats Station, CA

Measurement	Averaging Time	Duration and Sampling Frequency	Measurement Method/Instrument
SO_2	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Ion chromatography for sulfate on particle-free potassium carbonate impregnated cellulose fiber filters (Dionex 2020i Ion Chromatographic System)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	
NO_2	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Automated colorimetry for nitrate on particle-free triethanolamine (TEA) impregnated cellulose fiber filter extracts (TRAACS 800 System)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	
NH_3	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Automated colorimetry for ammonium on particle-free citric acid impregnated cellulose fiber filter extracts (TRAACS 800 System)
	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	

Table 2-1 (continued)

Aerometric Measurements Acquired at the Barton Flats Station, CA

	Measurement	Averaging Time	Duration and Sampling Frequency	Measurement Method/Instrument
	Denuder Difference Nitric Acid (HNO_3)	0600 to 1800, 1800 to next day 0600 PST.	Two consecutive samples every sixth day between 11/2/91 and 09/28/93 and between 06/01/94 and 08/30/94.	Ion Chromatography on nylon backup filter extracts (Dionex 2020i Ion Chromatographic System)
	Denuder Difference Nitric Acid (HNO_3) (cont.)	0600 to 1200, 1200 to 1800, 1800 to next day 0600 PST.	Three samples per day between 07/18/93 and 07/31/93.	
II.	***Wet Deposition***			
	Wet Deposition Sampler	Weekly	Once/Week	Aerochem Metrics Model 301 Precipitation Collector
	pH	Weekly	Once/Week	Orion pH Meter on wet samples (Model 720A)
	Conductivity	Weekly	Once/Week	YSI Conductivity Meter on wet samples (Model 32FL)
	Cl^-, NO_3^- and $SO_4^=$	Weekly	Once/Week	Ion Chromatography on wet samples (Dionex 2020i Ion Chromatographic System)
	NH_4^+	Weekly	Once/Week	Automated colorimetry on wet samples (TRAACS 800 System)

Table 2-1 (continued)

Aerometric Measurements Acquired at the Barton Flats Station, CA

	Measurement	Averaging Time	Duration and Sampling Frequency	Measurement Method/Instrument
	Na^+, Mg^{++}, K^+, and Ca^{++}	Weekly	Once/Week	Atomic Absorption Spectrophotometry on wet samples (Perkin-Elmer Model 2380 System)
	Rainfall Rate	1-Hour during events	Daily, 24 hr/day	Belfort Model 5-780 Universal Recording Rain Gauge
III.	*Gas*			
	O_3	1 hour	Daily, 24 hr/day	Dasibi 1008 AH ultraviolet absorption monitor
IV.	*Meteorology*			
	Wind Speed	1 hour	Daily, 24 hr/day	Met-One Model 014A 3-cup Anemometer with magnetic activated reed switch
	Wind Direction	1 hour	Daily, 24 hr/day	Met-One Model 024A Wind Vane
	Sigma Theta	1 hour	Daily, 24 hr/day	Met-One Model 024A Wind Vane
	Temperature	1 hour	Daily, 24 hr/day	Campbell Model 207 Thermister
	Relative Humidity	1 hour	Daily, 24 hr/day	Campbell Model 207 Humidity Sensor
	Solar Radiation	1 hour	Daily, 24 hr/day	Li-Cor Model 200SZ Pyranometer (silicon photodiode)
	Leaf Wetness	1 hour	Daily, 24 hr/day	Model 237 Leaf Wetness Sensor

Table 2-2
Standard Operating Procedures Applied to Aerometric Measurements at the Barton Flats Station, CA

Subject	Observable/Method	Title	Date of Last Revision
I. FIELD OPERATIONS			
Meteorological Sampling	Wind Speed, Wind Direction, Temperature, Relative Humidity, Solar Radiation, and Leaf Wetness	Operation Maintenance of meteorological Instruments (DRI SOP 1-312.3)	1st Quarter, 1994
		Operation and Maintenance of the Campbell 21X Datalogger (DRI SOP 1-529.1)	1st Quarter, 1994
Air Quality Sampling	Ozone (O_3)	Operation and Maintenance of the Dasibi 1008 AH Ozone Analyzer (DRI SOP 1-112.3)	1st Quarter, 1994
		Operation and Maintenance of the Dasibi 1003 PC Ozone Calibrator (DRI SOP 1-113.2)	1st Quarter, 1994
	$PM_{2.5}$, Nitric Acid (HNO_3), Nitrogen Dioxide (NO_2), Ammonia (NH_3), and Sulfur Dioxide (SO_2)	DRI MEDVOL Gas/$PM_{2.5}$ Particle Sampler Operation, Maintenance, and Field Calibration (DRI SOP 1-231.1)	1st Quarter, 1994
	Precipitation	Operation of the Aerochem Metrics Model 301 Precipitation Collector (DRI SOP 1-228.2)	1st Quarter, 1994
	Precipitation	Operation/Calibration of the Belfort Model 5-780 Universal Rain Gauge (DRI SOP 1-229.2)	1st Quarter, 1994
II. LABORATORY OPERATIONS			
Chain-of-Custody	Filter Pack Handling	Filter Pack Assembling, Disassembling, and Cleaning Procedure (DRI SOP 2-208.3)	4th Quarter, 1994
	Shipping and Receiving	Sample Shipping, Receiving, and Chain-of-Custody (DRI SOP 2-209.3)	4th Quarter, 1994
Sample Pretreatment	Filter Impregnations	Impregnating, Drying, and Acceptance Testing of Filters for sampling Gases in Air (DRI SOP 2-104.3)	4th Quarter, 1994
	Nylon Filter Prewashing	Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling (DRI SOP 2-105.3)	4th Quarter, 1994

Table 2-2 (continued)
Standard Operating Procedures Applied to Aerometric Measurements at the Barton Flats Station, CA

Subject	Observable/Method	Title	Date of Last Revision
Sample Pretreatment (cont.)	Quartz Filter Pre-Firing	Pre-firing of Quartz Fiber Filters for Carbonaceous Material Sampling (DRI SOP 2-106.3)	4th Quarter, 1994
Chemical Analysis	Filter Sectioning	Sectioning of Teflon Filter Samples (DRI SOP 2-201.3)	2nd Quarter, 1994
	Filter Extraction	Extraction of Ionic Species from Filter Samples (DRI SOP 2-202.3)	4th Quarter, 1994
	Mass	Gravimetric Analysis Procedure (DRI SOP 2-102.3)	3rd Quarter, 1994
	Chloride (Cl^-), Nitrate (NO_3^-), and Sulfate ($SO_4^=$)	Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography (DRI SOP 2-203.4)	4th Quarter, 1994
	Ammonium (NH_4^+)	Analysis of Filter Extracts and Precipitation Samples by Automated Colormetric Analysis (DRI SOP 2-207.3)	2nd Quarter, 1994
	Sodium (Na^+), Magnesium (Mg^{++}), Potassium (K^+), and Calcium (Ca^{++})	Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy (DRI SOP 2-206.3)	4th Quarter, 1994
	Nitrite (NO_2^-)	Nitrite Analysis by Technicon TRAACS 800 (DRI SOP ARB 2260-401)	3rd Quarter, 1988
	Conductivity	Operation and Maintenance of the YSI Model 32FL Conductivity Meter (DRI SOP 2-210.2)	1st Quarter, 1992
	pH	Operation and Maintenance of Orion Model 720A pH Meter (DRI SOP 2-211.1)	4th Quarter, 1991
III. DATA PROCESSING AND DATA VALIDATION			
	Aerosol/Gas Data	Dry Deposition Field, Mass, and Chemical Data Processing and Data Validation (DRI SOP 3-003.4)	4th Quarter, 1994
	Meteorological Data	Meteorological and Continuous Gaseous Data Processing and Validation (DRI SOP 3-109.2)	4th Quarter, 1994

Table 2-3

Summary of Aerometric Data Base Files Acquired at the Barton Flats Station, CA

Category	Data Base File	File Description	Number of Records	Data Base Structure Reference
Dry deposition	FOCON.DBF and FOCON.FPT	Contains $PM_{2.5}$ mass and Cl^-, NO_3^-, $SO_4^=$, NH_4^+ concentrations, and gaseous NH_3, SO_2, NO_2 and HNO_3 concentrations. Includes data for daytime and nighttime 12-hour samples (06:00 to 18:00 and 18:00 to 06:00 PST the following day) collected from 11/2/91 to 9/28/93 and from 6/1/94 to 8/30/94 on the U.S. EPA every sixth-day sampling schedule. Also includes data for the intensive sampling period which consisted of 06:00 to 12:00, 12:00 to 18:00, and 18:00 to 06:00 PST samples collected daily from 7/18/93 through 7/31/93.	304	Table A2-2
Wet deposition	FOWET.DBF and FOWET.FPT	Contains Cl^-, NO_3^-, $SO_4^=$, NH_4^+, Na^+, Mg^{++}, K^+ and Ca^{++} concentrations, and pH and conductivity of wet deposition samples. Includes data for samples collected weekly each Tuesday from 11/5/91 through 9/28/93 and from 5/31/94 through 8/30/94. Also includes daily and weekly precipitation amounts.	116	Table A2-3
Meteorology and ozone	FOMET.DBF and FOMET.FPT	Contains hourly average wind speed, wind direction, sigma theta, temperature, relative humidity, solar radiation, leaf wetness, and ozone concentration for the period 10/30/91 through 11/30/94.	27,063	Table A2-4

Table 2-3 (continued)

Summary of Aerometric Data Base Files Acquired at the Barton Flats Station, CA

Category	Data Base File	File Description	Number of Records	Data Base Structure Reference
	SCMET.DBF	Contains hourly average wind speed and wind direction for 33 sites in the South Coast Air Basin. Data provided by South Coast Air Quality Management District.	578,952	Table A2-5
	SCSITES.DBF	Contains site codes, locations, latitude and longitude of sites in SCMET.DBF.	33	Table A2-6
Data Base Documentation	README.DOC	Project and data description file, Microsoft Word 6.0 format.	N/A	N/A
	README.TXT	ASCII text version of README.DOC	N/A	N/A
	FOFLDNAM.DBF	Defines field names and measurement units used in the FoxPro dry and wet deposition and meteorological data bases.		Table A2-1
	DRYSTRU.TXT	Dry deposition data base structure documentation, ASCII text format.	N/A	N/A
	WETSTRU.TXT	Wet deposition data base structure documentation, ASCII text format.	N/A	N/A
	METSTRU.TXT	Meteorological and ozone data base structure documentation, ASCII text format.	N/A	N/A
	SCMTSTRU.TXT	Supplementary South Coast meteorological data base structure documentation, ASCII text format.	N/A	N/A

Table 2-3 (continued)

Summary of Aerometric Data Base Files Acquired at the Barton Flats Station, CA

Category	Data Base File	File Description	Number of Records	Data Base Structure Reference
	SCSTSTRU.TXT	Supplementary South Coast site data base structure documentation, ASCII test format.	N/A	N/A
	FLDFLAG.TXT	Field validation flag definitions, ASCII text format.	N/A	N/A
	CHMFLAG.TXT	Analysis validation flag definitions, ASCII text format.	N/A	N/A
	METFLAG.TXT	Meteorological/ozone validation flag definitions, ASCII text format.	N/A	N/A

Table 2-4

Field Blank Concentrations and Precisions Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93 and Between 06/01/94 and 08/30/94

Species[a]	Blank[b] Subtracted (B_i)	Blank[c] Precision (s_{Bi})	Average Field Blank	Field Blank Std. Dev. (STD_{Bi})	Root Mean Squared Blank Precision (s_{RMS})[d]	Total No. of Blanks in Average
I. Dry Deposition Sample Field Blanks (μg/filter)						
Inclusive Sampling Period (11/02/91 to 03/31/92)						
PM_{10} Mass	0.0000	8.7560	-7.0000	8.7560	5.9530	4
Chloride (Cl^-)	0.2880	0.2203	0.2880	0.2203	0.0929	5
Nitrate (NO_3^-)	0.0000	0.2415	0.1080	0.2415	0.0449	5
Sulfate ($SO_4^=$)	0.2240	0.2161	0.2240	0.2161	0.0322	5
Ammonium (NH_4^+)	0.5300	0.0643	0.5300	0.0643	0.0586	5
Ammonia (NH_3) as NH_4^+	0.7348	0.1386	0.7348	0.1386	0.0088	5
Sulfur Dioxide (SO_2) as $SO_4^=$	3.2400	1.2939	3.2400	1.2939	0.1025	5
Nitrogen Dioxide (NO_2)	1.5008	0.8902	1.5008	0.8902	0.0618	5
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.4180	0.2890	0.4180	0.2890	0.0225	5
Inclusive Sampling Period (04/06/92 to 07/29/92)						
PM_{10} Mass	0.0000	11.1766	-13.7500	11.1766	4.4730	4
Chloride (Cl^-)	0.8950	0.0772	0.8950	0.0772	0.0655	4
Nitrate (NO_3^-)	0.9300	0.3412	0.9300	0.3412	0.0087	4
Sulfate ($SO_4^=$)	0.4200	0.1608	0.4200	0.1608	0.0020	4
Ammonium (NH_4^+)	0.6675	0.1723	0.6675	0.1723	0.0183	4
Ammonia (NH_3) as NH_4^+	2.7273	0.7341	2.7273	0.7341	0.0382	4
Sulfur Dioxide (SO_2) as $SO_4^=$	3.2450	2.3961	3.2450	2.3961	0.2541	4
Nitrogen Dioxide (NO_2)	1.4750	0.5043	1.4750	0.5043	0.0071	4
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	1.1275	0.1997	1.1275	0.1997	0.0143	4
Inclusive Sampling Period (08/04/92 to 11/26/92)						
PM_{10} Mass	0.0000	16.2147	-3.7500	16.2147	7.2380	4
Chloride (Cl^-)	0.7000	0.3333	0.7000	0.0712	0.3333	4
Nitrate (NO_3^-)	0.0000	0.3333	0.2000	0.2332	0.3333	4
Sulfate ($SO_4^=$)	0.5700	0.3333	0.5700	0.2877	0.3333	4
Ammonium (NH_4^+)	0.0000	0.3333	0.1355	0.0664	0.3333	4

Table 2-4 (continued)

Field Blank Concentrations and Precisions Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93 and Between 06/01/94 and 08/30/94

Species[a]	Blank[b] Subtracted (B_i)	Blank[c] Precision (s_{Bi})	Average Field Blank	Field Blank Std. Dev. (STD_{Bi})	Root Mean Squared Blank Precision (s_{RMS})[d]	Total No. of Blanks in Average
Ammonia (NH_3) as NH_4^+	1.9568	0.4986	1.9568	0.4986	0.1667	4
Sulfur Dioxide (SO_2) as $SO_4^=$	1.9750	0.8333	1.9750	0.1323	0.8333	4
Nitrogen Dioxide (NO_2)	1.7953	1.5886	1.7953	1.5886	0.1667	4
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.3075	0.1667	0.3075	0.1005	0.1667	4
Inclusive Sampling Period (12/02/92 to 04/25/93)						
PM_{10} Mass	0.0000	4.7450	1.8000	4.6583	4.7450	5
Chloride (Cl^-)	0.4320	0.3333	0.4320	0.1339	0.3333	5
Nitrate (NO_3^-)	0.0000	0.3333	0.0600	0.1342	0.3333	5
Sulfate ($SO_4^=$)	0.0000	0.3333	0.1840	0.1734	0.3333	5
Ammonium (NH_4^+)	0.7584	0.3333	0.7584	0.3064	0.3333	5
Ammonia (NH_3) as NH_4^+	3.0105	0.5759	3.0105	0.5759	0.3333	4
Sulfur Dioxide (SO_2) as $SO_4^=$	1.3480	0.3807	1.3480	0.3807	0.3333	5
Nitrogen Dioxide (NO_2)	0.7460	0.4637	0.7460	0.4637	0.1667	5
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.2760	0.1845	0.2760	0.1845	0.1667	5
Inclusive Sampling Period (05/01/93 to 09/28/93)						
PM_{10} Mass	0.0000	10.5093	-2.2222	10.5093	8.2870	9
Chloride (Cl^-)	0.5733	0.3333	0.5733	0.0755	0.3333	9
Nitrate (NO_3^-)	0.0000	0.3333	0.2444	0.2908	0.3333	9
Sulfate ($SO_4^=$)	0.3711	0.3333	0.3711	0.2867	0.3333	9
Ammonium (NH_4^+)	0.0000	0.3333	0.1898	0.0359	0.3333	9
Ammonia (NH_3) as NH_4^+	1.7198	0.4532	1.7198	0.4532	0.1667	9
Sulfur Dioxide (SO_2) as $SO_4^=$	3.1667	0.8333	3.1667	0.7378	0.8333	9
Nitrogen Dioxide (NO_2)	1.5970	0.8212	1.5970	0.8212	0.1667	9
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.2000	0.1667	0.2000	0.1603	0.1667	9
Inclusive Sampling Period (06/01/94 to 08/30/94)						
PM_{10} Mass	0.0000	10.0167	-6.6667	10.0167	9.1140	3
Chloride (Cl^-)	1.0200	0.5000	1.0200	0.0794	0.5000	3

Table 2-4 (continued)
Field Blank Concentrations and Precisions Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93 and Between 06/01/94 and 08/30/94

Species[a]	Blank[b] Subtracted (B_i)	Blank[c] Precision (s_{Bi})	Average Field Blank	Field Blank Std. Dev. (STD_{Bi})	Root Mean Squared Blank Precision (s_{RMS})[d]	Total No. of Blanks in Average
Nitrate (NO_3^-)	0.0000	0.5000	0.0000	0.0000	0.5000	3
Sulfate ($SO_4^=$)	0.0000	0.5000	0.0000	0.0000	0.5000	3
Ammonium (NH_4^+)	0.0000	0.5000	0.3850	0.1110	0.5000	3
Ammonia (NH_3) as NH_4^+	2.4037	0.1667	2.4037	0.0800	0.1667	3
Sulfur Dioxide (SO_2) as $SO_4^=$	0.0000	0.1667	0.1567	0.0702	0.1667	3
Nitrogen Dioxide (NO_2)	0.3835	0.1667	0.3835	0.1280	0.1667	2
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.4967	0.2120	0.4967	0.2120	0.1667	3
II Wet Deposition Sample Field Blanks (μg/ml)						
Inclusive Sampling Period (11/12/91 to 08/23/94)						
Chloride (Cl^-)	0.0431	0.0269	0.0431	0.0269	0.0167	31
Nitrate (NO_3^-)	0.0282	0.0617	0.0282	0.0617	0.0167	31
Sulfate ($SO_4^=$)	0.0144	0.0167	0.0144	0.0165	0.0167	31
Ammonium (NH_4^+)	0.0133	0.0167	0.0133	0.0155	0.0167	31
Soluble Sodium (Na^+)	0.0200	0.0276	0.0200	0.0276	0.0019	31
Soluble Magnesium (Mg^{++})	0.0017	0.0036	0.0017	0.0036	0.0007	31
Soluble Potassium (K^+)	0.0058	0.0101	0.0058	0.0101	0.0021	31
Soluble Calcium (Ca^{++})	0.0337	0.0311	0.0337	0.0311	0.0093	31

[a] See Table A-2 for species identification.

[b] Values used in data processing. Non-zero average blank concentrations are subtracted when the average blank exceeds its standard deviation.

[c] Larger of either the analytical precision or standard deviation from the field.

[d] RMS precision is the square root of the sum of the squared uncertainties of the observations divided by the number of observations.

Table 2-5
Analytical Specification of 12-Hour Dry Deposition and Weekly Wet Deposition Measurements at the Barton Flats Station, CA

I. Dry Deposition	Analysis Method[a]	MDL[b] [μg/m³]	RMS[c] [μg/m³]	LQL[d] [μg/m³]	No. Values[e]	No. > LQL
PM_{10} Mass	Gravimetry	0.4859	0.4844	1.4832	285	234
Chloride (Cl^-)	IC	0.0035	0.0213	0.0425	295	43
Nitrate (NO_3^-)	IC	0.0035	0.0211	0.0504	295	278
Sulfate ($SO_4^=$)	IC	0.0035	0.0210	0.0421	295	291
Ammonium (NH_4^+)	AC	0.0035	0.0211	0.0422	295	271
Ammonia (NH_3)	AC	0.0035	0.0122	0.1188	291	267
Sulfur Dioxide (SO_2)	IC	0.0035	0.0400	0.2030	291	206
Nitrogen Dioxide (NO_2)	AC	0.0347	0.0098	0.1258	294	250
Total Particulate Nitrate (NO_3^-)	IC	0.0035	0.0099	0.0484	284	263
Nitric Acid (HNO_3^-)	IC	0.0060	0.0253	0.0926	284	222

II. Wet Deposition	Analysis Method[a]	MDL[b] [μg/ml]	RMS[c] [μg/ml]	LQL[d] [μg/ml]	No. Values[e]	No. > LQL
Chloride (Cl^-)	IC	0.0500	0.0167	0.0537	51	45
Nitrate (NO_3^-)	IC	0.0500	0.0167	0.1234	51	40
Sulfate ($SO_4^=$)	IC	0.0500	0.0167	0.0334	51	50
Ammonium (NH_4^+)	AC	0.0500	0.0167	0.0334	51	39
Soluble Sodium (Na^+)	AAS	0.0500	0.0019	0.0551	51	31
Soluble Magnesium (Mg^{++})	AAS	0.0030	0.0007	0.0071	51	36
Soluble Potassium (K^+)	AAS	0.0100	0.0021	0.0202	51	17
Soluble Calcium (Ca^{++})	AAS	0.0025	0.0093	0.0623	51	31

[a] IC: Ion Chromatography
AC: Automated Colorimetry
AAS: Atomic Absorption Spectrophotometry

[b] Minimum Detectable Limits (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero. Typical sample volumes are 1.44 m^2 for NO_2 sampling port and 14.4 m^3 for the other sampling ports.

[c] RMS or root mean squared precision is the square root of the sum of the square uncertainties of the observations divided by the number of observations.

[d] LQL or lower quantifiable limit is equal to two times the uncertainty of the field blank. The LQL is expressed here in terms of mass per cubic meter, after dividing by 14.4 m^3, (the nominal volume of a 12-hour sample at 20 L/min) for every sampling port but NO_2 in the dry deposition sampler and dividing by 1.44 m^3 (the nominal volume of a 12-hour sample at 2 L/min) for the NO_2 sampling port.

[e] Number of non-voided (with -99) values reported.

Table 2-6a

Summary of the Dry Deposition Sampling System Flow Check Results at the Barton Flats Station, CA

I. Sequential Gas/Particle Sampler Flow Rate Performance Checks

Date	Filter Pack	Port	Setpoint Flow Rate (lpm)	Test Flow Rate (lpm)	Difference[a] (%)
11/29/91	TK	1	39.25	40.63	+3.5
	TK	2	39.24	40.63	+3.6
	DN	4	39.02	40.63	+4.1
	DN	5	39.99	40.63	+1.6
	QN	7	39.67	40.63	+2.4
	QN	8	39.82	40.63	+2.0
	GT	10	1.850	1.934	+4.5
	GT	11	1.850	1.934	+4.5
	Make up		98.85	100.87	+2.0
01/06/92	TK	1	39.25	42.30	+7.8
	TK	2	38.78	41.52	+7.1
	DN	4	39.02	41.91	+7.4
	DN	5	39.99	41.52	+3.8
	QN	7	38.95	40.63	+4.3
	QN	8	39.82	41.03	+3.0
	GT	10	1.850	1.934	+4.5
	GT	11	1.850	1.934	+4.5
	Make up		98.85	102.79	+4.0
02/04/92	TK	1	39.25	41.03	+4.5
	TK	2	39.24	40.63	+3.6
	DN	4	39.02	40.63	+4.1
	DN	5	39.62	40.44	+2.1
	QN	7	38.95	40.05	+2.8
	QN	8	39.82	40.44	+1.6
	GT	10	1.850	1.934	+4.5
	GT	11	1.872	1.934	+3.3
	Make up		98.85	102.79	+4.0
03/12/92	TK	1	39.25	40.63	+3.5
	TK	2	39.69	41.22	+3.9
	DN	4	39.02	40.63	+4.1
	DN	5	40.35	40.63	+0.7
	QN	7	38.95	40.05	+2.8
	QN	8	40.21	40.63	+1.0
	GT	10	1.850	1.934	+4.5
	GT	11	1.872	1.934	+3.3
	Make up		98.85	100.87	+2.0

Table 2-6a (continued)

Summary of the Dry Deposition Sampling System Flow Check Results at the Barton Flats Station, CA

I. Sequential Gas/Particle Sampler Flow Rate Performance Checks

Date	Filter Pack	Port	Setpoint Flow Rate (lpm)	Test Flow Rate (lpm)	Difference[a] (%)
04/17/92	TK	1	39.25	40.63	+3.5
	TK	2	39.69	40.63	+2.4
	DN	4	39.02	40.63	+4.1
	DN	5	39.99	40.63	+1.6
	QN	7	38.95	40.05	+2.8
	QN	8	40.21	40.63	+1.0
	GT	10	1.850	1.934	+4.5
	GT	11	1.872	1.934	+3.3
	Make up		98.85	103.76	+5.0
05/22/92	TK	1	41.50	40.63	-2.1
	TK	2	41.35	40.63	-1.7
	DN	4	40.38	40.63	+0.6
	DN	5	41.05	40.63	-1.0
	QN	7	40.06	40.05	0.0
	QN	8	40.89	40.63	-0.6
	GT	10	1.913	1.934	+1.1
	GT	11	1.737	1.934	+11.3
	Make up		103.80	100.87	-2.8
06/22/92	TK	1	41.50	40.63	-2.1
	TK	2	41.35	40.63	-1.7
	DN	4	40.38	40.05	-0.8
	DN	5	40.75	40.63	-0.3
	QN	7	40.06	40.05	0.0
	QN	8	40.57	40.63	+0.2
	GT	10	1.913	1.934	+1.1
	GT	11	1.737	1.934	+11.3
	Make up		103.80	100.87	-2.8
07/24/92	TK	1	41.50	40.63	-2.1
	TK	2	41.35	40.63	-1.7
	DN	4	40.38	40.05	-0.8
	DN	5	41.05	40.63	-1.0
	QN	7	40.06	40.05	0.0
	QN	8	40.25	40.63	+1.0
	GT	10	1.913	1.934	+1.1
	GT	11	1.737	1.934	+11.3
	Make up		103.80	119.15	+14.8

Table 2-6a (continued)

Summary of the Dry Deposition Sampling System Flow Check Results at the Barton Flats Station, CA

I. Sequential Gas/Particle Sampler Flow Rate Performance Checks

Date	Filter Pack	Port	Setpoint Flow Rate (lpm)	Test Flow Rate (lpm)	Difference[a] (%)
08/27/92	TK	1	41.50	40.63	-2.1
	TK	2	41.35	40.63	-1.7
	DN	4	40.38	40.63	+0.6
	DN	5	41.05	40.63	-1.0
	QN	7	40.06	40.05	0.0
	QN	8	40.89	40.63	-0.6
	GT	10	1.913	1.934	+1.1
	GT	11	1.737	1.934	+11.3
	Make up		103.80	102.79	-1.0
09/28/92	TK	1	38.40	36.12	-5.9
	TK	2	38.39	36.12	-5.9
	DN	4	38.21	36.61	-4.2
	DN	5	38.57	36.61	-5.1
	QN	7	38.17	37.10	-2.8
	QN	8	38.26	37.10	-3.0
	GT	10	1.807	1.826	+1.1
	GT	11	1.581	1.826	+15.5
	Make up		96.92	112.41	+16.0
10/29/92	TK	1	38.40	39.07	+1.7
	TK	2	38.39	39.07	+1.8
	DN	4	38.21	39.56	+3.5
	DN	5	38.90	39.56	+1.7
	QN	7	38.17	39.07	+2.4
	QN	8	38.60	39.07	+1.2
	GT	10	1.807	1.826	+1.1
	GT	11	1.581	1.826	+15.5
	Make up		96.92	102.79	+6.1
11/27/92	TK	1	38.40	35.63	-7.2
	TK	2	37.94	35.63	-6.1
	DN	4	38.21	37.59	-1.6
	DN	5	39.21	37.59	-4.1
	QN	7	38.17	37.59	-1.5
	QN	8	38.26	37.59	-1.7
	GT	10	1.807	1.867	+3.4
	GT	11	1.581	1.867	+18.1
	Make up		96.92	113.38	+17.0

Table 2-6a (continued)

Summary of the Dry Deposition Sampling System Flow Check Results at the Barton Flats Station, CA

I. Sequential Gas/Particle Sampler Flow Rate Performance Checks

Date	Filter Pack	Port	Setpoint Flow Rate (lpm)	Test Flow Rate (lpm)	Difference[a] (%)
01/04/93	TK	1	37.94	38.09	+0.4
	TK	2	37.54	38.09	+1.5
	DN	4	38.48	38.58	+0.3
	DN	5	37.53	38.58	+2.8
	QN	7	37.83	38.58	+2.0
	QN	8	38.00	38.58	+1.5
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	100.87	-10.7
02/11/93	TK	1	37.94	37.59	-0.9
	TK	2	37.54	37.59	+0.2
	DN	4	38.48	38.09	-1.0
	DN	5	37.53	38.09	+1.5
	QN	7	37.83	38.58	+2.0
	QN	8	38.00	38.58	+1.5
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	100.87	-10.7
03/11/93	TK	1	37.94	37.10	-2.2
	TK	2	37.54	37.10	-1.2
	DN	4	38.48	38.09	-1.0
	DN	5	37.53	38.09	+1.5
	QN	7	37.83	38.09	+0.7
	QN	8	38.68	38.09	-1.5
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	102.79	-9.0
04/23/93	TK	1	37.94	37.10	-2.2
	TK	2	37.54	37.10	-1.2
	DN	4	38.48	37.59	-2.3
	DN	5	37.18	37.59	+1.1
	QN	7	37.83	38.09	+0.7
	QN	8	38.00	38.09	+0.2
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	107.60	-4.7

Table 2-6a (continued)

Summary of the Dry Deposition Sampling System Flow Check Results at the Barton Flats Station, CA

I. Sequential Gas/Particle Sampler Flow Rate Performance Checks

Date	Filter Pack	Port	Setpoint Flow Rate (lpm)	Test Flow Rate (lpm)	Difference[a] (%)
05/24/93	TK	1	37.94	37.10	-2.2
	TK	2	37.54	37.10	-1.2
	DN	4	38.48	37.59	-2.3
	DN	5	37.59	37.59	0.0
	QN	7	37.83	38.09	+0.7
	QN	8	38.34	38.09	-0.7
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	109.53	-3.0
06/29/93	TK	1	37.94	36.12	-4.8
	TK	2	37.07	36.12	-2.5
	DN	4	38.48	37.10	-3.6
	DN	5	37.53	37.10	-1.1
	QN	7	37.83	37.59	-0.6
	QN	8	38.00	37.59	-1.1
	GT	10	1.973	1.826	-7.5
	GT	11	1.962	1.826	-6.9
	Make up		112.95	107.60	-4.7
09/30/93	TK	1	37.51	37.10	-1.1
	TK	2	37.46	37.10	-0.9
	DN	4	37.72	37.59	-0.3
	DN	5	37.13	37.59	+1.3
	QN	7	37.07	37.59	+1.4
	QN	8	37.20	37.59	+1.1
	GT	10	1.826	1.826	0.0
	GT	11	1.872	1.826	-2.5
	Make up		108.33	119.15	+10.0
08/31/94	TK	1	38.47	39.07	+1.6
	TK	2	39.30	39.07	-0.6
	DN	4	38.30	37.10	-3.1
	DN	5	37.03	37.10	+0.2
	QN	7	38.17	38.58	+1.1
	QN	8	37.96	38.58	+1.6
	GT	10	1.806	1.826	+1.1
	GT	11	1.736	1.826	+5.2
	Make up		98.17	97.98	-0.2

[a] 100 x (Test Flow Rate - Setpoint Flow Rate) / Setpoint Flow Rate

Table 2-6b

Summary of the Ozone Audit Results at the Barton Flats Station, CA

II. Ozone Analyzer

Date	Audit Type	Analyzer	Site Ozone (ppb)	Audit Ozone (ppb)	Difference[a] (%)
10/23/91	In lab check	Dasibi 1008AH	436.2	442.0	-1.3
		S.N. 4776	331.7	336.0	-1.3
		ambient monitor	218.0	220.6	-1.2
			98.7	100.0	-1.3
			19.3	18.9	+2.1
10/30/91	After field installation	Dasibi 1008AH	477.1	482.3	-1.1
		S.N. 4776	365.3	368.0	-0.7
		ambient monitor	216.0	217.1	-0.5
			142.0	142.7	-0.5
			49.0	49.2	-0.4
10/30/91	After field installation	Dasibi 1003PC	480.3	488.8	-1.7
		S.N. 5528	356.6	362.4	-1.6
		calibrator	222.0	225.6	-1.6
			174.2	176.6	-1.4
			81.2	83.4	-2.6
05/13/92	As is	Dasibi 1008 AH	395.6	418.8	-5.5
		S.N. 4776	309.3	328.3	-5.8
		ambient monitor	200.0	211.9	-5.6
			101.7	107.8	-5.7
			46.7	49.1	-4.9
05/15/92	After maintenance	Dasibi 1008 AH	390.7	446.9	-12.6
		S.N. 4776	317.5	363.0	-12.5
		ambient monitor	211.0	236.5	-10.8
			85.0	94.9	-10.4
05/16/92	Replacement analyzer	Dasibi 1008 AH	414.7	411.9	+0.7
		S.N. 4759	304.0	301.8	+0.7
		ambient monitor	201.4	198.7	+1.4
			98.0	96.2	+1.9
			48.0	46.5	+3.2
05/13/92	As is	Dasibi 1003 PC	409.9	405.0	+1.2
		S.N. 5528	306.9	303.8	+1.0
		calibrator	204.6	201.0	+1.8
			97.6	94.2	+3.6
			47.0	44.8	+4.9
05/16/94	After maintenance	Dasibi 1003 PC	413.3	410.9	+0.6
		S.N. 5528	303.0	301.5	+0.5
		calibrator	199.7	198.4	+0.7
			98.0	96.8	+1.2
			46.8	46.1	+1.5

Table 2-6b (continued)

Summary of the Ozone Audit Results at the Barton Flats Station, CA

II. Ozone Analyzer

Date	Audit Type	Analyzer	Site Ozone (ppb)	Audit Ozone (ppb)	Difference[a] (%)
11/14/92	As is	Dasibi 1008 AH	373.7	382.5	-2.3
		S.N. 4759	282.5	290.3	-2.7
		ambient monitor	197.9	202.4	-2.2
			95.8	97.9	-2.2
			41.2	40.7	+1.2
11/14/92	As is	Dasibi 1003 PC	409.9	390.5	+5.0
		S.N. 5528	291.6	279.5	+4.3
		calibrator	210.7	202.2	+4.2
			101.9	97.6	+4.4
			54.6	52.7	+3.6
07/15/93	As is	Dasibi 1008 AH	426.6	440.3	-3.1
		S.N. 4759	341.4	350.3	-2.5
		ambient	244.4	251.2	-2.7
			141.1	144.7	-2.5
			46.0	46.3	-0.7
07/15/93	As is	Dasibi 1003 PC	444.4	436.5	+1.8
		S.N. 5528	355.2	349.4	+1.7
		calibrator	254.6	250.2	+1.8
			146.8	144.0	+1.9
			49.7	47.5	+4.6
07/15/93	Collocated analyzer	Dasibi 1008 AH	432.5	442.3	-2.2
		S.N. 4776	346.8	353.7	-2.0
		collocated	249.7	252.8	-1.2
			145.5	145.6	-0.1
			48.4	45.6	+6.1
05/24/94	As is	Dasibi 1008 AH	389.4	404.4	-3.7
		S. N. 4759	287.4	300.6	-4.4
		ambient monitor	194.4	200.4	-3.0
			96.0	96.7	-0.7
			45.7	45.0	+1.6
05/25/94	After maintenance	Dasibi 1008 AH	397.8	407.0	-2.3
		S.N. 4759	296.0	302.9	-2.3
		ambient monitor	198.5	203.4	-2.4
			94.7	97.0	-2.4
			45.9	49.7	-7.6
05/27/94	After maintenance	Dasibi 1008 AH	391.9	405.7	-3.4
		S. N. 4759	289.9	298.7	-3.0
		ambient monitor	195.4	203.9	-4.2
			95.7	99.2	-3.5
			46.3	45.7	+1.3

Table 2-6b (continued)

Summary of the Ozone Audit Results at the Barton Flats Station, CA

II. Ozone Analyzer

Date	Audit Type	Analyzer	Site Ozone (ppb)	Audit Ozone (ppb)	Difference[a] (%)
05/24/94	As is	Dasibi 1003 PC	403.8	408.6	-1.2
		S. N. 5528	301.3	305.3	-1.3
		calibrator	201.8	202.9	-0.5
			96.6	94.5	+2.2
			46.0	44.3	+3.8
05/27/94	After maintenance	Dasibi 1003 PC	409.1	407.3	+0.4
		S.N. 5528	301.8	300.1	+0.6
		calibrator	204.3	205.2	-0.4
			101.1	99.8	+1.3
			49.1	48.5	+1.2

[a] 100 x (Site Ozone - Audit Ozone) / Audit Ozone

Table 2-6c

Summary of the Meteorological Instrument Audit Results at the Barton Flats Station, CA

I. Wind Speed

Date	Site Wind Speed (m/s)	Audit Wind Speed (m/s)	Difference[a] (m/s)
10/30/91	8.8	8.4	+0.4
10/30/91	16.4	16.4	0.0
10/30/91	48.8	48.4	+0.4
05/14/92	8.4	8.4	0.0
05/14/92	16.4	16.4	0.0
05/14/92	48.6	48.4	+0.2
11/13/92	8.6	8.4	+0.2
11/13/92	16.8	16.4	+0.4
11/13/92	49.2	48.4	+0.8
07/16/93	8.4	8.4	0.0
07/16/93	16.8	16.4	+0.4
07/16/93	48.4	48.4	0.0
05/24/94	8.4	8.4	0.0
05/24/94	16.8	16.4	+0.4
05/24/94	48.4	48.4	0.0

II. Wind Direction Sensor

Date	Site Wind Direction (degrees)	Target Bearing (degrees)	Difference[a] (degrees)
10/30/91	[b]	[b]	
05/14/92	[b]	[b]	
11/13/92	360[c]	0[c]	0
11/13/92	179[c]	180[c]	-1
07/16/93	359[c]	0[c]	-1
07/16/93	178[c]	180[c]	-2
07/16/93	92[c]	90[c]	+2
07/16/93	275[c]	270[c]	+5
05/24/94	277	278	-1
05/24/94	1	0	+1
05/24/94	180	180	0
05/24/94	181	180	+1

Table 2-6c (continued)

Summary of the Meteorological Instrument Audit Results at the Barton Flats Station, CA

III. Temperature Sensor

Date	Site Temperature (°C)	Audit Temperature (°C)	Difference[a] (°C)
10/30/91	6.8	6.5	+0.3
05/19/92	16.2	17.4	-1.2
11/13/92	15.4	14.5	+0.9
11/13/92	15.6	16.6	-1.0
11/13/92	15.7	17.1	-1.4
07/16/93	17.8	20.0	-2.2
07/16/93	16.0	17.2	-1.2
07/16/93	16.1	16.8	-0.7
05/24/94	18.6	22.5	-3.9[d]
05/24/94	18.5	19.4	-0.9
05/24/94	19.6	21.6	-2.0

IV. Relative Humidity Sensor

Date	Site Relative Humidity (%)	Audit Relative Humidity (%)	Difference[a] (%)
10/30/91	24.8	17.6	+7.2
05/16/92	56.5	52.1	+4.4
05/16/92	57.3	17.4	-0.1
11/13/92	15.5	15.1	+0.4
11/13/92	15.6	16.8	-1.2
07/16/93	16.7	15.6	+0.8
07/16/93	44.3	50.7	-6.4
07/16/93	44.3	49.7	-5.4
05/24/94	15.7	28.5	-12.8[e]
05/24/94	15.7	30.9	-15.2[e]
05/24/94	15.1	22.9	-7.8

Table 2-6c (continued)

Summary of the Meteorological Instrument Audit Results at the Barton Flats Station, CA

V. Solar Radiation

Date	Site Solar Radiation (W/m^2)	Audit Solar Radiation (W/m^2)	Difference (W/m^2)
05/15/92	625	610	+15
05/15/92	566	559	+7
05/15/92	541	530	+11
07/16/93	838	833	+5
07/16/93	728	716	+12
07/16/93	670	727	-57
05/24/94	931	930	+1
05/24/94	978	1033	-55
05/24/94	899	930	-31

[a] Site sensor value – audit value

[b] Could not sight targets because of trees and haze. Crossarm aligned along magnetic North/South line ± 5 degrees when installed.

[c] Could not sight targets due to trees and magnetic interference from shelter and tower. Checked alignment of vane with crossarm.

[d] Temperature data collected between 10/01/93 and 07/27/94 flagged as suspect. New sensor installed 07/27/94.

[e] Time series of relative humidity data shows marked change in response on audit date. Data collected 10/01/93 to 05/23/94 flagged as suspect. Data collected 05/24/94 to 07/27/94 invalidated. New sensor installed 07/27/94.

Table 2-7

Correlations of Dry and Wet Deposition Measurements at the Barton Flats Station, CA, Between 10/31/91 and 09/30/93 and Between 06/01/94 and 08/31/94

I. Dry Deposition, Ozone, and Meteorological Measurements[a]

	$PM_{2.5}$ Mass	Chloride (Cl^-)	Nitrate (NO_3^-)	Sulfate ($SO_4^=$)	Ammonium (NH_4^-)	Ammonia (NH_3)	Sulfur Dioxide (SO_2)	Nitrogen Dioxide (NO_2)	$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	Nitric Acid (HNO_3)	Ozone (O_3)	Temp.
$PM_{2.5}$ Mass												
Chloride (Cl^-)	0.031											
Nitrate (NO_3^-)	0.563	0.055										
Sulfate ($SO_4^=$)	0.827	0.077	0.257									
Ammonium (NH_4^+)	0.845	0.076	0.859	0.701								
Ammonia (NH_3)	0.617	0.106	0.163	0.620	0.441							
Sulfur Dioxide (SO_2)	0.479	0.153	0.117	0.474	0.310	0.573						
Nitrogen Dioxide (NO_2)	0.667	-0.020	0.439	0.523	0.580	0.502	0.466					
$PM_{2.5}$ Total Particulate Nitrate (NO_3^-)	0.828	0.060	0.695	0.628	0.842	0.628	0.394	0.572				
Nitric Acid (HNO_3)	0.328	0.053	-0.113	0.509	0.170	0.693	0.499	0.217	0.270			
Ozone (O_3)	0.578	0.035	0.085	0.591	0.314	0.702	0.693	0.407	0.449	0.670		
Temperature	0.451	-0.008	-0.023	0.505	0.197	0.663	0.592	0.458	0.217	0.645	0.733	
Relative Humidity	-0.051	0.126	0.158	0.036	0.130	-0.179	-0.235	0.039	0.100	-0.309	-0.434	-0.552

II. Wet Deposition Data[b]

	Chloride (Cl^-)	Nitrate (NO_3^-)	Sulfate ($SO_4^=$)	Ammonium (NH_4^-)	Soluble Sodium (Na^+)	Soluble Magnesium (Mg^+)	Soluble Potassium (K^+)	Soluble Calcium (Ca^+)	Conductivity	pH
Chloride (Cl^-)										
Nitrate (NO_3^-)	0.593									
Sulfate ($SO_4^=$)	0.611	0.927								
Ammonium (NH_4^+)	0.663	0.807	0.781							
Soluble Sodium (Na^+)	0.906	0.600	0.666	0.518						
Soluble Magnesium (Mg^{++})	0.819	0.782	0.792	0.674	0.894					
Soluble Potassium (K^+)	0.603	0.431	0.491	0.508	0.706	0.775				
Soluble Calcium (Ca^{++})	0.512	0.876	0.846	0.649	0.572	0.847	0.548			
Conductivity	0.618	0.951	0.947	0.695	0.724	0.827	0.514	0.838		
pH	0.011	-0.393	-0.370	-0.231	-0.048	-0.110	0.008	-0.255	-0.392	
Precipitation Amount	-0.251	-0.374	-0.372	-0.356	-0.273	-0.336	-0.320	-0.342	-0.370	0.169

[a] No. of sample pairs is between 284 and 295

[b] No. of sample pairs is 51

Table 2-8

Statistical Summary of Seasonal Gas/Particle Ambient Concentrations Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93

Summer[a] (Daytime[e])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	9.7	3.5	16.	2.8	29
Chloride (Cl^-)	0.026	0.015	0.06	0.005	29
Non-volatilized Nitrate (NO_3^-)	0.98	1.02	3.9	0.19	29
Sulfate ($SO_4^=$)	1.60	0.64	3.2	0.51	29
Ammonium (NH_4^+)	0.838	0.416	1.82	0.208	29
Ammonia (NH_3)	3.92	1.60	7.0	0.91	29
Sulfur Dioxide (SO_2)	0.82	0.41	1.8	0.12	29
Nitrogen Dioxide (NO_2)	3.1	1.1	5.2	1.4	29
Total Particulate Nitrate (NO_3^-)	3.87	2.46	9.6	0.28	29
Nitric Acid (HNO_3)	2.46	1.09	4.3	0.01	29
Sum of Ionic Species	3.44	1.62	7.1	0.91	29

Winter[b] (Daytime[e])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	1.6	1.8	7.4	0.0	28
Chloride (Cl^-)	0.025	0.020	0.10	0.002	29
Non-volatilized Nitrate (NO_3^-)	0.33	0.63	2.9	0.00	29
Sulfate ($SO_4^=$)	0.37	0.36	1.55	0.02	29
Ammonium (NH_4^+)	0.166	0.240	1.18	0.000	29
Ammonia (NH_3)	0.34	0.25	1.10	0.10	27
Sulfur Dioxide (SO_2)	0.24	0.33	1.2	0.00	27
Nitrogen Dioxide (NO_2)	0.8	0.8	2.8	0.0	29
Total Particulate Nitrate (NO_3^-)	0.62	1.04	3.9	0.01	25
Nitric Acid (HNO_3)	0.15	0.10	0.41	0.00	25
Sum of Ionic Species	0.89	1.11	5.3	0.03	29

Summer[a] (Nighttime[f])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	8.8	4.0	19.	0.7	29
Chloride (Cl^-)	0.019	0.014	0.07	0.002	29
Non-volatilized Nitrate (NO_3^-)	0.79	0.89	3.8	0.11	29
Sulfate ($SO_4^=$)	1.35	0.62	2.6	0.37	29
Ammonium (NH_4^+)	0.721	0.389	1.91	0.189	29
Ammonia (NH_3)	1.81	1.19	4.9	0.24	29
Sulfur Dioxide (SO_2)	0.54	0.38	1.5	0.00	29
Nitrogen Dioxide (NO_2)	3.2	1.5	7.3	1.2	29
Total Particulate Nitrate (NO_3^-)	1.84	1.50	7.2	0.39	29
Nitric Acid (HNO_3)	0.35	0.32	1.2	0.00	29
Sum of Ionic Species	2.89	1.57	7.8	0.90	29

Winter[b] (Nighttime[f])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	2.0	1.8	6.5	0.0	26
Chloride (Cl^-)	0.021	0.020	0.08	0.000	28
Non-volatilized Nitrate (NO_3^-)	0.19	0.33	1.52	0.00	28
Sulfate ($SO_4^=$)	0.39	0.40	1.46	0.02	28
Ammonium (NH_4^+)	0.132	0.142	0.51	0.000	28
Ammonia (NH_3)	0.16	0.16	0.66	0.00	28
Sulfur Dioxide (SO_2)	0.19	0.26	0.9	0.00	28
Nitrogen Dioxide (NO_2)	0.4	0.7	2.9	0.0	28
Total Particulate Nitrate (NO_3^-)	0.43	0.69	3.0	0.00	24
Nitric Acid (HNO_3)	0.07	0.07	0.28	0.00	24
Sum of Ionic Species	0.73	0.68	2.4	0.04	28

Table 2-8 (continued)

Statistical Summary of Seasonal Gas/Particle Ambient Concentrations Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93

Spring[c] (Daytime[e])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	6.7	5.0	18.	0.2	30
Chloride (Cl^-)	0.029	0.024	0.10	0.000	31
Non-volatilized Nitrate (NO_3^-)	1.36	1.98	9.0	0.05	31
Sulfate ($SO_4^=$)	1.08	0.64	2.7	0.08	31
Ammonium (NH_4^+)	0.777	0.801	3.3	0.000	31
Ammonia (NH_3)	1.74	1.46	4.8	0.31	31
Sulfur Dioxide (SO_2)	0.59	0.38	1.5	0.01	31
Nitrogen Dioxide (NO_2)	2.0	1.2	4.1	0.0	31
Total Particulate Nitrate (NO_3^-)	3.34	3.02	11.2	0.15	31
Nitric Acid (HNO_3)	0.65	0.61	2.5	0.00	31
Sum of Ionic Species	3.24	3.10	13.9	0.16	31

Fall[d] (Daytime[e])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	7.7	6.5	28.	0.0	25
Chloride (Cl^-)	0.024	0.014	0.05	0.002	25
Non-volatilized Nitrate (NO_3^-)	2.30	3.47	14.1	0.06	25
Sulfate ($SO_4^=$)	1.15	0.85	3.5	0.09	25
Ammonium (NH_4^+)	1.031	1.266	5.4	0.042	25
Ammonia (NH_3)	2.08	1.75	7.0	0.05	25
Sulfur Dioxide (SO_2)	0.69	0.49	1.5	0.00	25
Nitrogen Dioxide (NO_2)	3.2	2.4	10.2	0.0	25
Total Particulate Nitrate (NO_3^-)	3.62	3.68	13.9	0.05	25
Nitric Acid (HNO_3)	1.12	1.02	3.4	0.00	25
Sum of Ionic Species	4.51	5.37	23.1	0.23	25

Spring[c] (Nighttime[f])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	5.8	4.7	17.	0.3	29
Chloride (Cl^-)	0.033	0.045	0.23	0.000	31
Non-volatilized Nitrate (NO_3^-)	1.35	1.81	7.7	0.02	31
Sulfate ($SO_4^=$)	0.95	0.51	2.22	0.12	31
Ammonium (NH_4^+)	0.703	0.683	2.9	0.000	31
Ammonia (NH_3)	0.88	0.76	3.0	0.05	31
Sulfur Dioxide (SO_2)	0.27	0.23	0.8	0.00	31
Nitrogen Dioxide (NO_2)	1.7	1.3	4.2	0.0	31
Total Particulate Nitrate (NO_3^-)	2.15	2.14	7.5	0.04	30
Nitric Acid (HNO_3)	0.10	0.23	0.5	0.00	30
Sum of Ionic Species	3.03	2.74	11.9	0.17	31

Fall[d] (Nighttime[f])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	5.1	5.1	20.	0.0	25
Chloride (Cl^-)	0.023	0.014	0.06	0.005	25
Non-volatilized Nitrate (NO_3^-)	1.38	2.33	10.1	0.04	25
Sulfate ($SO_4^=$)	0.82	0.65	2.00	0.07	25
Ammonium (NH_4^+)	0.675	0.835	3.6	0.038	25
Ammonia (NH_3)	0.78	0.72	3.2	0.00	25
Sulfur Dioxide (SO_2)	0.37	0.30	0.9	0.00	25
Nitrogen Dioxide (NO_2)	1.8	2.3	7.2	0.0	25
Total Particulate Nitrate (NO_3^-)	1.82	2.55	10.8	0.00	24
Nitric Acid (HNO_3)	0.14	0.26	0.5	0.00	24
Sum of Ionic Species	2.90	3.55	15.5	0.28	25

[a] Summer includes June, July, and August of 1992 and 1993.

[b] Winter includes December of 1991, January, February, and December of 1992, and January and February of 1993.

[c] Spring includes March, April, and May of 1992 and 1993.

[d] Fall includes November of 1991, September, October, and November of 1992, and September of 1993.

[e] Daytime = 0601 to 1800 PST.

[f] Nighttime = 1801 to next day 0600 PST.

Table 2-9

Statistical Summary of Gas/Particle Ambient Concentrations Acquired at the Barton Flats Station, CA, During Summer Intensive Period Between 07/18/93 and 07/31/93

	Concentrations in $\mu g/m^3$					Concentrations in $\mu g/m^3$				
	Morning (0600 to 1200 PST)					Afternoon (1200 to 1800 PST)				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	4.	2.	8.	0.	13	15.	4.	22.	7.	14
Chloride (Cl^-)	0.02	0.02	0.07	0.00	14	0.03	0.03	0.11	0.00	14
Non-volatilized Nitrate (NO_3^-)	0.30	0.03	0.35	0.24	14	0.58	0.32	1.55	0.30	14
Sulfate ($SO_4^=$)	0.91	0.40	1.51	0.31	14	3.31	1.07	5.1	1.20	14
Ammonium (NH_4^+)	0.38	0.14	0.60	0.16	14	1.46	0.44	2.1	0.59	14
Ammonia (NH_3)	1.79	0.68	3.6	0.90	14	5.4	1.7	9.0	2.2	14
Sulfur Dioxide (SO_2)	0.4	0.2	0.7	0.0	14	0.9	0.4	1.6	0.1	14
Nitrogen Dioxide (NO_2)	1.	1.	3.	0.	13	3.	2.	6.	2.	14
Total Particulate Nitrate (NO_3^-)	0.61	0.35	1.28	0.21	14	6.8	2.5	10.7	2.2	14
Nitric Acid (HNO_3)	3.4	0.8	4.4	2.3	14	4.9	0.9	6.7	3.5	14
Sum of Ionic Species	1.62	0.55	2.5	0.78	14	5.4	1.6	7.5	2.3	14

	Concentrations in $\mu g/m^3$					Concentrations in $\mu g/m^3$				
	Daytime (0600 to 1800 PST)[a]					Nighttime (1800 to next day 0600 PST)				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	9.	2.	13.	6.	13	7.8	3.2	16.0	4.1	13
Chloride (Cl^-)	0.03	0.02	0.06	0.00	14	0.01	0.01	0.03	0.00	14
Non-volatilized Nitrate (NO_3^-)	0.44	0.16	0.90	0.32	14	0.40	0.39	1.53	0.08	14
Sulfate ($SO_4^=$)	2.11	0.69	3.1	0.89	14	1.42	0.40	2.3	0.89	14
Ammonium (NH_4^+)	0.92	0.27	1.3	0.42	14	0.69	0.23	1.11	0.39	14
Ammonia (NH_3)	3.60	0.87	5.1	1.72	14	1.25	0.73	3.2	0.62	14
Sulfur Dioxide (SO_2)	0.6	0.3	1.0	0.1	14	0.29	0.14	0.61	0.11	14
Nitrogen Dioxide (NO_2)	2.	1.	4.	1.	13	2.1	1.1	4.5	0.8	14
Total Particulate Nitrate (NO_3^-)	3.7	1.4	5.8	1.2	14	1.64	1.09	3.2	0.24	14
Nitric Acid (HNO_3)	4.2	0.8	5.5	3.1	14	0.5	0.2	0.9	0.2	14
Sum of Ionic Species	3.5	1.0	4.9	1.7	14	2.52	0.87	3.9	1.36	14

[a] Calculated from daily averages of Morning and Afternoon concentrations.

Table 2-10

Statistical Summary of Gas/Particle Ambient Concentrations Acquired at the Barton Flats Station, CA, Between 06/01/94 and 08/31/94

Summer[a] (Daytime[b])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	7.4	2.9	13.	3.4	15
Chloride (Cl^-)	0.04	0.02	0.06	0.00	16
Non-volatilized Nitrate (NO_3^-)	0.40	0.18	0.75	0.11	16
Sulfate ($SO_4^=$)	1.50	0.79	3.2	0.50	16
Ammonium (NH_4^+)	0.62	0.32	1.34	0.23	16
Ammonia (NH_3)	3.80	1.52	6.5	1.10	15
Sulfur Dioxide (SO_2)	1.18	0.39	1.9	0.60	15
Nitrogen Dioxide (NO_2)	3.0	0.8	4.6	1.9	16
Total Particulate Nitrate (NO_3^-)	2.96	1.92	6.8	0.39	16
Nitric Acid (HNO_3)	4.5	2.4	12.2	1.2	16
Sum of Ionic Species	2.4	1.3	5.1	0.0	17

Summer[a] (Nighttime[c])	Concentrations in $\mu g/m^3$				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
$PM_{2.5}$ Mass	6.8	2.6	12.	2.7	15
Chloride (Cl^-)	0.04	0.02	0.10	0.00	16
Non-volatilized Nitrate (NO_3^-)	0.31	0.24	1.06	0.11	16
Sulfate ($SO_4^=$)	1.39	0.66	2.8	0.50	16
Ammonium (NH_4^+)	0.64	0.29	1.28	0.27	16
Ammonia (NH_3)	1.30	0.83	3.9	0.35	15
Sulfur Dioxide (SO_2)	0.71	0.36	1.63	0.21	15
Nitrogen Dioxide (NO_2)	2.4	0.8	3.8	1.0	16
Total Particulate Nitrate (NO_3^-)	1.29	0.92	3.7	0.33	15
Nitric Acid (HNO_3)	0.99	0.63	2.6	0.04	15
Sum of Ionic Species	2.2	1.2	4.8	0.0	17

[a] Summer includes June, July, and August of 1994.

[b] Daytime = 0600 to 1800 PST.

[c] Nighttime = 1800 to next day 0600 PST.

Table 2-11

Statistical Summary of Weekly[a] Wet Deposition Measurements Acquired at the Barton Flats Station, CA, Between 11/05/91 and 09/28/93 and Between 05/31/94 and 08/30/94

	Concentrations in μg/ml (except as noted)									
	All Data Points					**Fall[b]**				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
Precipitation (inches)	1.085	1.648	8.74	0.001	54	0.289	0.263	0.634	0.053	4
Conductivity (Field) (μS/cm)	13.07	13.75	63.	1.70	54	18.4	9.8	29.	6.8	4
Conductivity (Lab) (μS/cm)	11.40	12.98	68.	0.61	54	16.4	10.0	29.	6.1	4
pH (Field) (pH units)	5.90	1.02	8.43	4.24	54	6.13	1.09	7.51	4.90	4
pH (Lab) (pH units)	5.91	0.77	8.25	4.35	54	5.95	0.34	6.37	5.55	4
Chloride (Cl^-)	0.30	0.50	3.2	0.03	51	0.73	0.67	1.38	0.12	4
Nitrate (NO_3^-)	1.93	2.58	11.7	0.04	51	1.88	1.30	3.81	0.98	4
Sulfate ($SO_4^=$)	0.82	1.04	5.1	0.03	51	1.03	0.46	1.38	0.37	4
Ammonium (NH_4^+)	0.49	0.66	2.7	0.00	51	0.52	0.41	1.07	0.07	4
Soluble Sodium (Na^+)	0.192	0.332	1.6	0.005	51	0.578	0.664	1.48	0.059	4
Soluble Magnesium (Mg^{++})	0.0476	0.0737	0.30	0.0013	51	0.1033	0.1091	0.25	0.0134	4
Soluble Potassium (K^+)	0.040	0.070	0.346	0.000	51	0.141	0.155	0.346	0.017	4
Soluble Calcium (Ca^{++})	0.318	0.501	2.17	0.006	51	0.383	0.282	0.78	0.130	4

Table 2-11 (continued)

Statistical Summary of Weekly[a] Wet Deposition Measurements Acquired at the Barton Flats Station, CA, Between 11/05/91 and 09/28/93 and Between 05/31/94 and 08/30/94

	Concentrations in μg/ml (except as noted)									
	Spring[c]					**Summer[d]**				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
Precipitation (inches)	0.589	0.727	2.461	0.052	10	0.439	0.336	1.138	0.001	10
Conductivity (Field) (μS/cm)	16.9	13.9	43.	3.7	10	21.2	18.9	63.	3.1	10
Conductivity (Lab) (μS/cm)	14.1	12.2	39.	2.0	10	19.0	19.6	68.	3.2	10
pH (Field) (pH units)	5.35	0.48	6.02	4.64	10	5.03	0.52	5.72	4.24	10
pH (Lab) (pH units)	5.58	0.47	6.53	4.97	10	5.50	0.60	6.50	4.51	10
Chloride (Cl^-)	0.53	0.95	3.2	0.09	10	0.26	0.21	0.79	0.06	10
Nitrate (NO_3^-)	2.85	2.73	8.1	0.22	10	3.36	3.52	11.7	0.33	10
Sulfate ($SO_4^=$)	1.10	1.15	3.3	0.15	10	1.68	1.46	5.1	0.19	10
Ammonium (NH_4^+)	0.76	0.96	2.7	0.07	10	0.74	0.57	1.74	0.00	10
Soluble Sodium (Na^+)	0.293	0.480	1.6	0.053	10	0.198	0.293	1.01	0.014	10
Soluble Magnesium (Mg^{++})	0.0775	0.1055	0.30	0.0113	10	0.0613	0.0692	0.24	0.0046	10
Soluble Potassium (K^+)	0.059	0.077	0.228	0.000	10	0.039	0.049	0.165	0.000	10
Soluble Calcium (Ca^{++})	0.489	0.645	1.93	0.049	10	0.611	0.654	2.17	0.064	10

Table 2-11 (continued)

Statistical Summary of Weekly[a] Wet Deposition Measurements Acquired at the Barton Flats Station, CA, Between 11/05/91 and 09/28/93 and Between 05/31/94 and 08/30/94

	Concentrations in μg/ml (except as noted)									
	Winter[e]					Summer 94[f]				
	Average	Std. Dev.	Maximum	Minimum	No. in Avg.	Average	Std. Dev.	Maximum	Minimum	No. in Avg.
Precipitation (inches)	1.864	2.128	8.741	0.081	25	0.11	0.216	0.495	0.001	5
Conductivity (Field) (μS/cm)	5.43	6.61	31.	1.70	25	23.1	14.8	43.	5.9	5
Conductivity (Lab) (μS/cm)	4.74	6.18	30.	0.61	25	20.1	13.1	33.	4.4	5
pH (Field) (pH units)	6.50	1.03	8.43	4.38	25	5.47	0.42	5.93	4.95	5
pH (Lab) (pH units)	6.19	0.94	8.25	4.35	25	5.93	0.19	6.26	5.75	5
Chloride (Cl^-)	0.13	0.14	0.57	0.03	25	0.68	0.04	0.71	0.65	2
Nitrate (NO_3^-)	0.65	1.31	5.70	0.04	25	6.27	0.75	6.8	5.74	2
Sulfate ($SO_4^=$)	0.24	0.29	1.24	0.03	25	2.07	0.28	2.3	1.87	2
Ammonium (NH_4^+)	0.16	0.26	1.09	0.01	25	1.92	0.05	1.96	1.89	2
Soluble Sodium (Na^+)	0.073	0.088	0.33	0.005	25	0.378	0.158	0.49	0.267	2
Soluble Magnesium (Mg^{++})	0.0119	0.0124	0.0466	0.0013	25	0.166	0.078	0.22	0.111	2
Soluble Potassium (K^+)	0.009	0.014	0.056	0.000	25	0.139	0.062	0.183	0.095	2
Soluble Calcium (Ca^{++})	0.058	0.067	0.294	0.006	25	1.12	0.66	1.59	0.65	2

[a] Precipitation samples collected weekly on Tuesday at 09:00 PST.

[b] Fall includes November of 1991, September, October, and November of 1992, and September of 1993.

[c] Spring includes March, April, and May of 1992 and 1993.

[d] Summer includes June, July, and August of 1992 and 1993.

[e] Winter includes December of 1991, January, February, and December of 1992, and January and February of 1993.

[f] From 05/31/94 to 08/30/94.

Table 2-12
Statistical Summary of Hourly Average Ambient Ozone Concentrations Acquired at the Barton Flats Station, CA Between 11/01/91 and 11/30/94
(concentrations in ppb)

	Daily[a]					Daytime[b]					Nighttime[c]					Afternoon[d]				
	Ave.	Std. Dev.	Max	Min	No.	Ave.	Std. Dev.	Max	Min	No.	Ave.	Std. Dev.	Max	Min	No.	Ave.	Std. Dev.	Max	Min	No.
Nov. 1991-Nov. 1994	51.5	23.8	220	5	26331	57.7	27.2	220	5	13131	45.4	17.7	186	5	13200	68.7	32.8	220	11	6552
Dec. 1991-Nov. 1992	51.0	24.8	220	5	8669	57.1	28.2	220	5	4317	44.8	18.9	186	5	4352	68.3	33.9	220	11	2151
Winter[e] 1991/1992	37.1	7.4	72	6	2135	38.3	7.9	72	9	1064	35.9	6.8	52	6	1071	39.3	8.6	71	13	525
Spring[f] 1992	52.1	22.7	182	15	2179	60.3	25.3	182	15	1087	43.9	16.0	134	15	1092	72.1	29.3	182	29	538
Summer[g] 1992	63.3	32.8	220	5	2178	73.1	35.2	220	5	1081	53.6	26.9	186	5	1097	94.0	36.4	220	11	532
Fall[h] 1992	51.1	21.4	157	13	2177	56.5	25.0	157	14	1085	45.8	15.3	117	13	1092	67.5	29.1	157	18	544
Dec. 1992-Nov. 1993	52.0	23.0	187	11	8348	58.6	26.8	187	17	4166	45.4	16.0	178	11	4182	70.3	32.2	187	17	2080
Winter 1992/1993	39.1	5.8	63	14	2076	40.1	6.1	60	17	1042	38.0	5.3	63	14	1034	40.6	6.3	60	17	520
Spring 1993	52.6	18.0	156	18	2204	59.8	19.9	156	18	1100	45.4	12.2	148	19	1104	70.9	21.5	156	27	549
Summer 1993	66.2	31.6	187	14	2190	78.1	34.3	187	22	1090	54.4	23.3	178	14	1100	103	31.3	187	29	538
Fall 1993	48.9	18.6	156	11	1878	55.0	22.1	156	18	934	43.0	11.7	116	11	944	65.1	25.6	156	23	467
Dec. 1993-Nov. 1994	52.9	23.8	213	10	8600	58.8	27.0	213	10	4292	47.0	18.4	180	10	4308	69.8	32.7	213	14	2141
Winter 1993/1994	40.6	6.0	72	18	2046	41.9	6.4	72	18	1025	39.4	5.2	53	21	1021	42.6	6.8	72	18	511
Spring 1994	51.6	18.1	145	15	2195	59.1	20.4	145	22	1092	44.2	11.5	136	15	1103	69.1	22.8	145	25	543
Summer 1994	70.3	32.5	213	10	2209	80.0	34.8	213	14	1104	60.5	26.6	180	10	1105	104	33.1	213	14	546
Fall 1994	47.9	18.4	160	10	2151	52.6	20.9	160	10	1071	43.1	14.1	132	11	1080	61.5	24.6	160	26	535

a) 0000 to 2400 PST
b) 0600 to 1800 PST
c) 1800 to next day 0600 PST
d) 1200 to 1800 PST
e) December, January, February
f) March, April, May
g) June, July, August
h) September, October, November

Table 2-13
Statistical Summary of Hourly Average Air Temperature, Relative Humidity and Solar Radiation Acquired at the Barton Flats Station, CA Between 11/01/91 and 11/30/94

	Daily[a] Temperature (°C)					Daily[a] Relative Humidity (%)					Daily[a] Solar Radiation (W/m^2)				
	Ave.	Std. Dev.	Max	Min	No.	Ave.	Std. Dev.	Max	Min	No.	Ave.	Std. Dev.	Max	Min	No.
Nov. 1991-Nov. 1994	10.1	7.4	30.5	-10.1	27010	42.2	25.2	105	11.3	25460	224	315	1095	0	27007
Dec. 1991-Nov. 1992	10.5	6.9	26.9	-6.1	8784	46.2	27.0	105	12.1	8784	219	310	1058	0	8784
Winter[b] 1991/1992	4.2	4.5	16.9	-6.1	2160	52.3	31.1	104	15.1	2160	126	210	818	0	2160
Spring[c] 1992	8.9	5.8	21.5	-2.8	2208	55.0	26.8	100	13.5	2208	248	334	1058	0	2208
Summer[d] 1992	16.6	4.7	26.9	2.3	2208	46.0	21.5	93.8	12.8	2208	310	364	1055	0	2208
Fall[e] 1992	12.2	5.9	25.5	-1.9	2184	31.4	21.0	105	12.1	2184	197	280	955	0	2184
Dec. 1992-Nov. 1993	9.8	7.3	28.3	-10.1	8760	40.5	25.3	91.6	11.3	8760	231	325	1078	0	8758
Winter 1992/1993	1.8	4.2	14.6	-10.1	2160	59.5	28.1	91.6	15.8	2160	107	189	817	0	2160
Spring 1993	9.4	4.8	21.0	-4.3	2208	40.7	21.9	89.6	13.9	2208	283	358	1078	0	2208
Summer 1993	16.6	4.8	28.3	-1.8	2208	32.0	18.3	86.8	11.8	2208	329	383	1055	0	2206
Fall 1993	11.2	6.2	27.7	-4.3	2184	30.2	20.6	91.5	11.3	2184	203	288	959	0	2184
Dec. 1993-Nov. 1994	10.2	8.0	30.5	-8.3	8750	39.6	22.6	102	11.8	7200	228	316	1095	0	8749
Winter 1993/1994	4.1	4.9	17.9	-7.7	2160	34.4	22.3	84.3	15.0	2160	141	221	829	0	2160
Spring 1994	7.9	5.8	21.5	-5.7	2208	38.7	21.2	81.2	14.2	2016	257	340	1095	0	2198
Summer 1994	19.4	4.2	30.5	7.2	2199	39.5	18.8	89.0	11.8	840	316	371	1062	0	2208
Fall 1994	9.3	7.0	24.0	-8.3	2184	45.7	24.1	102	14.3	2184	197	281	1056	0	2184

a) 0000 to 2400 PST
b) December, January, February
c) March, April, May
d) June, July, August
e) September, October, November

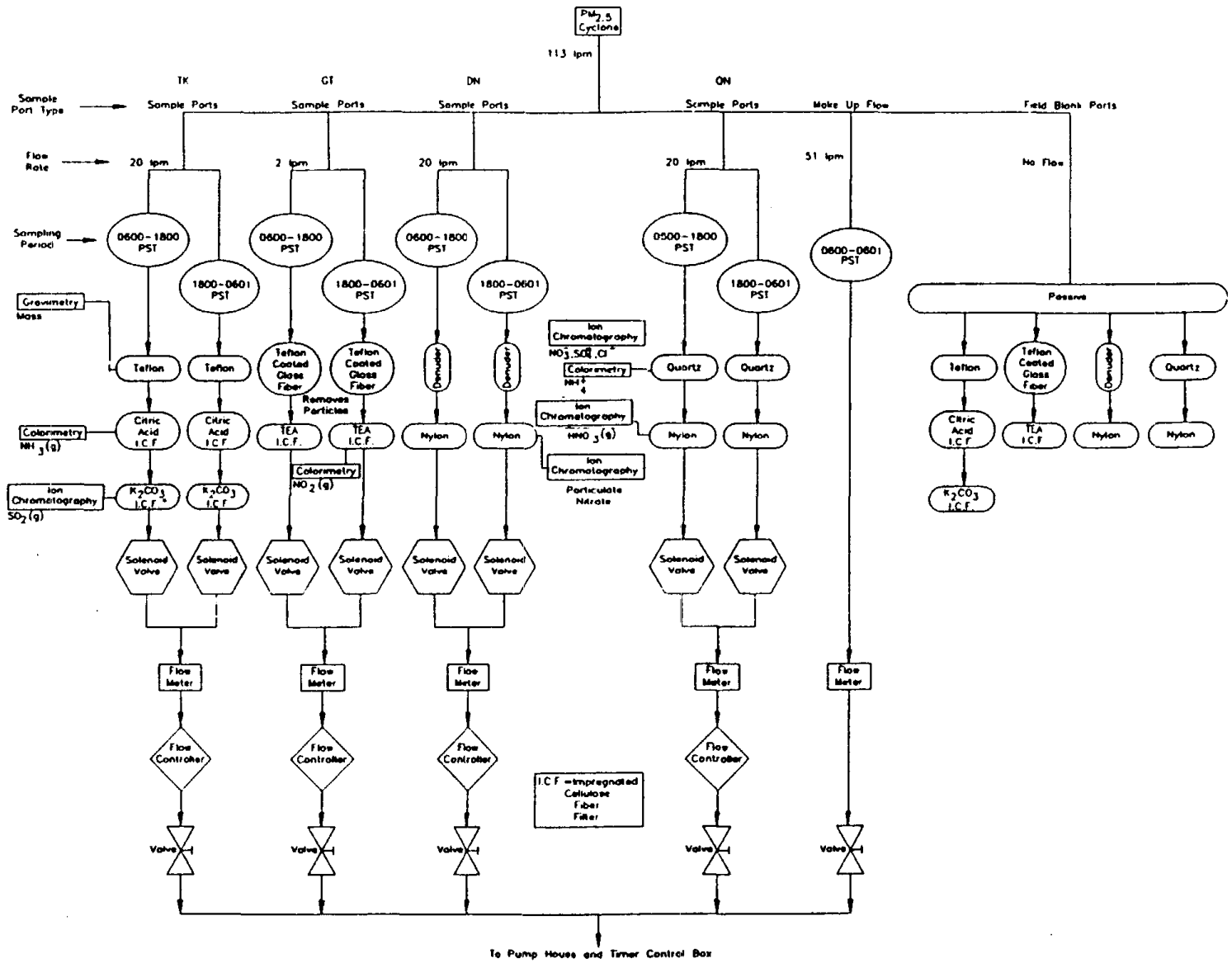

Figure 2-1. Flow Diagram of the Dry Deposition Sampling System at the Barton Flats Station, CA.

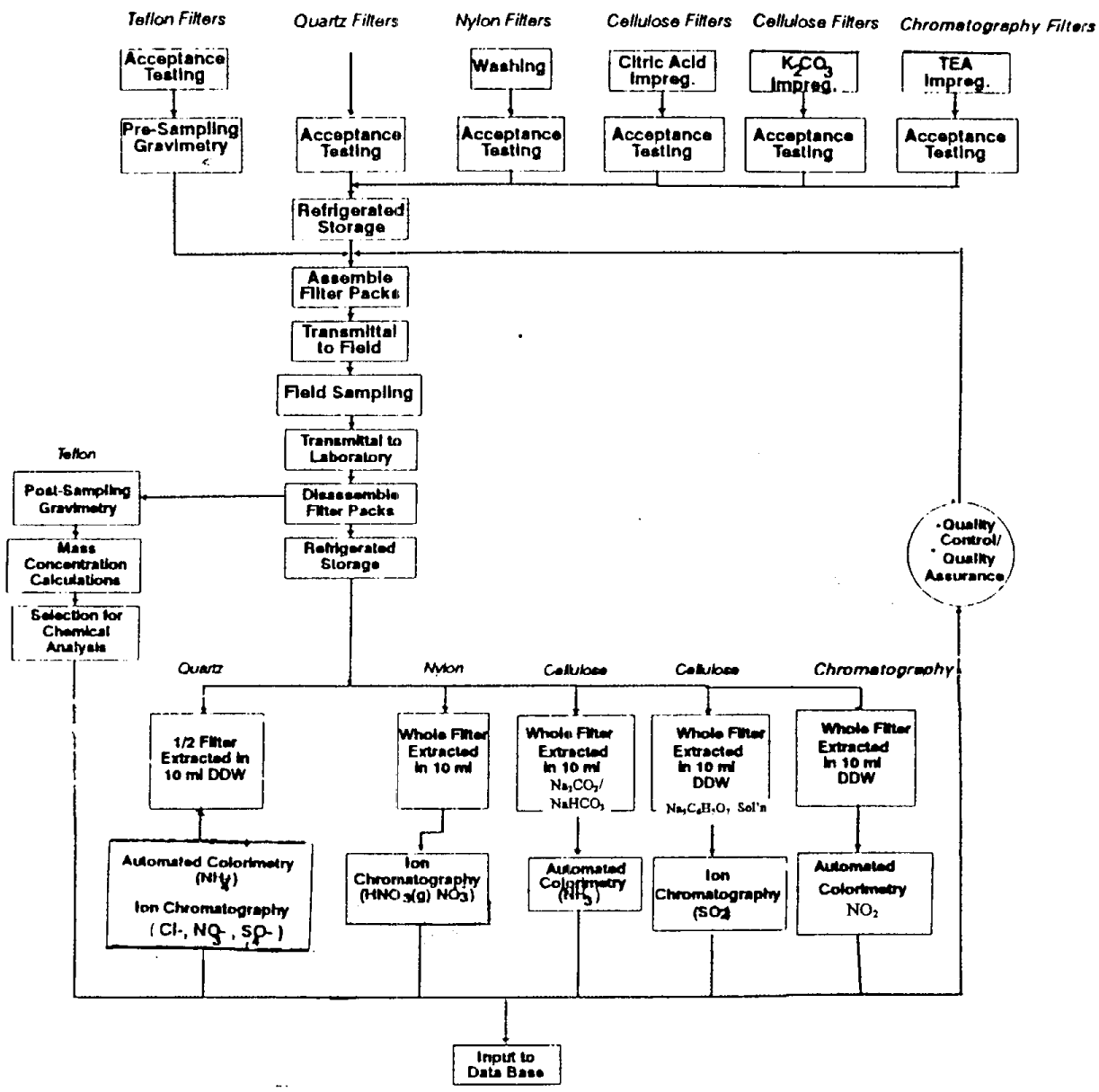

Figure 2-2. Flow Diagram of Filter Processing and Chemical Analysis Activities for the Aerosol and Gaseous Sampling System at the Barton Flats Station, CA.

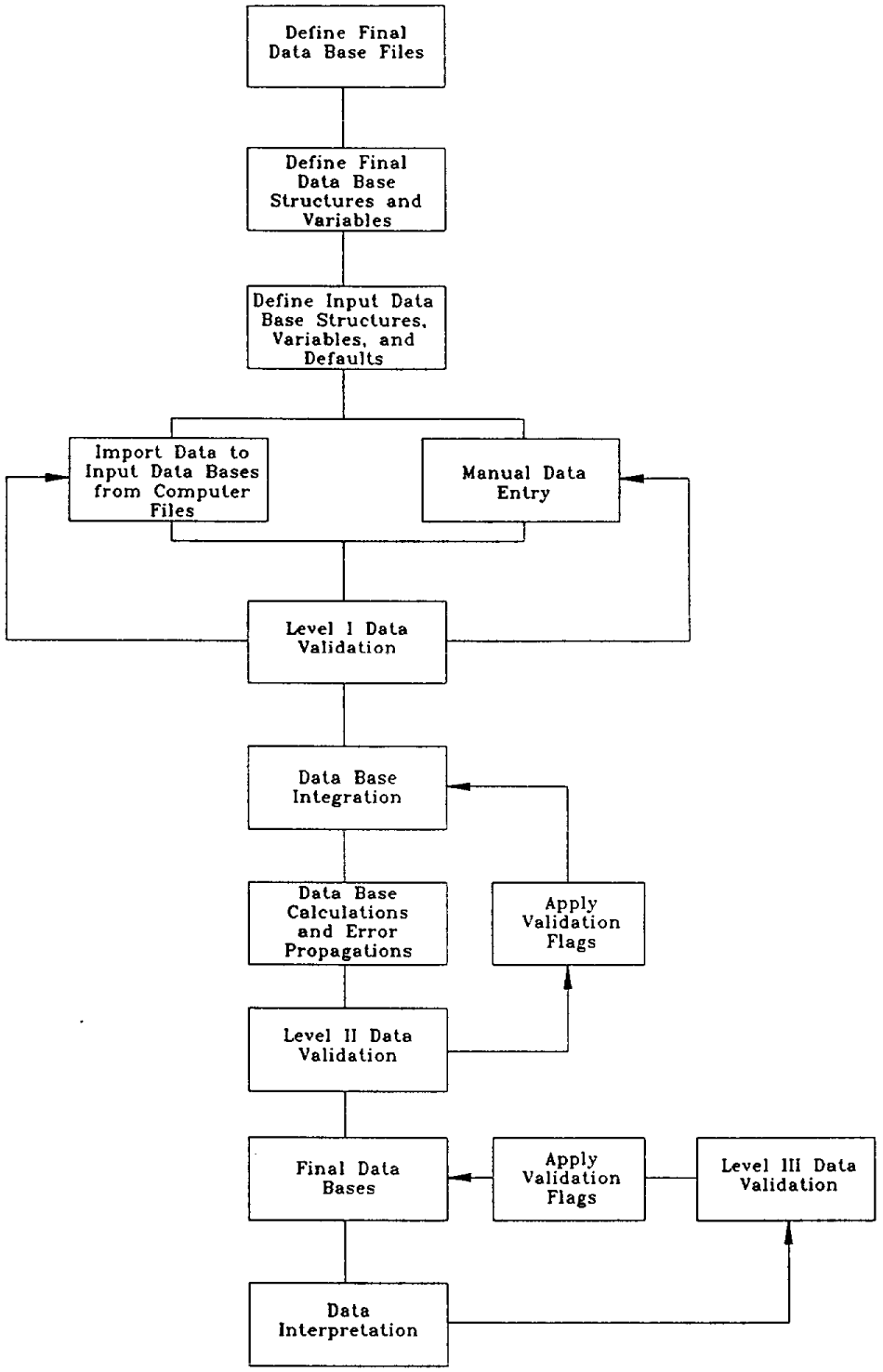

Figure 2-3. Flow Diagram of the Data Base Management System

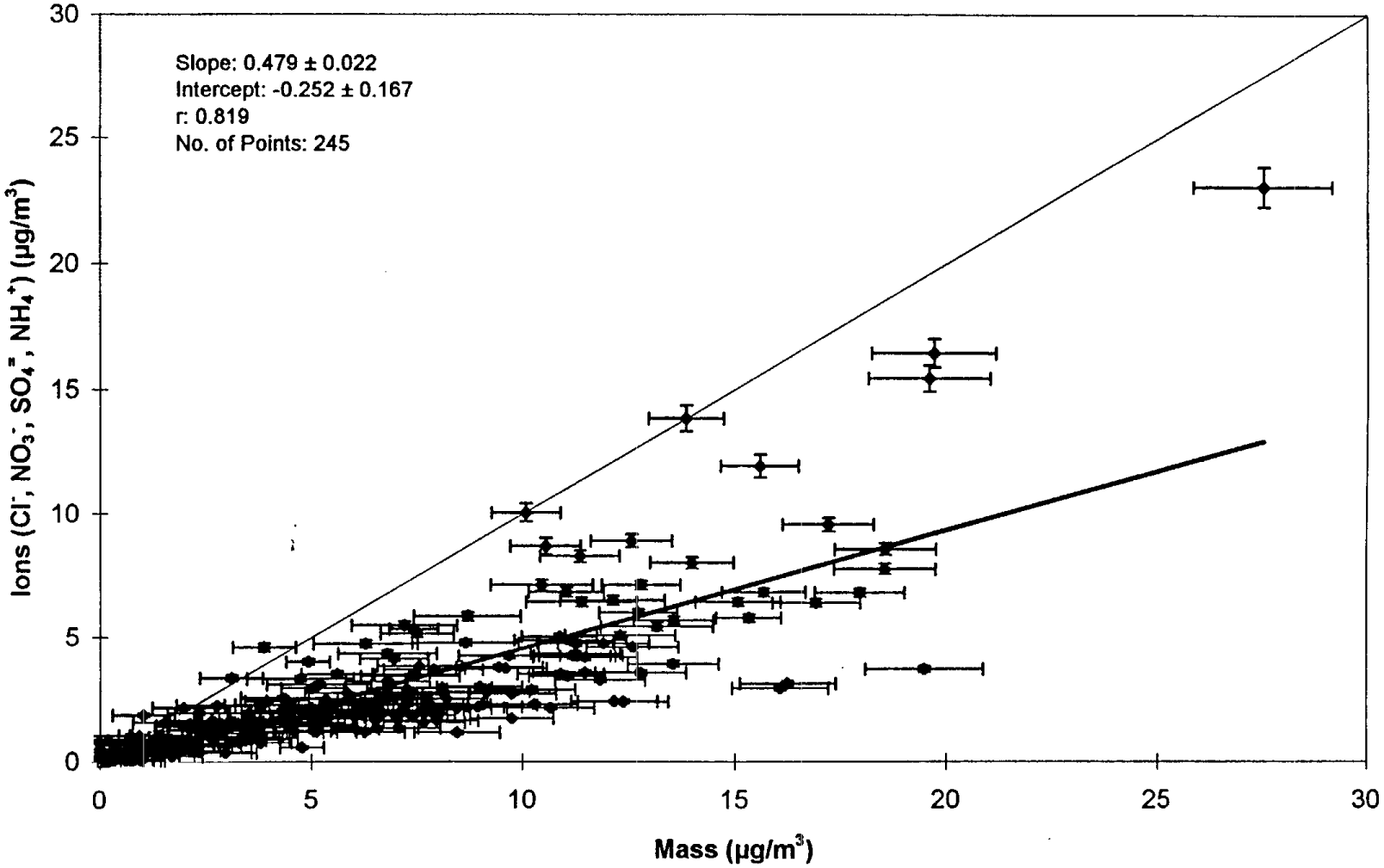

Figure 2-4. Sum of Ionic Species Versus Mass Concentrations for $PM_{2.5}$ Samples Acquired at the Barton Flats Station, CA, Between 11/02/91 and 09/28/93 and Between 06/01/94 and 08/30/94.

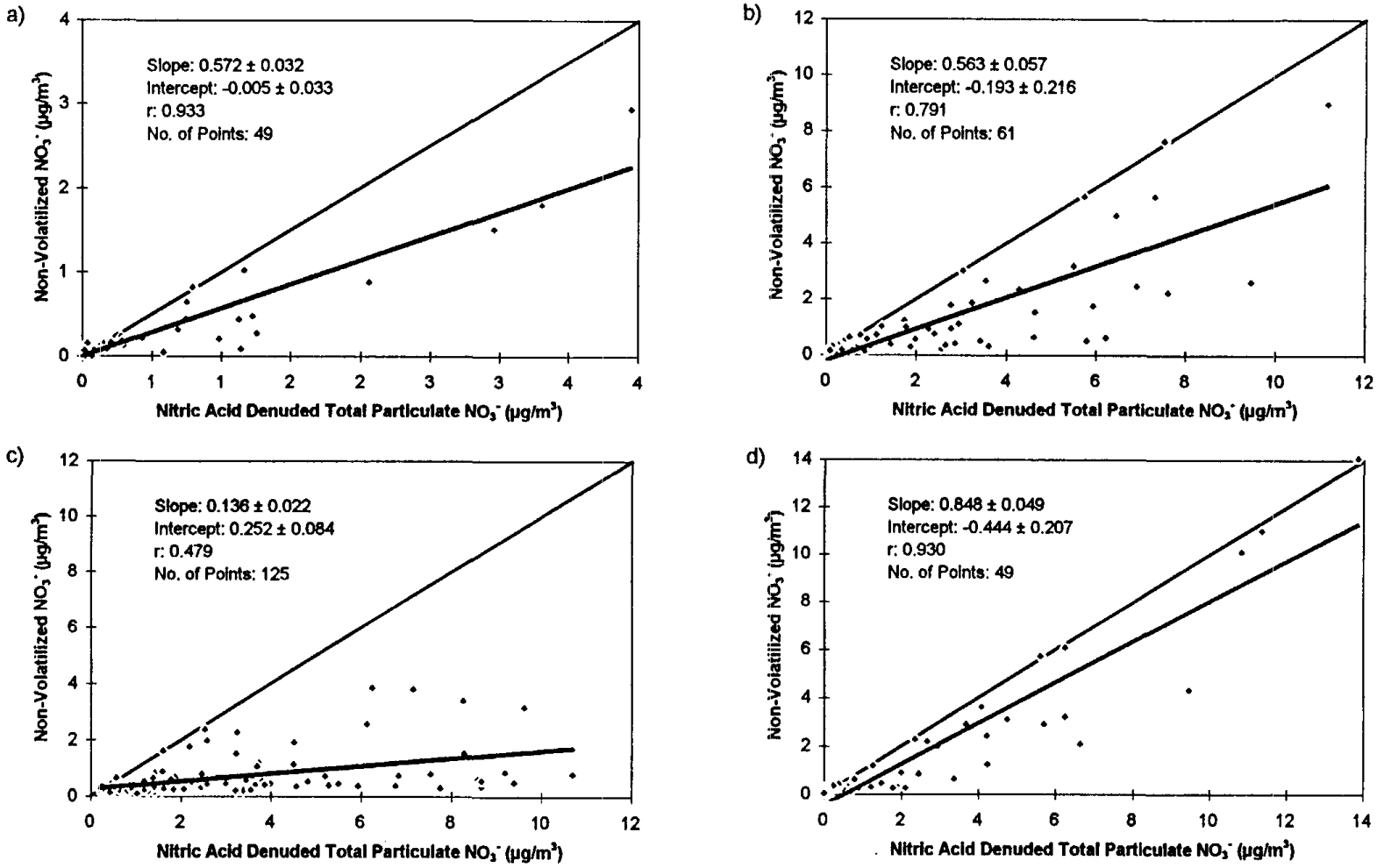

Figure 2-5. Scatter Plots of $PM_{2.5}$ Non-Volatilized Nitrate Versus Nitric Acid Denuded Nitrate at the Barton Flats Station, CA, During: a) Winter (December of 1991, January, February, and December of 1992, and January and February of 1993), b) Spring (March, April, and May of 1992 and 1993), c) Summer (June, July, and August of 1992, 1993, and 1994), and d) Fall (November of 1991, September, October, and November of 1992, and September of 1993).

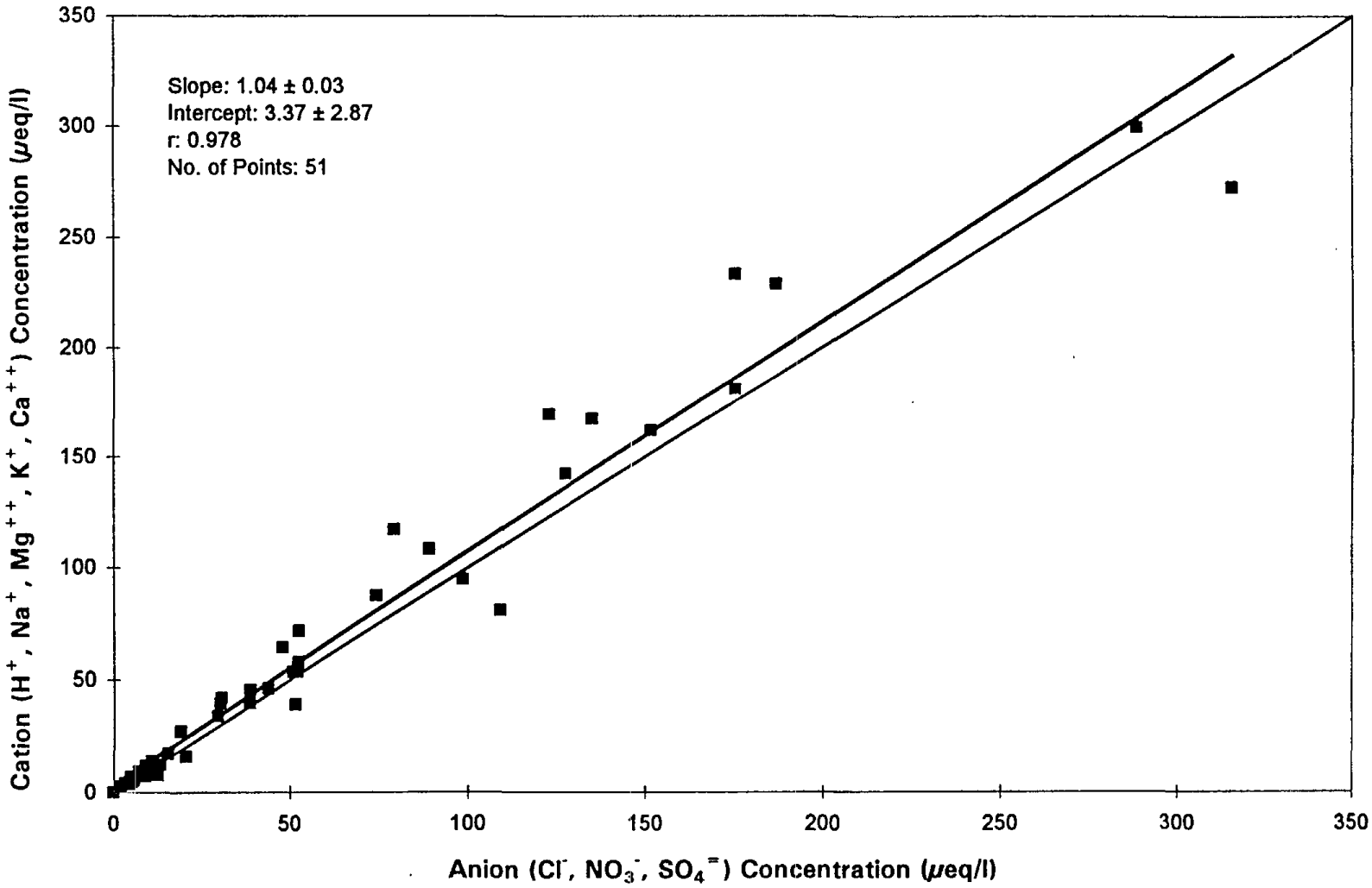

Figure 2-6. Cation Versus Anion Balances for the Wet Deposition Samples Acquired at the Barton Flats Station, CA, Between 11/05/92 and 09/28/93 and Between 05/31/94 and 08/30/94.