Final Report

Prepared for California Air Resources Board
California Air Resources Board Contract No. 93-332

REGIONAL ESTIMATES OF ACID DEPOSITION FLUXES IN CALIFORNIA FOR 1985-1994

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April 30, 1996

DISCLAIMER

ABSTRACT

Acidic deposition occurs via precipitation, fog, cloud water, and dry deposition. Each of these processes is potentially important in California. The specific objectives of this project were to (1) evaluate the quality of the available deposition data; (2) compute estimates of the deposition of each species of interest, by mode of deposition, at each monitoring location in California having sufficient data available; (3) generalize the estimated deposition amounts to larger regions of interest, to the extent possible; (4) compare the magnitudes of wet and dry deposition; and (5) identify measurement and methodological requirements for improving the results. A previous report (Blanchard and Michaels, 1994) covered the periods July 1984 through June 1990 (wet deposition) and early 1988 through September 1991 (dry deposition). This report extends the previous work to cover the period from July 1984 through June 1994.

The California Acid Deposition Monitoring Program (CADMP) operated 25 to 35 wet-deposition and 10 dry-deposition monitoring sites during the periods 1984 through 1994 and 1988 through 1994, respectively. In addition to the CADMP, the California Air Resources Board (CARB) funded a 10-site alpine wet-deposition network, which was operated by the Univeristy of California at Santa Barbara from 1990 through 1994. The National Atmospheric Deposition Program / National Trends Network (NAPD/NTN) also operated 8 wet-deposition monitoring sites in California. Precipitation-chemistry data from these three networks were combined and used for generating annual regional estimates of wet-deposition fluxes throughout California. Because so much fewer data were available from the dry-deposition network, estimates of dry-deposition fluxes were generated only for the monitoring locations and were not generalized to broader regions. Estimates of the magnitudes of wet plus dry deposition were also generated for the ten locations having both wet- and dry-deposition data available.

In all years (1985 through 1994) and at all monitoring sites, the magnitudes of deposition of sulfate and nitrate by precipitation were each no greater than 12 kilograms per hectare per year (kg ha^{-1} yr^{-1}), and were usually less than 6 kg ha^{-1} yr^{-1}. Excess sulfate (i.e., excluding the estimated sea-salt contribution) was no greater than 10 kg ha^{-1} yr^{-1} in all years at all sites and was usually less than 4 kg ha^{-1} yr^{-1}. Ammonium deposition was less than 5 kg ha^{-1} yr^{-1} in all years at all sites.

Regionally-averaged wet-deposition fluxes were lower than the site maxima listed above. During all years and for all regions, (1) mean nitrate deposition via precipitation was less than 6 kg ha^{-1} yr^{-1}; (2) excess sulfate (i.e., excluding sea-salt sulfate) and sulfate deposition were less than 4 kg ha^{-1} yr^{-1}; and (3) ammonium deposition was less than 2 kg ha^{-1} yr^{-1}. The interpolation uncertainties for wet deposition were generally less than 20 percent in the South Coast Air Basin, which has a large number of monitors. Elsewhere in California, wet deposition interpolation uncertainties were no more than 40 percent (southern California) and 60 percent (northern California) for sulfate, excess sulfate and nitrate. Interpolation uncertainties were up to 100 percent for acidity, because acidity deposition rates were typically close to zero g ha^{-1} yr^{-1}.

The estimated dry deposition fluxes of nitric acid (HNO_3) at the 10 dry-deposition monitoring sites, averaged over 1989 through 1993, ranged from 1 to 86 kg ha^{-1} yr^{-1}. The dry-deposition flux estimates are subject to uncertainties on the order of 50 percent. At the 7 urban sites, HNO_3 deposition accounted for about 30 to 80 percent of the deposition of oxidized nitrogen species and 20 to 70 percent of the total nitrogen deposition.

At the three nonurban monitoring sites (Gasquet, Yosemite National Park, and Giant Forest in Sequoia National Park), wet nitrate and nonseasalt-sulfate deposition approximately equalled (within 0.7 kg ha^{-1} yr^{-1}) dry deposition of oxidized nitrogen and sulfur species. The multi-year average sum of wet and dry deposition at these three sites were 1-2 kg N ha^{-1} yr^{-1} (from oxidized species), 1-2 kg S ha^{-1} yr^{-1}, and 1-2 kg N ha^{-1} yr^{-1} (from reduced species).

At the seven urban sites, dry sulfur deposition was approximately 1 to 3 times the magnitude of wet sulfur deposition; dry deposition of oxidized nitrogen species at the urban sites ranged from about 10 to 30 times the magnitude of wet nitrate deposition. At all sites, dry deposition of reduced nitrogen species (ammonia and particulate ammonium) was about a factor of 2 greater than wet ammonium deposition. The multi-year average sum of wet and dry deposition at these seven sites were 5-30 kg N ha^{-1} yr^{-1} (from oxidized species), 1-3 kg S ha^{-1} yr^{-1}, and 1-4 kg N ha^{-1} yr^{-1} (from reduced species).

ACKNOWLEDGMENTS

We wish to thank N. Motallebi, our contract manager, who obtained data, located missing information, provided advice, and, in numerous other ways, facilitated this project.

This report was submitted in fulfillment of contract number 93-332, "Regional Estimates of Acid Deposition Fluxes in California," under the sponsorship of the California Air Resources Board. Work was completed April 30, 1996.

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GLOSSARY

°C	degrees Celsius
Ca^{2+}	calcium ion
CADMP	California Acid Deposition Monitoring Program
CARB	California Air Resources Board
CCSS	California Cooperative Snow Survey
Cl^-	chloride ion
cm	centimeter
CV	coefficient of variation
EPA	Environmental Protection Agency
eq	equivalent
g	gram
H^+	hydrogen ion
ha	hectare
HNO_3	nitric acid
K^+	potassium ion
kg	kilogram
km	kilometer
L	liter
m	meter
M	molar
mb	millibar
Mg^{2+}	magnesium ion
ml	milliliter
mm	millimeter
μg	microgram
$\mu g\ m^{-3}$	micrograms per cubic meter
$\mu eq\ L^{-1}$	micro-equivalents per liter (a unit of concentration)
$\mu S\ cm^{-1}$	micro-Siemen per cm (a unit of conductance)
N	nitrogen
Na^+	sodium ion
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NH_3	ammonia
NH_4^+	ammonium ion
NO_x	nitrogen oxides
NO_3^-	nitrate ion
NWS	National Weather Service
O_3	ozone
pH	negative base 10 logarithm of the hydrogen ion concentration
PM10	particulate matter 10 microns and smaller
PM2.5	particulate matter 2.5 microns and smaller
pNH_4^+	particulate ammonium
pNO_3^-	particulate nitrate

pSO_4^{2-}	particulate sulfate
ppb	parts per billion
pphm	parts per hundred million
ppm	parts per million
QA/QC	quality assurance/quality control
S	sulfur
SoCAB	South Coast Air Basin
SO_2	sulfur dioxide
SO_4^{2-}	sulfate ion
TDLAS	Tunable Diode Laser Absorption Spectroscopy
UCSB	University of California, Santa Barbara
V_d	deposition velocity
VOC	volatile organic compound
W	Watt
xSO_4^{2-}	excess sulfate: sulfate concentration with estimated sea-salt sulfate concentration removed
yr	year

SUMMARY

INTRODUCTION

Acidic deposition occurs via precipitation, fog, cloud water, and dry deposition. Each of these processes is potentially important in California.

The California Acid Deposition Monitoring Program (CADMP) was established to provide information about the concentrations and mass fluxes of acidic species delivered by precipitation, fog, cloud water, and dry deposition. The CADMP has four objectives:

- To identify the range of chemical concentrations and mass deposition occurring in California;
- To provide data to be used as inputs for studies of the effects of acidic deposition in California;
- To provide data that may be useful in establishing relationships between regions that are sources of precursor emissions and regions that receive acidic deposition;
- To identify possible time trends in concentration or deposition amounts.

This project updates our previous report (Blanchard and Michaels, 1994; hereinafter referred to as the March 1994 report), which covered the first of these objectives for the periods July 1984 through June 1991 (for wet deposition) and early 1988 through September 1991 (for dry deposition). The present report covers the time periods through June 1994 (for wet deposition) and April 1994 (for dry deposition).

OBJECTIVES

The specific objectives of this project are to

1. Evaluate the quality of the available deposition data;
2. Compute estimates of the deposition of each species of interest, by mode of deposition, at each monitoring location in California having sufficient data available;
3. Generalize the estimated deposition amounts to larger regions of interest, to the extent possible;
4. Compare the magnitudes of wet and dry deposition;
5. Identify measurement and methodological requirements for improving the results.

APPROACH

We used precipitation-chemistry data from the CADMP (25-35 sites), the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (8 California sites), and a 10-site alpine wet-deposition network, which was operated by the Univeristy of California at Santa Barbara, to calculate the fluxes of chemical species delivered via precipitation. We then interpolated from the monitoring sites to the state as a whole by using a statistical procedure, kriging, which quantifies both the interpolated values and the interpolation errors, thus yielding estimates for the uncertainties in isopleths. We carried out calculations for four sampling years, from July 1990 through June 1994. Summary results for the period 1985-1994 are also presented.

The CADMP dry-deposition network (10 sites) was designed with the intent of implementing a procedure known as the inferential method. In this approach, the flux of a particular species is calculated as the product of its ambient concentration and a velocity, known as the deposition velocity, V_d. Deposition velocity generally depends on both the nature of the pollutant and the surface. We used a set of calculational procedures, developed at Oak Ridge National Laboratory, to carry out the calculations. The period covered in this report is October 1991 through April 1994. Results for the entire period of record commencing in early 1988 through April 1994 are also presented. Because so much fewer data were available from the dry-deposition network, estimates of dry-deposition fluxes were generated only for the monitoring locations and were not generalized to broader regions. Estimates of the magnitudes of wet plus dry deposition were also generated for the ten locations having both wet- and dry-deposition data available.

PRINCIPAL FINDINGS

Wet Deposition

For the period July 1990 through June 1994, nitrate deposition via precipitation was less than 6 kilograms per hectare per year (kg ha^{-1} yr^{-1}); excess sulfate (i.e., excluding sea-salt sulfate) and sulfate deposition were less than 4 kg ha^{-1} yr^{-1}; and ammonium deposition was less than 2 kg ha^{-1} yr^{-1}. For comparison, wet sulfate and nitrate deposition in portions of eastern North America exceed 25 and 15 kg ha^{-1} yr^{-1}, respectively (Sisterson, 1991); ammonium deposition is less than about 4 kg ha^{-1} yr^{-1} in almost all parts of eastern North America (Sisterson, 1991). Calcium was not interpolated due to questions about the validity of the data.

Interpolation uncertainties were generally less than 20 percent in the South Coast Air Basin, which has a large number of monitors. Elsewhere in California, interpolation uncertainties were no more than 40 percent (southern California) and 60 percent (northern California) for sulfate, excess sulfate and nitrate. Uncertainties can be up to 100 percent for acidity, because acidity deposition rates were typically close to zero g ha^{-1} yr^{-1}.

Dry Deposition

The estimates of dry-deposition fluxes at 10 CADMP sites in California provide an indication of the magnitude of dry deposition at key locations in California. However, the calculations are limited in numerous important respects and they could likely be improved over time with additional effort. The dry-deposition flux estimates are subject to uncertainties of approximately 50 percent.

Estimated deposition of HNO_3 at the 10 sites ranges from 1 to 86 kg ha^{-1} yr^{-1}. At the urban sites, HNO_3 deposition accounts for 30 to 80 percent of the deposition of oxidized nitrogen species and 20 to 70 percent of the total nitrogen deposition.

Annual rates of deposition of oxidized nitrogen species at the three rural sites (Gasquet, Sequoia, and Yosemite) are about one-tenth to one-half as great as the values reported by Meyers et al. (1991) for sites in the eastern United States. The deposition rates calculated for the rural CADMP sites are quite uncertain because many of the measurements were below the limits of quantification. The rates of nitrogen deposition at Azusa, Bakersfield, Long Beach, and Los Angeles exceed those reported by Meyers et al. (1991) by factors of 2 to 17.

The Sum of Wet and Dry Deposition

At the three nonurban sites (Gasquet, Yosemite, and Sequoia), wet nitrate and nonseasalt-sulfate deposition approximately equalled (within 0.7 kg ha^{-1} $yr^{-1)}$ dry deposition of oxidized nitrogen and sulfur species. The multi-year average sum of wet and dry deposition at these three sites were 1-2 kg N ha^{-1} yr^{-1} (from oxidized species), 1-2 kg S ha^{-1} yr^{-1}, and 1-2 kg N ha^{-1} yr^{-1} (from reduced species).

At the seven urban sites, dry sulfur deposition [SO_2 and particulate sulfate (pSO_4^{2-})] was approximately 1 to 3 times the magnitude of wet sulfur deposition; dry deposition of oxidized nitrogen species [HNO_3, NO_2, and particulate nitrate (pNO_3^-)] at the urban sites ranged from about 10 to 30 times the magnitude of wet nitrate deposition. At all sites, dry deposition of reduced nitrogen species [ammonia (NH_3) and particulate ammonium (pNH_4^+)] was about a factor of 2 greater than wet ammonium deposition. The multi-year average sum of wet and dry deposition at these seven sites were 5-30 kg N ha^{-1} yr^{-1} (from oxidized species), 1-3 kg S ha^{-1} yr^{-1}, and 1-4 kg N ha^{-1} yr^{-1} (from reduced species).

Comparison of Deposition and Emissions

The calculated rates of deposition of oxidized nitrogen species at the South Coast Air Basin (SoCAB) stations ranged from 16 to 37 percent of the rate of emissions of NO_x within the SoCAB. The sum of wet plus dry nitrogen deposition rates at Fremont was about 11 percent of the NO_x emissions rate occurring within the San Francisco Bay area. However, since Fremont does not experience the highest peak ozone concentrations in the

Bay area, concentrations of photochemical reaction products (including HNO_3) may be greater at other locations within the Bay area, implying that deposition rates in parts of the Bay area may also be greater than those calculated for Fremont. The estimated nitrogen deposition rates at Bakersfield and Sacramento were about 76 and 32 percent, respectively, of the emissions rates of Kern County and the area around Sacramento County.

Limitations

Wet-deposition flux estimates are based on data obtained using a proven monitoring technique and a reasonably dense network of stations. The most significant source of potential bias is underestimation of precipitation amounts in alpine regions. Calculations made with just CADMP data were compared with calculations made with both CADMP and UCSB alpine data. The uncertainties in our regionalized estimates of wet deposition vary spatially and among chemical species; they are typically in the range of 20 to 50 percent for the species and areas of greatest interest.

In contrast, both the measurements and the model used to calculate dry deposition are subject to potentially large uncertainties. At present, outstanding questions remain regarding the accuracy of the denuder difference HNO_3 concentrations. Moreover, the expected uncertainties in dry deposition flux estimates calculated according to the inferential method are on the order of 50 percent.

RECOMMENDATIONS

We offer the following recommendations for consideration:

1. Particular effort should be devoted to resolving the questions pertaining to accurate measurement of nitric acid. At many locations, it is the largest component of total nitrogen deposition. Therefore, accurate measurement is critical.

2. Comparison of results obtained from application of the inferential method and from micrometeorological studies would be highly desirable. Lacking such a comparison, we cannot evaluate the accuracies of the calculated deposition amounts.

3. If analyses of dry-deposition trends are of interest, they should be carried out for the ambient air concentrations, rather than the calculated dry-deposition fluxes, because many uncertainties are introduced in the process of calculating fluxes. For the urban locations, where dry deposition fluxes are many times the magnitude of wet deposition, trends in dry deposition may serve as a surrogate for trends in total deposition. At rural locations, where wet and dry deposition fluxes are of comparable magnitudes, consideration should be given to co-analyzing the time trends in wet and dry deposition.

PART I: WET DEPOSITION

INTRODUCTION

Objectives

The specific objectives of this part of the project are to

1. Evaluate the quality of the available precipitation-chemistry data;
2. Compute estimates of the wet deposition of each species of interest at each monitoring location in California having sufficient data;
3. Generalize the estimated deposition amounts to larger regions of interest.

Overview of Part I

We first summarize the methods used. We then briefly describe the data that are available and discuss the quality of these data. We identify the variables and the spatial and temporal scales of interest. Finally, we describe the methods used in uncertainty analysis and present summary results.

METHODS

Use of Kriging for Spatial Interpolation of Acidic Deposition

Kriging was used to interpolate the precipitation monitoring data. Kriging is a stochastic approach encompassing a family of procedures. These procedures were originally developed for geostatistical applications (Journel and Huijbregts, 1978). Kriging uses the similarities in the measurements taken at different sites to determine a set of weights; weighted averages of the observations are then used to generate the unknown point or regional estimates. Kriging is attractive because it quantifies the interpolation errors, thus yielding estimates for the uncertainties in isopleths. When the assumptions of the kriging methodology are fulfilled, kriging provides the best linear unbiased estimator in the sense that it minimizes the variance of the estimation error (Journel and Huijbregts, 1978). A more detailed description of the characteristics and limitations of kriging can be found in the March 1994 report.

Data Availability

We previously had available to us CADMP data from July 1984 through June 1990. For the present report, we obtained CADMP data for July 1990 through June 1994

(Takemoto et al., 1995b). We also obtained monthly-average precipitation-chemistry data from the NADP/NTN for California and for selected sites in Oregon, Nevada, and Arizona (for 1979 through 1994), and snowpack/precipitation-chemistry for CARB/University of California, Santa Barbara (UCSB) alpine sites in California (for October 1989 through September 1993) (Melack et al., 1995). Figure 1 shows the locations of CADMP, NADP/NTN, and CARB/UCSB sites used in our analyses.

Both CADMP and NADP/NTN use automated Aerochem Metrics collectors, which open automatically with the onset of precipitation and close when precipitation ceases. However, these collectors, which are now widely used for monitoring precipitation chemistry, fail to collect snow well under conditions of large snowfall or moderate-to-heavy winds. Consequently, the CADMP monitors are of limited accuracy at high elevations of the Sierra Nevada. To remedy this shortcoming, the CARB funded a special four-year project to measure wet-deposition fluxes at 10 alpine sites between the Lake Tahoe basin and the region near Mt. Whitney, which was carried out by UCSB (Melack et al, 1995).

We also obtained NWS precipitation-amount data from 492 stations in California, Arizona, Nevada, and Oregon (see Figure 2). Although the large number of stations provides good coverage of California, portions of the alpine Sierra and southeastern desert are not as well covered.

For future studies, consideration should be given to using data from the California Cooperative Snow Surveys (CCSS) conducted by the Department of Water Resources. The CCSS data base provides information on snowpack; for total yearly precipitation at these locations other data would also be needed. A comparison of CCSS and NWS sites shows that high elevations are better represented in the CCSS data base (see Table 1).

Table 1. Numbers of National Weather Service (NWS) and California Cooperative Snow Survey (CCSS) sites, by elevation.

Site Grouping	NWS	CCSS
Total number of sites	492	397
No. $\geq$ 10,000 ft.	0	29
No. 9,000-9,999 ft.	3	39
No. 8,000-8,999 ft.	4	70
No. 7,000-7,999 ft.	3	82

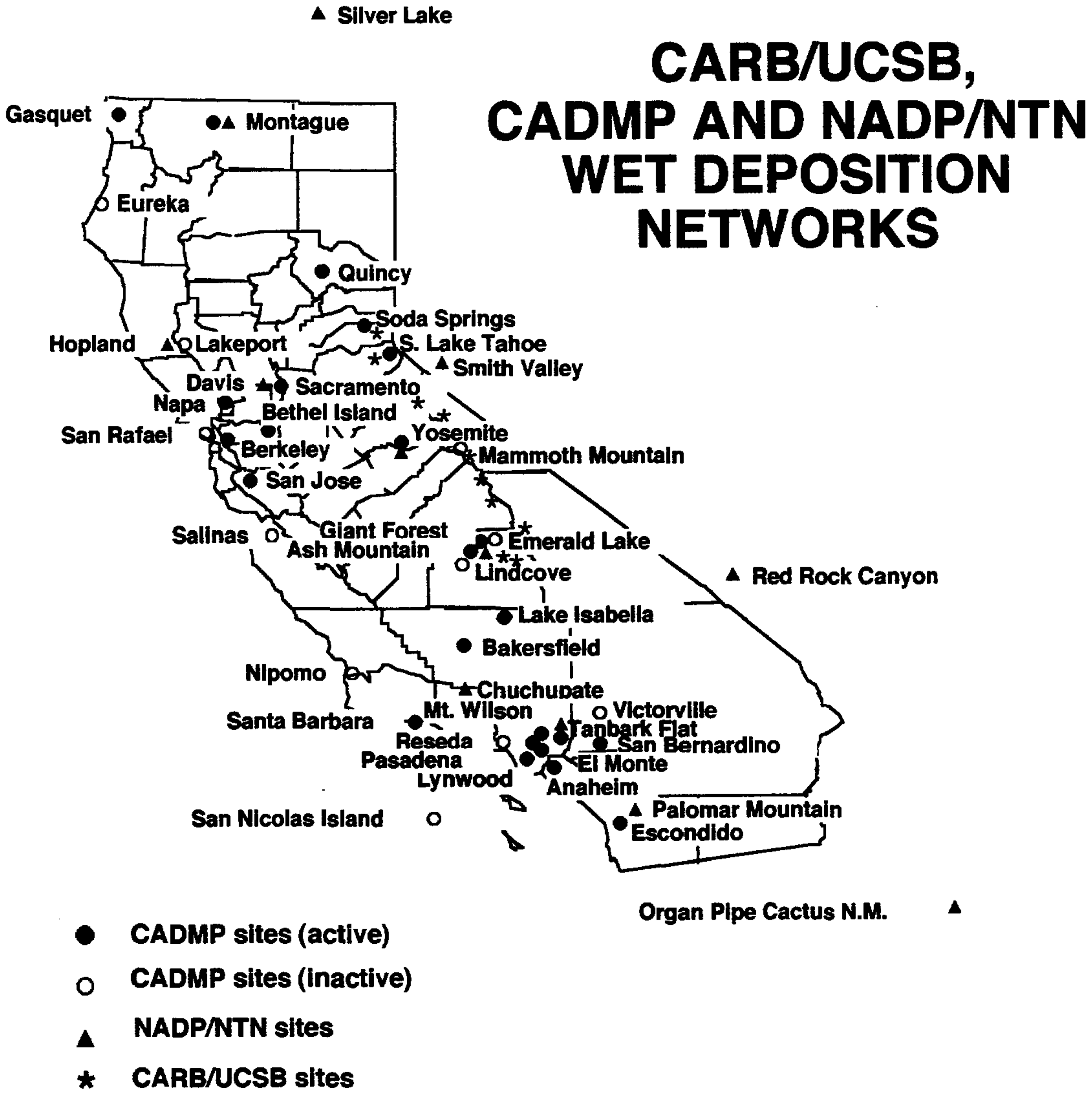

Figure 1. Locations of CARB/UCSB, CADMP and NADP/NTN monitoring sites.

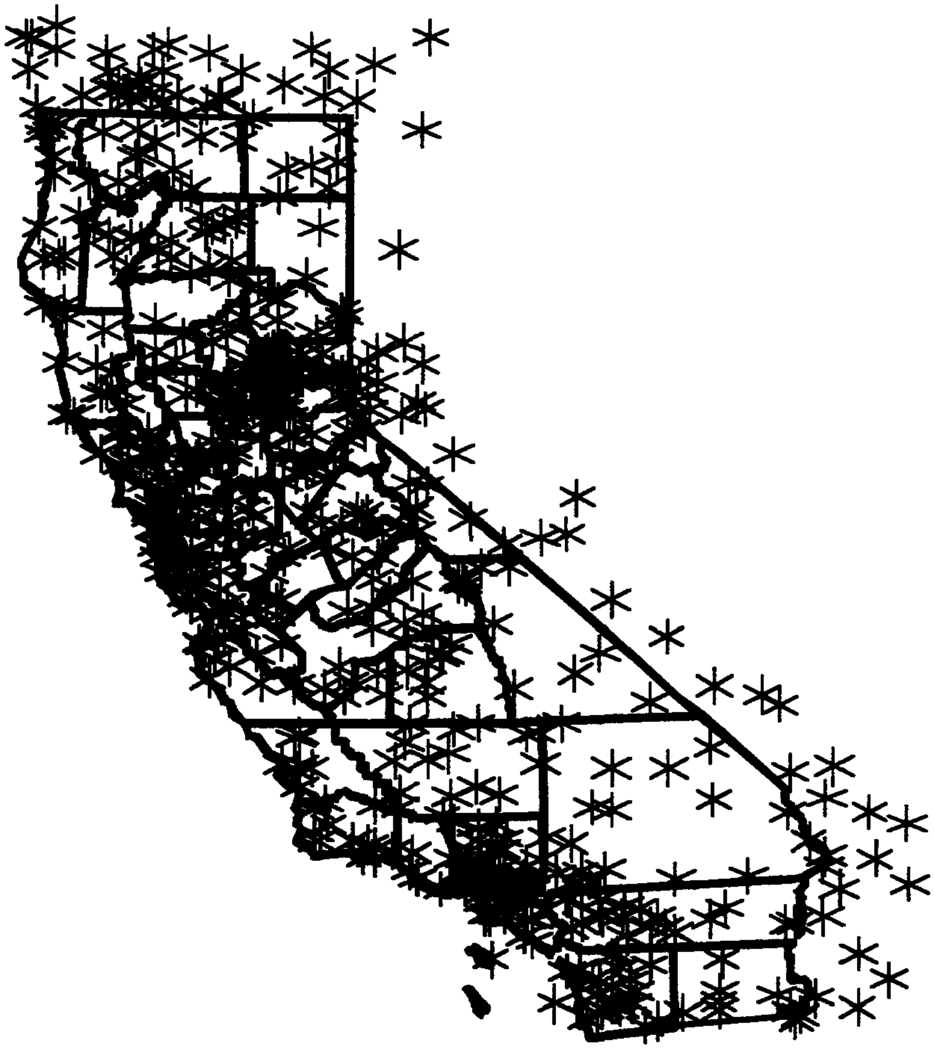

Figure 2. Locations of NWS precipitation stations.

Data Quality

The CADMP data for 1984 through 1987 had been carefully reviewed, first by the CARB's El Monte laboratory following the procedures described in Horrocks and Kowalski (1987), and, second, by that agency's Technical Services Division (TSD), which compiled the CADMP data base. Samples failing to meet quality assurance/quality control (QA/QC) checks were reanalyzed as described in Horrocks and Kowalski (1987). The data collected since July 1987 were reviewed by the ARB as described in Takemoto et al. (1995a) and Takemoto et al. (1995b). The NADP also follows rigorous QA/QC procedures (e.g., Bigelow, 1986; Lockard, 1987; Peden, 1988), which include external audits by the United States Geological Survey (USGS) (e.g., See et al., 1989).

For the period prior to 1990, the replicability and accuracy of CADMP data and their comparability to NADP data were described in our March 1994 report. In that report, we compared weekly NADP samples with CADMP samples. For the current report, we used only monthly-average NADP data. With these data, we compared annual averages at five locations (see Figures 3 and 4 for an example of one of these locations). Species including sulfate, nitrate, and ammonium replicated reasonably well. However, values for NADP measurements of calcium diverged from CADMP measurements for the years 1992, 1993 and 1994.

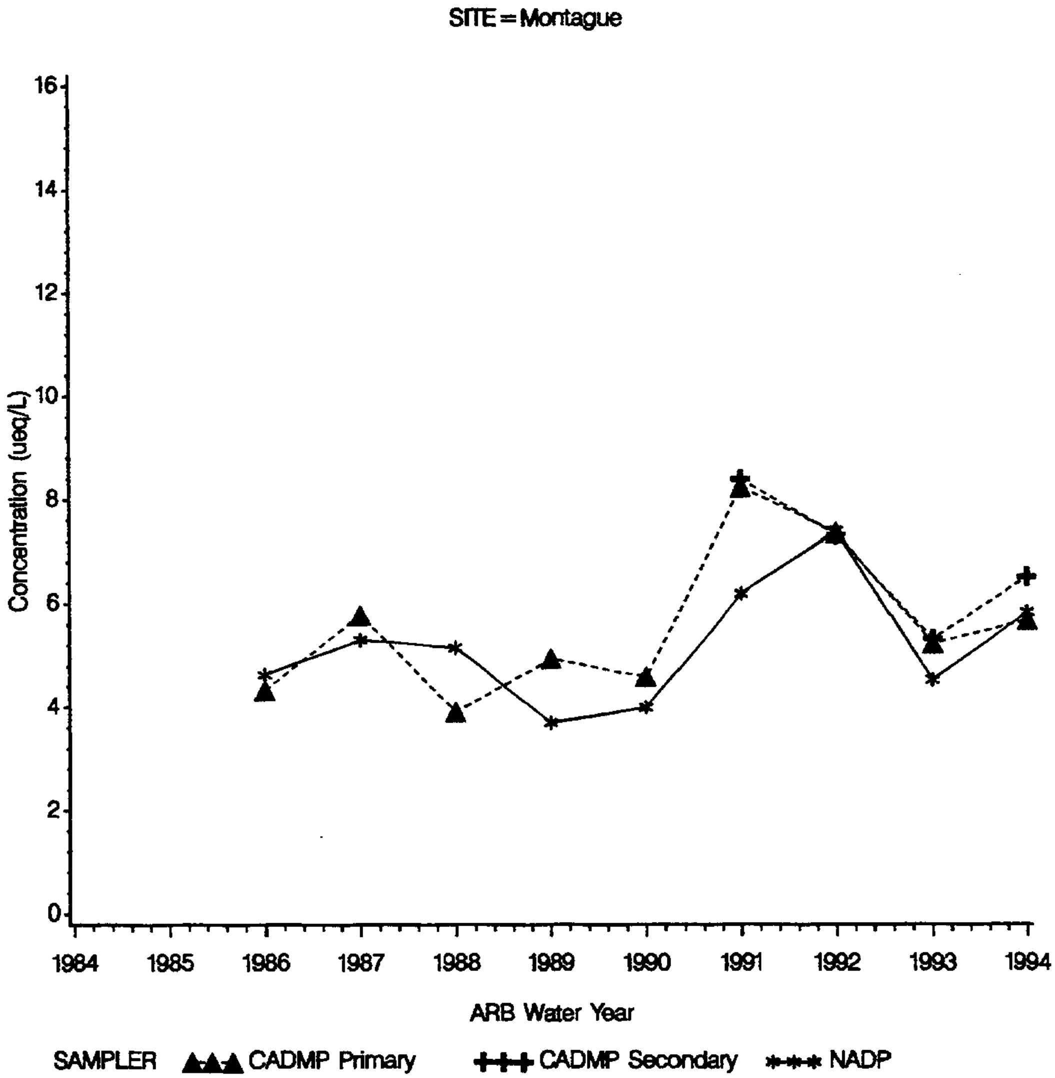

Figure 3. Annual average sulfate concentrations from collocated CADMP and NADP monitors at Montague.

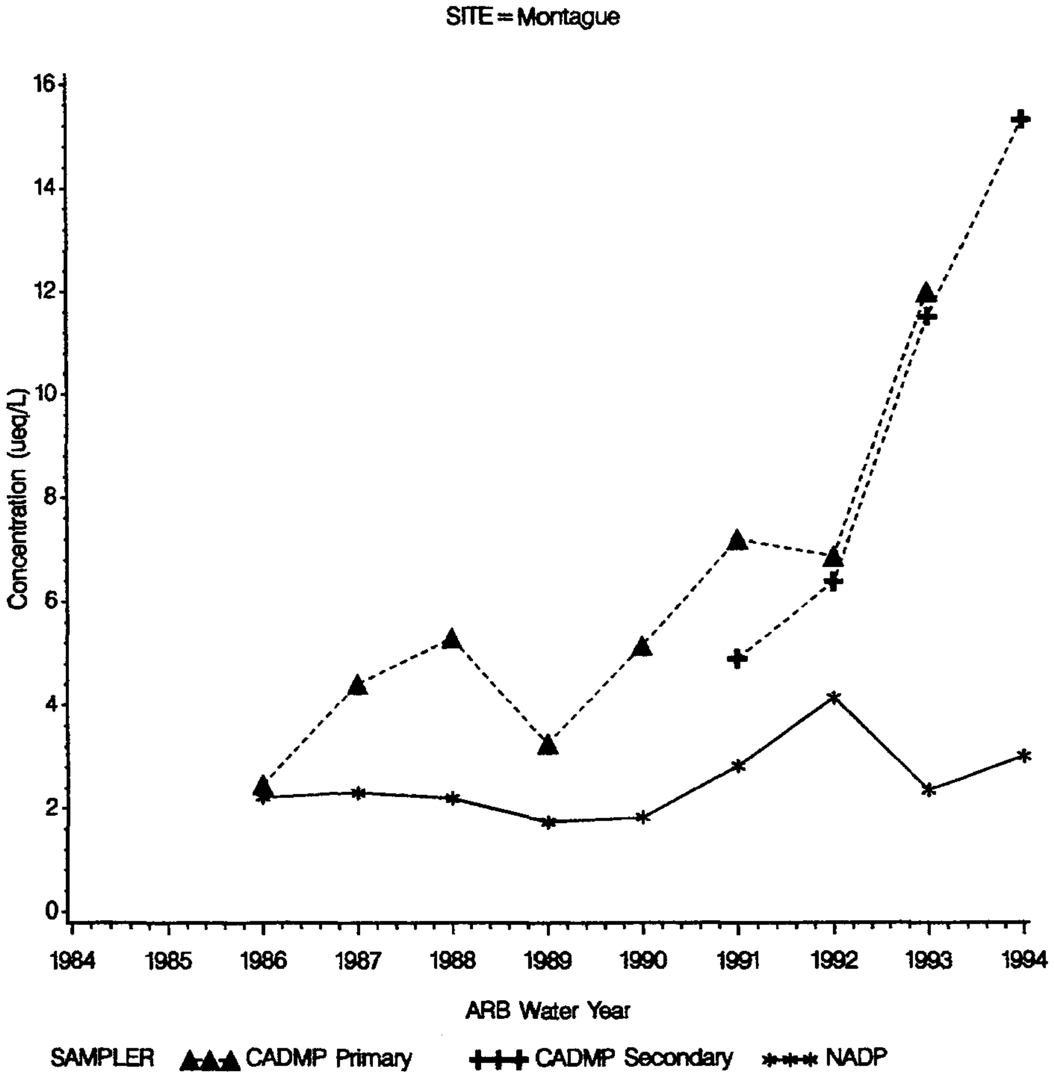

Figure 4. Annual average calcium concentrations from collocated CADMP and NADP monitors at Montague.

Sampling completeness. Sampling is seldom complete over periods such as a quarter. Most networks rely on measures of sampling completeness to determine the representativeness of period averages. We use the following four measures of sampling completeness, which are employed by NADP/NTN. In describing these measures, "samplers" or "collectors" refer to the devices that collect precipitation samples for chemical analysis:

- CI1 Portion of time that acceptable samples were taken for chemical analysis. Times when the sampler was broken or when the sample was contaminated would be excluded.
- CI2 Portion of time with precipitation depth measurements available. These measurements would normally be from rain gauges, but if a rain gauge were broken, depth measurements would be recorded from samplers.
- CI3 Portion of total recorded precipitation depth for which acceptable samples were taken.
- CI4 Portion of precipitation depth included in collectors relative to depth recorded by rain gauges for periods during which both were operational.

These indicators can be computed from the CADMP weekly data (Blanchard and Tonnessen, 1993) and are included in the monthly data provided by NADP/NTN. In compiling monthly, seasonal, or annual averages from weekly data, NADP requires criterion (2) to be at least 0.90 and the other three criteria to be 0.75. The CARB excludes any week in which the weekly CI4 is less than 0.70.

Sirois (1990) related CI1 and CI3 to the bias of monthly, seasonal, and annual average concentrations. The expected bias of annual average depth-weighted sulfate and nitrate concentrations were less than 6 and 10 percent, respectively, if indicators (1) and (3) were each greater than 80 percent.

Specification of Variables of Interest

Discussions with CARB staff indicated that the principal variables of interest were sulfate, nitrate, ammonium, calcium, and hydrogen ion deposition. Because the validity of recent calcium measurements appears questionable, we did not carry out calcium calculations. Further, because hydrogen ion is not conservative, we prefer to base our calculations on acidity. In a carbonate system, mineral acidity is (Stumm and Morgan, 1981)

$$[H\text{-}Acidity] = [H^{+}] - [HCO_3^{-}] - 2[CO_3^{2-}] - [OH^{-}] \quad , \qquad (1)$$

where all concentrations are in moles L^{-1}. We calculated acidity from pH, K_H (Henry's constant), and $p_{CO2} = 10^{-3.45}$ atm [350 parts per million (ppm) at 1 atmosphere]. For ease of comparison with other monitoring programs, we report results in units of kg ha^{-1} yr^{-1} for all species except acidity, which we report in grams (g) ha^{-1} yr^{-1}.

Temporal and Spatial Resolution

We carried out the calculations based on CARB's sampling years (1 July - 30 June). The alpine-network data are derived from sampling of the snow pack at the time of maximum accumulation. Rain samples are also collected for analysis at the alpine stations, and results are compiled as water-year averages (1 October - 30 September). We therefore recompiled the alpine data to match the CARB sampling year as closely as possible.

We created a 40 km by 40 km grid for the state of California. This choice was a compromise between too much and too little resolution. For most of the state, we have insufficient data to adopt a finer resolution (the Los Angeles and San Francisco areas may be exceptions). At the same time, grids coarser than about 40 km seemed likely to be too coarse.

For comparison, other studies involving the interpolation of acid-deposition data have used coarser grids than ours: Seilkop and Finkelstein (1987) used a 4° grid (about 300 to 400 km per side), Guertin et al. (1988) used a grid size of 127 km, Oehlert (1993) used rectangles of 1° latitude by 1.5° longitude (about 100 km per side), Haas (1990) and Haas (1992) used hexagons spaced approximately 150 to 200 km, and the National Acid Precipitation Program (NAPAP) used hexagons with 64 km spacing (Sisterson, 1991). Our network is somewhat denser than those used in the cited studies.

The projection method that we used was a modification of the standard procedure for converting latitude-longitude coordinates to Universal Transverse Mercator (UTM) coordinates. Because California spans two UTM zones, and because UTM zones cannot be aligned and combined, we projected a 12°-width strip (instead of the usual 6° width). It is centered at 120° W longitude (i.e., the California-Nevada border north of Lake Tahoe). The advantage of using UTM coordinates is that the distance scale is the same east-west as north-south.

Procedures for Uncertainty Analysis

We use two approaches to quantify the estimation uncertainties: cross-validation and kriging standard deviations. Cross-validation is a "leave-one-out" method for evaluating accuracy, which is carried out as follows. First, select one station, leave it out, and interpolate its measurement from other stations using the kriging procedures. Repeat this process for each station. Then, generate a file of residuals (observed measurement minus predicted measurement). Finally, summarize key statistics for the residuals, such as the mean error or range of errors.

Cross-validation yields straightforward estimates of the accuracy of the procedure when it is used to estimate point averages. However, because we are estimating cell averages, rather than point measurements, another procedure is also needed. We use the kriging standard deviation for this purpose. The kriging standard deviation is an estimate of the uncertainty of a cell average, which is generated from the set of kriging equations along with the kriging estimate of the cell average. It is analogous to the standard deviation of the mean of a set of numbers; however, it is a function of the sample locations and the variogram only.

Because the data do not fulfill the assumptions of the kriging methodology exactly, the kriging standard deviations are not always an accurate representation of the true uncertainties. However, as discussed in the March 1994 report, the kriging standard deviations and cross validation errors were usually comparable.

Implementation of Kriging Procedures

Precipitation amounts were kriged from annual averages of the NWS daily data. We included a site in the kriging analysis only if at least 95 percent of the days in the quarter had a valid precipitation amount (including zero). The data were log-transformed because this transformation yielded distributions that were very close to normal.

We kriged the annual averages of the precipitation-chemistry variables. We included a site in the kriging analysis only if both CI1 and CI3 were at least 75 percent.

As shown in the March 1994 report, interpolation uncertainties can be reduced by first accounting for the functional relationship between concentration (or deposition) and precipitation amount, then kriging residual concentration, and, finally, recombining the results with kriged precipitation amounts.

Both annual concentration and deposition vary spatially as functions of precipitation amount. We removed the functional relationship according to the following equations:

$$\ln(C_i) = \alpha + \beta \ln(P_i) + e_i \quad , \tag{2}$$

or

$$D_i = a + bP_i + e_i \quad , \tag{3}$$

where P_i represents precipitation amount for the i'th sample, C_i is concentration, D_i is deposition, and e_i is the error term, or residual. We used Equation 2 for all variables except acidity and kriged the residuals (retaining the log scale). Because acidity sometimes takes on negative values, we used Equation 3 for adjusting acidity.

We used ordinary block kriging to interpolate station data to the grid. We utilized the GEO-EAS package developed by the EPA (Englund and Sparks, 1991). Ordinary kriging requires specification of a search ellipse, which is centered on each cell. For each cell, only stations within the ellipse are used in estimating the cell average. We used a circle of radius 300 km; we found no differences in the results to suggest that an ellipse was more appropriate. We also examined the station weights that were computed by the program for selected grid cells. In general, the grid-cell averages were largely determined by sites within about 100 km of the cell center.

Variograms were calculated up to 300 km using about 15 km lag spacing. In all cases, we fit an exponential function to the observed variogram, with nugget (i.e., y-intercept) of zero. The zero nugget reflects our belief that monitors that are moved sufficiently close to each other (e.g., collocated samplers) would produce identical values (within the sampling error). When the lag spacing is reduced sufficiently (e.g., to 5 km), the variograms do show a zero nugget (as shown in the March 1994 report). We fit the observed variograms by adjusting the range and sill of the exponential functions. We tested for directional dependence, but found no evidence for it.

The variogram is a very simplified model of potentially complex spatial covariance. In areas where the concentration or deposition fields exhibit steep gradients, the variogram is likely to underestimate uncertainty.

RESULTS

Evaluation of the Methods

Comparison of methods for quantifying uncertainties. The March 1994 report contains a more detailed discussion of cross-validation. Briefly, for precipitation amount, over 75 percent of the cross-validation errors were less than 33 percent. A few precipitation sites (generally less than five per year out of 492) exhibited errors exceeding 100 percent. For ion deposition, the kriging uncertainties appeared to overestimate the true uncertainties in some areas and underestimate them in others. Most of the cross-validation errors were less than about 2σ, where σ is the kriging standard deviation. For both precipitation amount and ion deposition, the kriging standard deviations may underestimate the true interpolation uncertainties near the boundaries of our study domain and in areas with particularly steep deposition gradients.

Comparison of interpolated values to alpine measurements. For the 1989-1990 season, we compared our interpolated deposition amounts with measurements of precipitation, and sulfate, nitrate, and ammonium deposition made by the University of California at Santa Barbara (UCSB) at the alpine sites. The interpolations were carried out using concentration data from the CADMP and NADP/NTN networks and precipitation amounts from NWS sites (data from the alpine network were not used). The interpolations generated grid cell averages, where the grid cells are 40 x 40 km. The CARB/UCSB alpine-network measurements were made at 10 sites along the crest of the Sierra Nevada. The alpine measurements were taken as snowpack samples at the beginning of April 1990, which thus included the portion of the snowfall from October 1989 through April 1990 that did not melt; in addition, the alpine measurements included event samples of rainfall that occurred from late May or early June 1990 through September 1990. To permit comparison of the interpolations to the UCSB measurements, a point estimate was generated from the grid cell averages using bilinear interpolation of the values occurring in the four grid cells surrounding each UCSB site. Figure 5 shows the locations of the UCSB sites and surrounding grid cells. Table 2 lists the locations and elevations of all NWS sites within 40 km of each UCSB site.

The following points of agreement and disagreement are apparent:

- Interpolations from NWS precipitation amounts are consistently lower than UCSB measurements (see Figure 6a), particularly at UCSB sites where there are few nearby NWS stations and where the closest NWS sites are at significantly lower elevations (see also Table 2). Generally, interpolation estimates and UCSB measurements are most similar where more NWS sites are located and where the NWS sites are at higher elevations (see Figure 6a and Table 2). The most likely explanation of the discrepancies has to do with the averaging that occurs in the interpolation routines. Interpolation provides a good estimate for the average amount of precipitation throughout the 40 km x 40 km grid cells; a grid cell average would under- or overestimate, respectively, the high and low extremes occurring within the cell. Because the UCSB measurements were made at locations along the Sierra crest, where precipitation is maximal, the UCSB amounts exceed the interpolated values. The extent of discrepancy depends upon the number of high-elevation NWS stations located within each grid cell.

- The UCSB measurements of winter precipitation (October-March) are greater than interpolated predictions (October-March), following the same pattern as annual precipitation described above (see Figure 6b and Table 2).

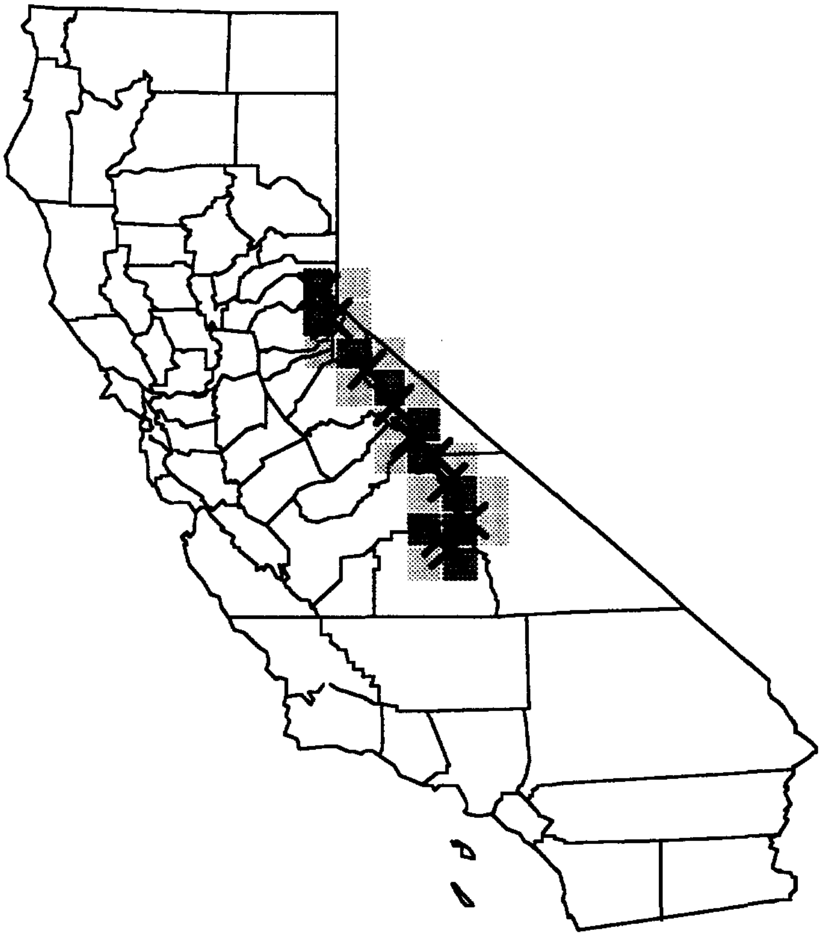

Figure 5. Locations of UCSB monitoring sites and interpolation grid cells. Dark shading denotes cells in which the UCSB sites are located and light shading denotes adjacent cells.

Table 2. National Weather Service (NWS) stations within 40 km of UCSB monitoring sites, with elevations.

UCSB Site	Elevation (m)	NWS Site	Elevation(m)
Alpine Meadows (AM)	2,164	Boca	1,700
		Truckee R S	1,835
		Donner Memorial St Pk	1,810
		Tahoe City	1,899
		Carson City	1,417
		Glenbrook	1,935
		Mt Rose Bowl	2,286
		Stateline-Harrahs	1,905
		Lake Spaulding	1,573
		Sagehen Creek	1,932
Angora Lake (ANG)	2,286	Echo Summit-Sierra Ski	2,240
		Twin Lakes	2,438
		Glenbrook	1,935
		Minden Airport	1,436
		Stateline-Harrahs	1,905
		Pacific House	1,048
		Tahoe City	1,899
		Woodfords	1,728
Sonora Pass (SP)	2,937	Bridgeport	1.972
Tioga Pass (TG)	2,993	Bridgeport	1,972
		Mono Lake	1,966
		Ellery Lake	2,941
		Gem Lake	2,734
		Bodie	2,551
		Yosemite Park HDQ	1,210
Mammoth Mountain(MM)	2,940	Ellery Lake	2,941
		Gem Lake	2,734
Eastern Brook Lk (EBL)	3,170	Lake Sabrina	2,764
		Bishop Creek Intake 2	2,484
		Bishop WSO AP	1,253
		South Lake	2,920
South Lake (SL)	3,010	Lake Sabrina	2,764
		South Lake	2,920
		Bishop Creek Intake 2	2,484
		Bishop WSO AP	1,253
Onion Valley (OV)	2,800	Independence	1,204

Table 2, continued

UCSB Site	Elevation (m)	NWS Site	Elevation(m)
Emerald Lake (EL)	2,824	Grant Grove	2,012
		Ash Mountain	521
		Lemon Cove	155
		Lodgepole	2,054
		Three RVR Edison P H 1	347
Mineral King (MK)	2,694	Ash Mountain	521
		Lodgepole	2,054
		Three RVR Edison P H 1	347

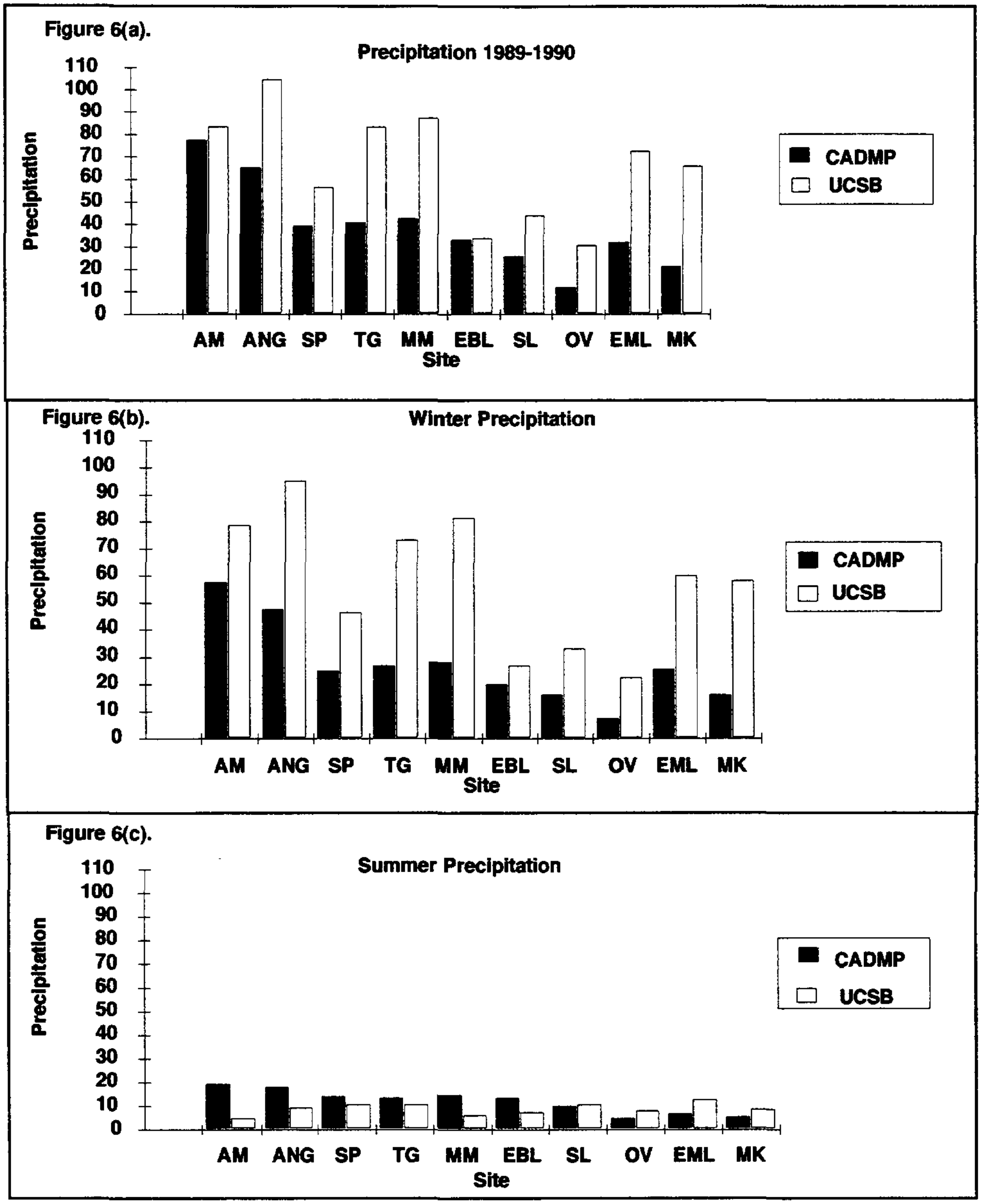

Figure 6. Precipitation amounts measured by UCSB at ten alpine sites and as determined from interpolation of NWS data: (a) annual amounts, October 1989 through September 1990, (b) winter amounts, October 1989 through March 1990, and (c) spring and summer amounts, April through September 1990.

- Interpolated values for summer precipitation (April-September) are greater than UCSB's measured levels at the six northern sites and lower at the four southern sites (see Figure 6c). This pattern appears to result from two factors. First, as described above, interpolation predictions tend to underestimate precipitation at the highest elevations; this underestimation is particularly noticeable at the four southern sites where the closest NWS stations are at much lower elevations than UCSB sites (see Table 2). Conversely, while UCSB collected some snow samples from the beginning of April through the end of May or early June, spring rain was not measured during this time period. The unsampled spring rain appears to account for UCSB's lower levels of summer precipitation at the northern sites. The missing spring rain would be less significant at the southern sites, where elevation differences between NWS and UCSB sites are more extreme.

- The UCSB measurements of sulfate, nitrate, and ammonium deposition were consistently lower than the interpolated values, with the exceptions of all species at Mineral King and sulfate at Onion Valley (see Figure 7). The most likely explanation for these differences is that the spring rains that were not sampled by UCSB (rainfall between April 1 and the end of May or early June) often contain elevated levels of sulfate, nitrate, and ammonium; the unsampled rainfall probably accounts for the discrepancy between UCSB measurements and the interpolations. Figure 8 shows that cumulative deposition of nitrate between April and June can account for a substantial fraction of the annual total at CADMP sites in the Sierra Nevada.

- The annual averaging period for the sulfate, nitrate, and ammonium interpolations was slightly different than the averaging period for the UCSB measurements: the UCSB annual total includes July through September 1990, whereas the interpolated annual total includes July through September 1989 (the overlap is the period October 1989 through June 1990). Because UCSB did not begin sampling until 1990 a comparison over identical averaging periods was not possible (comparison over exact time periods would be possible for later years; however, because the interpolations for CARB sample years later than 1990 included the alpine-network data, the interpolations would have to be recalculated to generate an independent comparison). Generally, the differences between summer 1989 and summer 1990 suggest that the CADMP interpolated estimates would be slightly lower than those shown in Figures 7 if the averaging period had been identical to that used by UCSB. For nitrate, the difference in sampling periods could account for approximately 0.1 to 1.0 kg ha^{-1} of the discrepancy between interpolations and UCSB measurements, with most differences less than 0.5 kg ha^{-1} (see Figure 8).

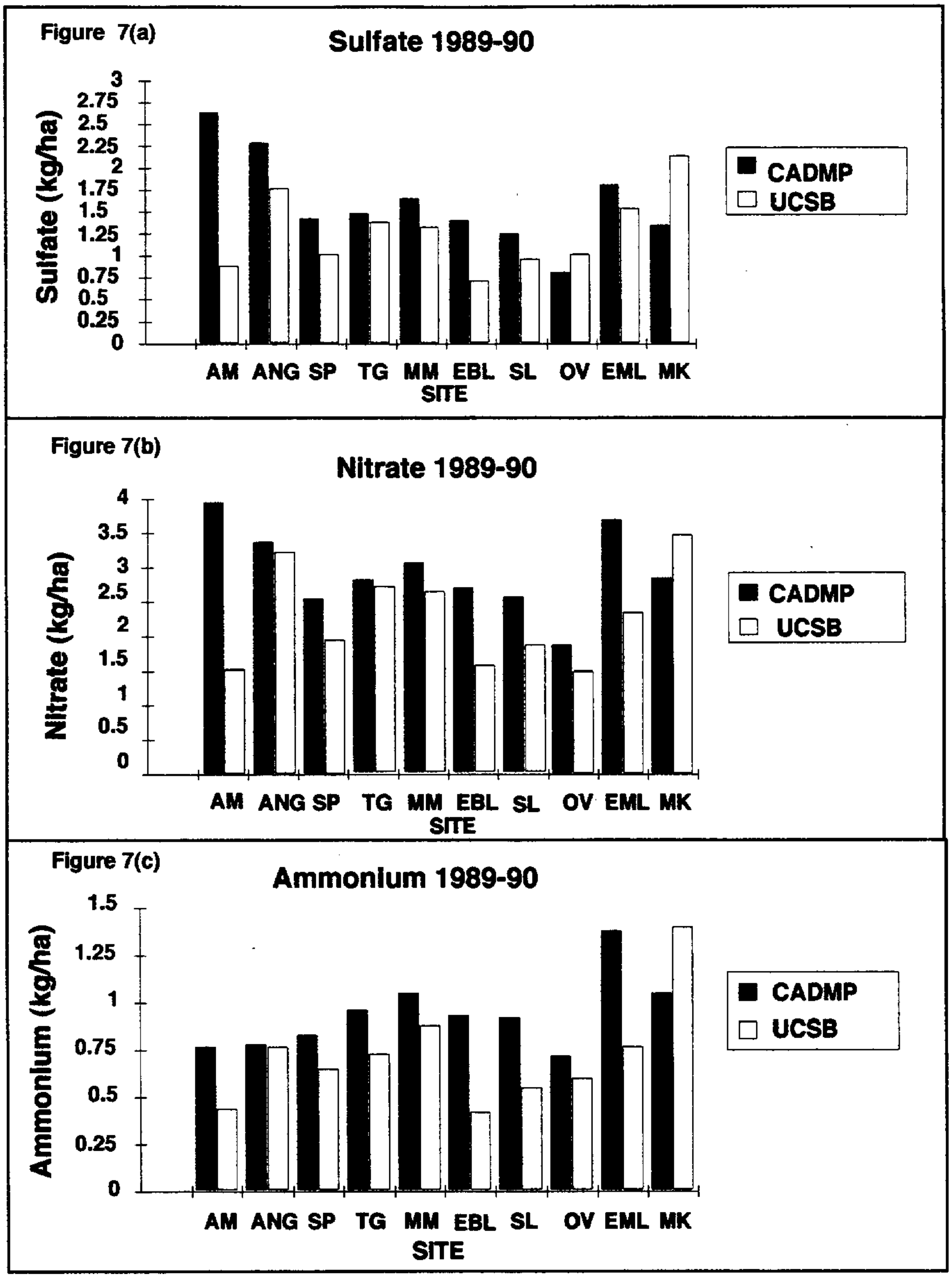

Figure 7. Sulfate, nitrate, and ammonium deposition measured by UCSB at ten alpine sites and as determined from interpolation of CADMP, NADP/NTN, and NWS data. The UCSB measurements were made during the period October 1989 through September 1990. The interpolations are for the period July 1989 through June 1990.

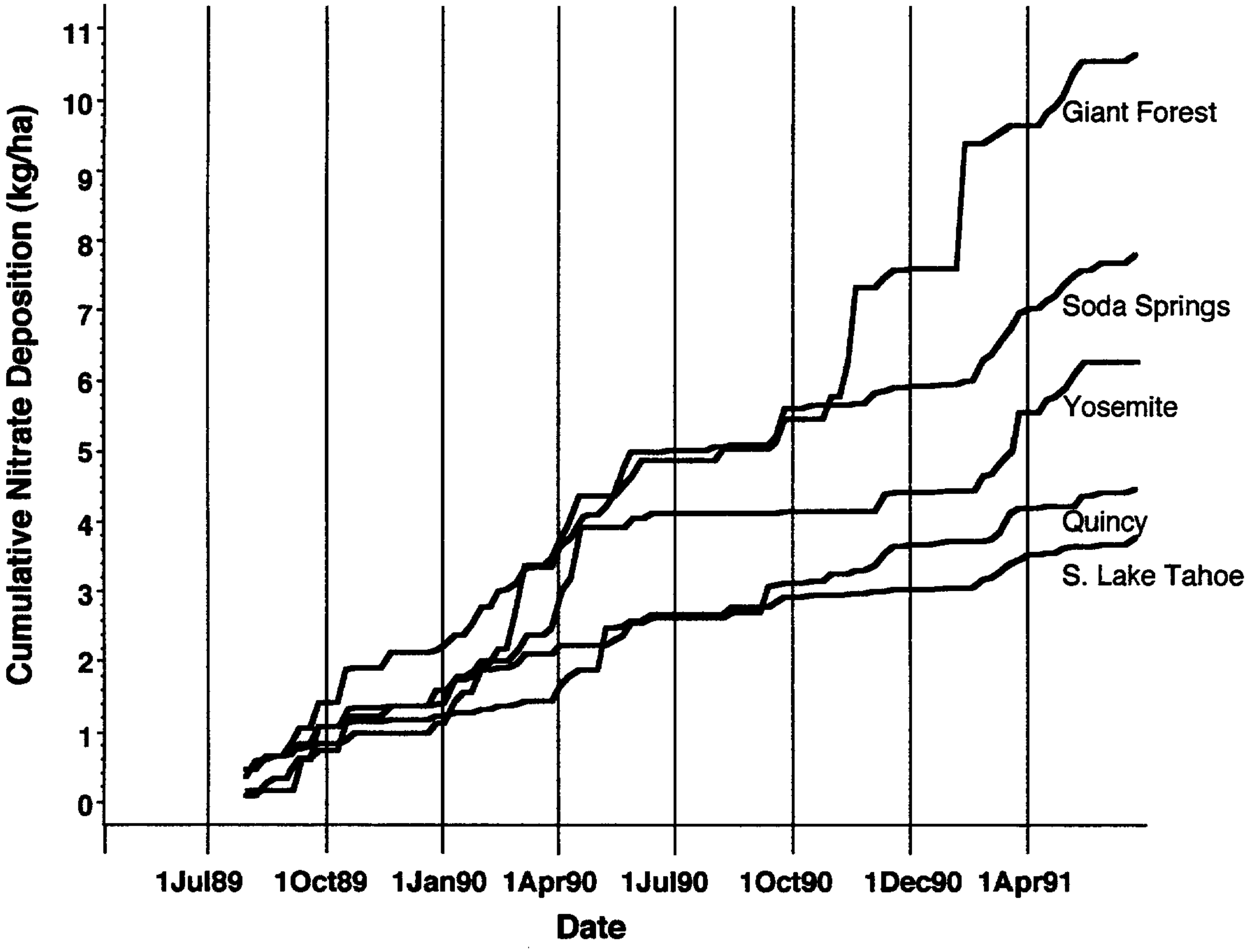

Figure 8. Cumulative nitrate deposition at five CADMP sites in the Sierra Nevada for the period July 1, 1989 through June 30, 1991.

In summary, the interpolation predictions using CADMP, NADP/NTN, and NWS sites appear to yield good estimates of spatial averages within each 40 km x 40 km grid cell. These predictions will underestimate total deposition at the highest elevations, where UCSB sites are located. The degree of underestimation of sulfate, nitrate, and ammonium deposition is larger than it appears in Figure 7 because the UCSB measurements did not include spring rain; if all rainfall had been measured, the UCSB values for precipitation and deposition levels would be higher than reported.

Due to the averaging that occurs in the interpolations and to the unsampled rainfall at the UCSB sites, the maximum deposition values occurring in the Sierra Nevada must be greater than both the interpolated values and the measurements reported by UCSB. However, based on spring deposition rates at lower elevations, it is unlikely that the underestimation would exceed 1 kg ha^{-1} for nitrate; it would be even less for sulfate and ammonium. Both the interpolations and the UCSB measurements show sulfate at 1-3 kg ha^{-1} at all sites; adding 1 kg ha^{-1} as a upper bound estimate of the bias, the maximum sulfate deposition in the Sierra Nevada would still be below 4 kg ha^{-1}. For comparison, Canadian and Scandinavian target thresholds for sulfate deposition range from 10 to 20 kg ha^{-1}.

Summary Results

Our results for 10-year averages are shown in the maps following this page (Figures 9 through 20). For each species, one map shows deposition and one shows the kriging CV. Appendix A shows maps for individual water years from 1991 through 1994.

For the period July 1990 through June 1994, nitrate deposition via precipitation was less than 6 kilograms per hectare per year (kg ha^{-1} yr^{-1}); excess sulfate (i.e., excluding sea-salt sulfate) and sulfate deposition were less than 4 kg ha^{-1} yr^{-1}; and ammonium deposition was less than 2 kg ha^{-1} yr^{-1}. For comparison, wet sulfate and nitrate deposition in portions of eastern North America exceed 25 and 15 kg ha^{-1} yr^{-1}, respectively (Sisterson, 1991); ammonium deposition is less than about 4 kg ha^{-1} yr^{-1} in almost all parts of eastern North America (Sisterson, 1991).

Wet deposition interpolation uncertainties were generally less than 20 percent in the South Coast Air Basin, which has a large number of monitors. Elsewhere in California, wet deposition intepolation uncertainties were no more than 40 percent (southern California) and 60 percent (northern California) for sulfate, excess sulfate and nitrate. Uncertainties can be up to 100 percent for acidity, because acidity deposition rates are typically close to zero g ha^{-1} yr^{-1}.

The value of each grid cell represents a spatial average and thus can differ from the value for a particular station that might be located in the grid cell. For example, the network maximum nitrate deposition was often located at Tanbark Flat. For each year, this maximum exceeds the grid cell average because other monitors, recording lower deposition amounts, are also located within or close to the same grid cell. A finer grid would help resolve particular maxima. For comparison, Tables 3 through 6 list nitrate, sulfate, excess sulfate, and ammonium deposition by station (site) and year. Table 7 lists mean deposition of nitrate, sulfate, excess sulfate, and ammonium over all available years.

Grid cells can be summed or averaged to yield either basin totals or averages. Appendix B presents time series plots of each species over the water years 1985 through 1994, for each air basin.

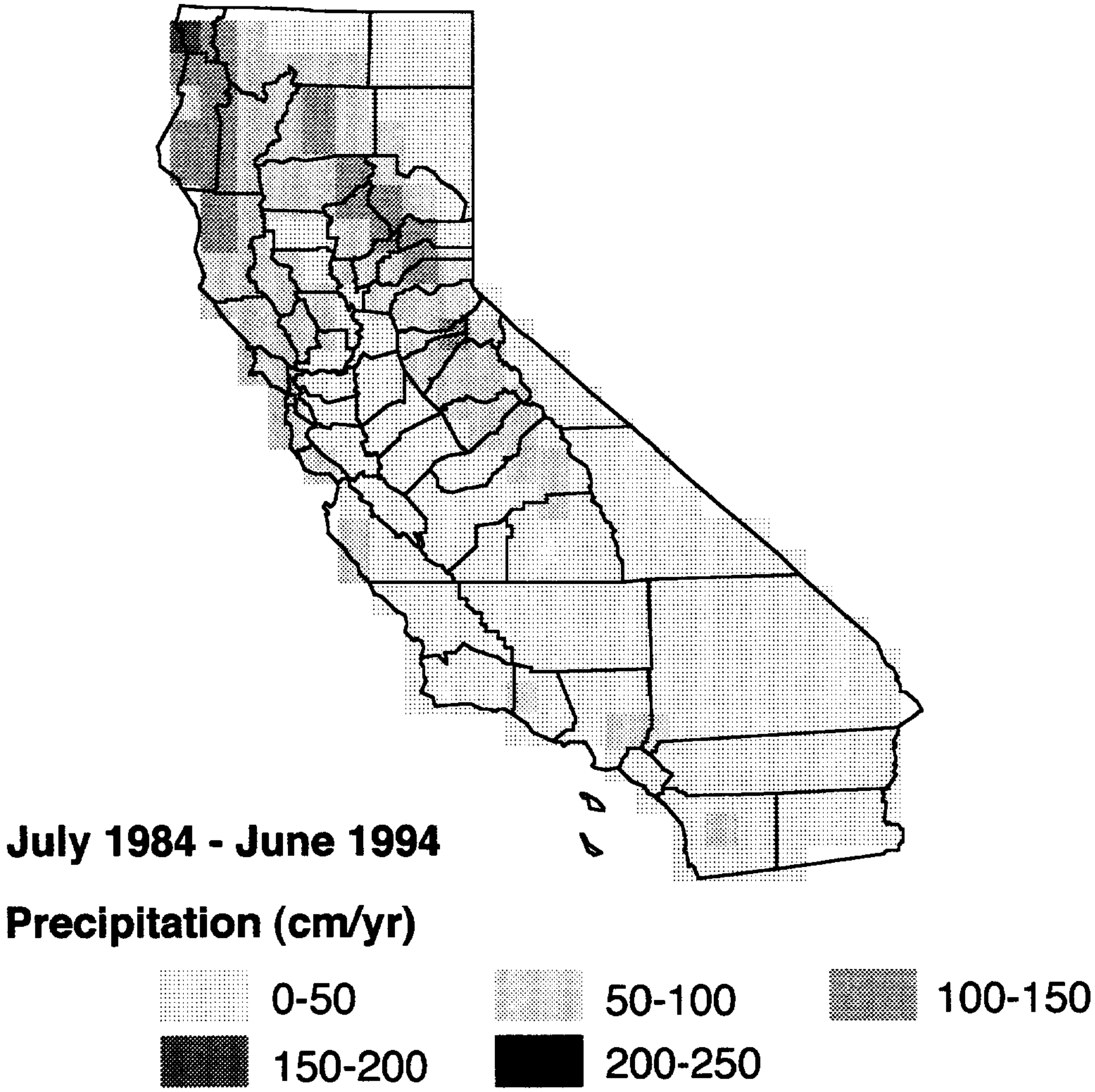

Figure 9. Ten-year average of annual interpolated precipitation amounts, July 1984 through June 1994.

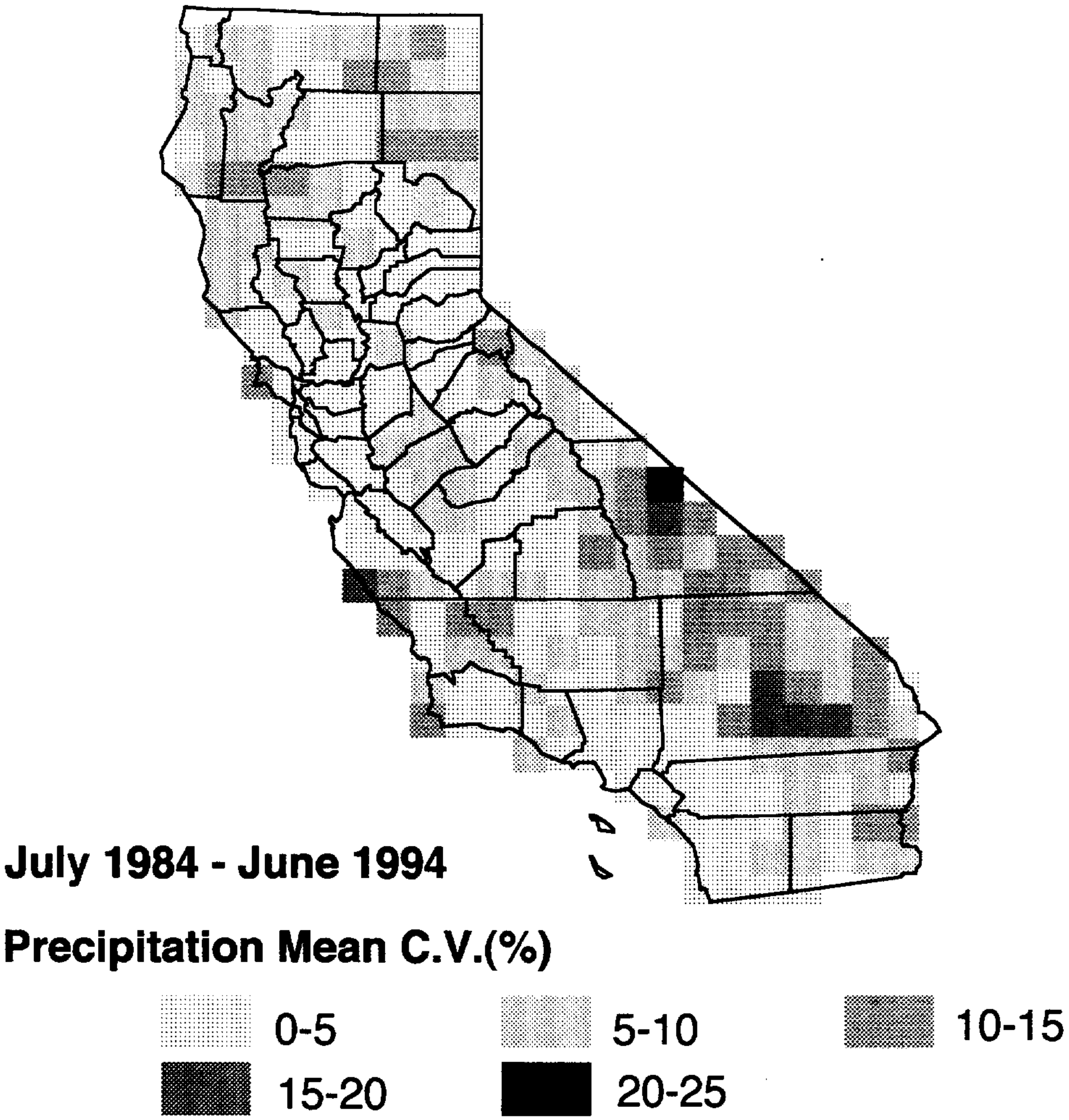

Figure 10. Ten-year average of annual coefficients of variation of interpolated precipitation amounts, July 1984 through June 1994.

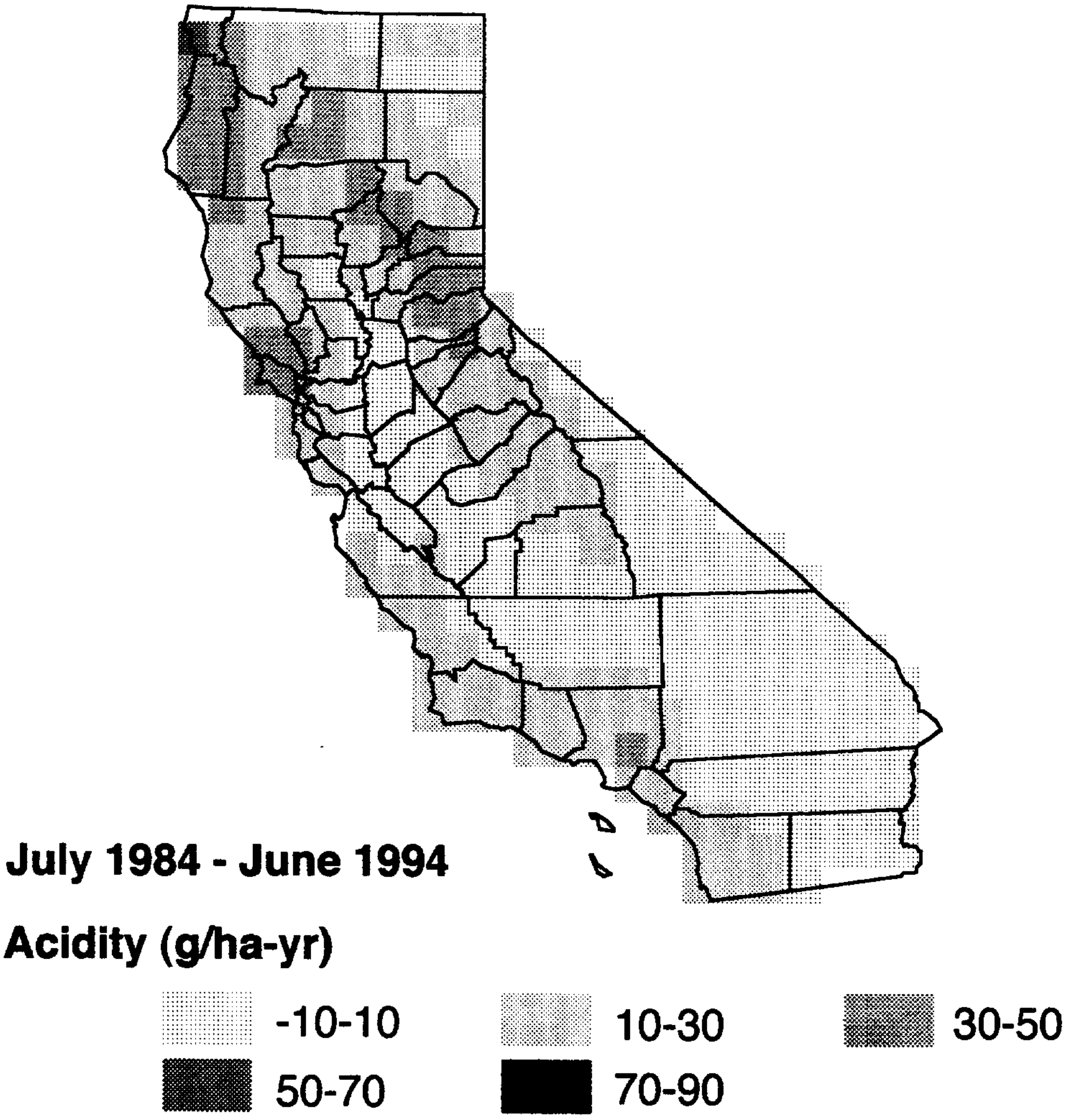

Figure 11. Ten-year average of annual interpolated acidity deposition, July 1984 through June 1994.

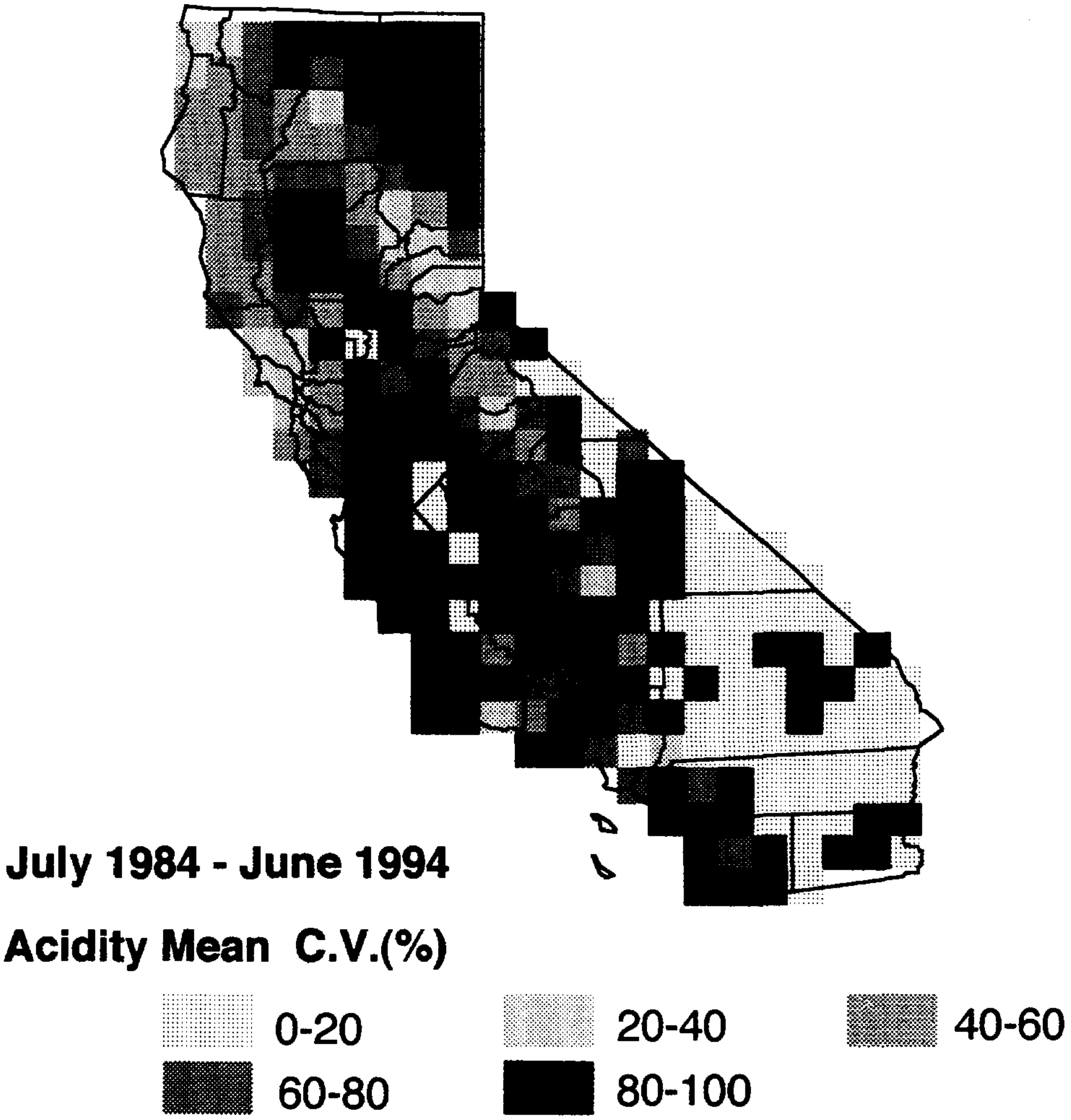

Figure 12. Ten-year average of annual coefficients of variation of interpolated acidity deposition, July 1984 through June 1994.

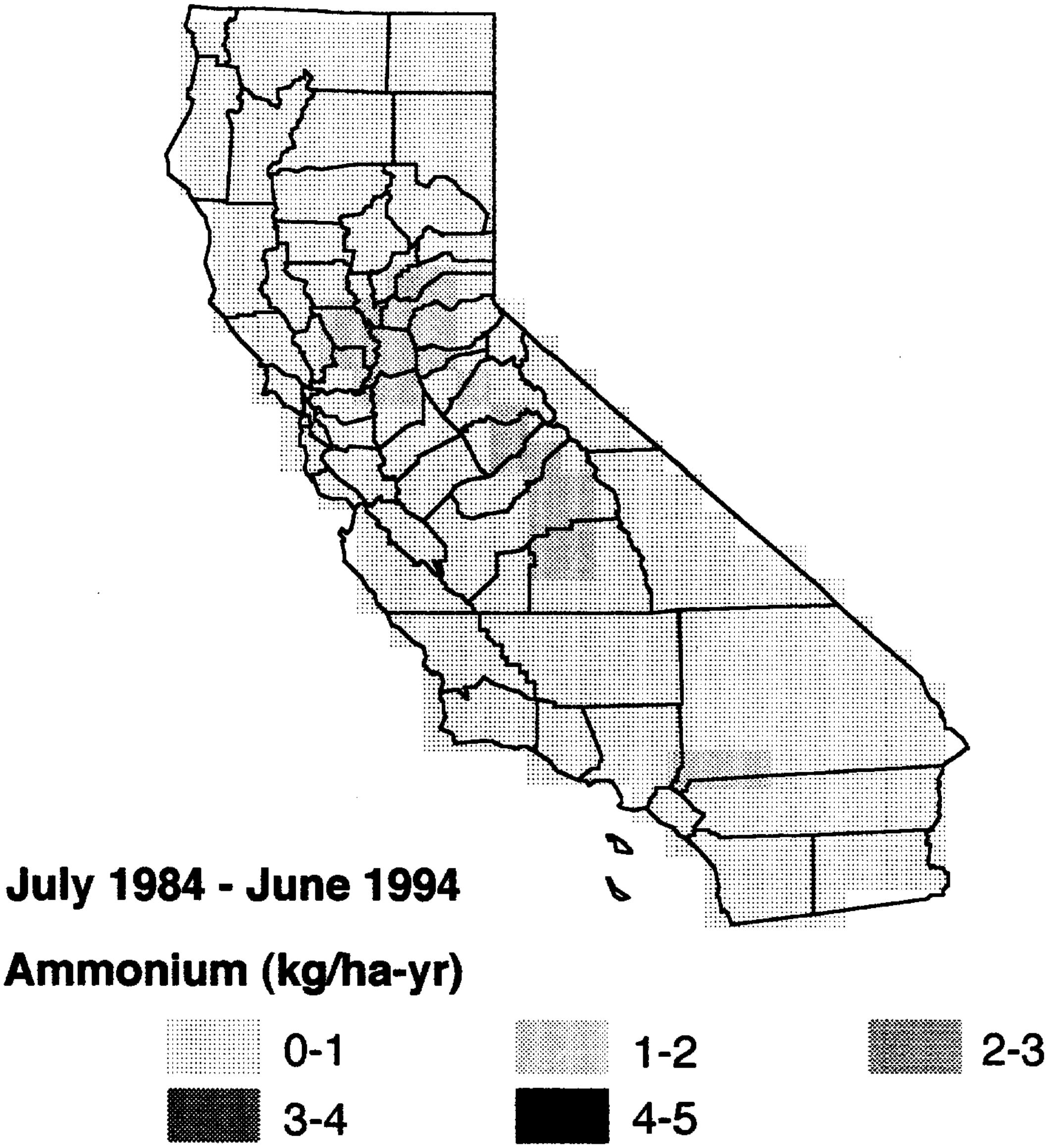

Figure 13. Ten-year average of annual interpolated ammonium deposition, July 1984 through June 1994.

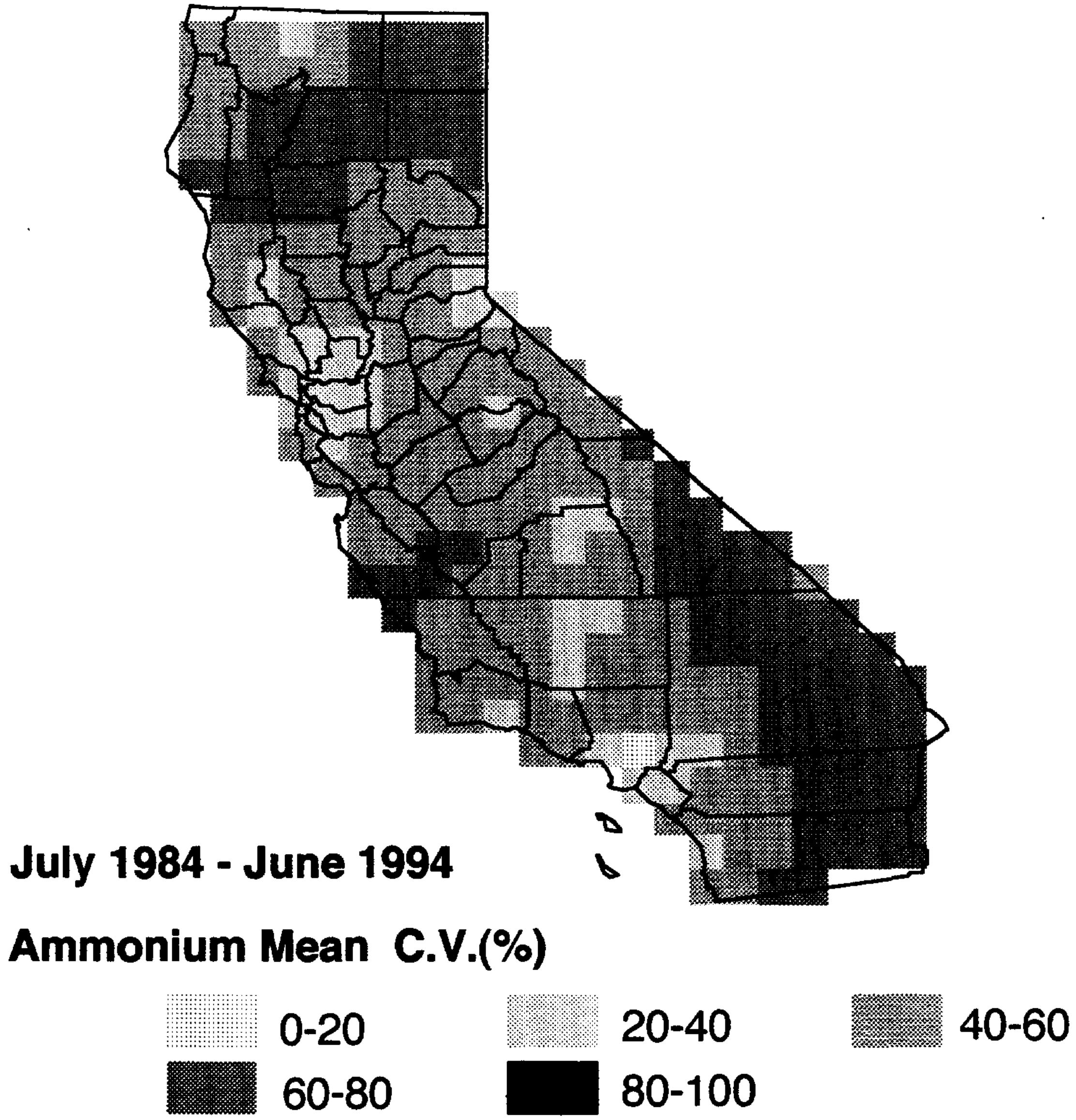

Figure 14. Ten-year average of annual coefficients of variation of interpolated ammonium deposition, July 1984 through June 1994.

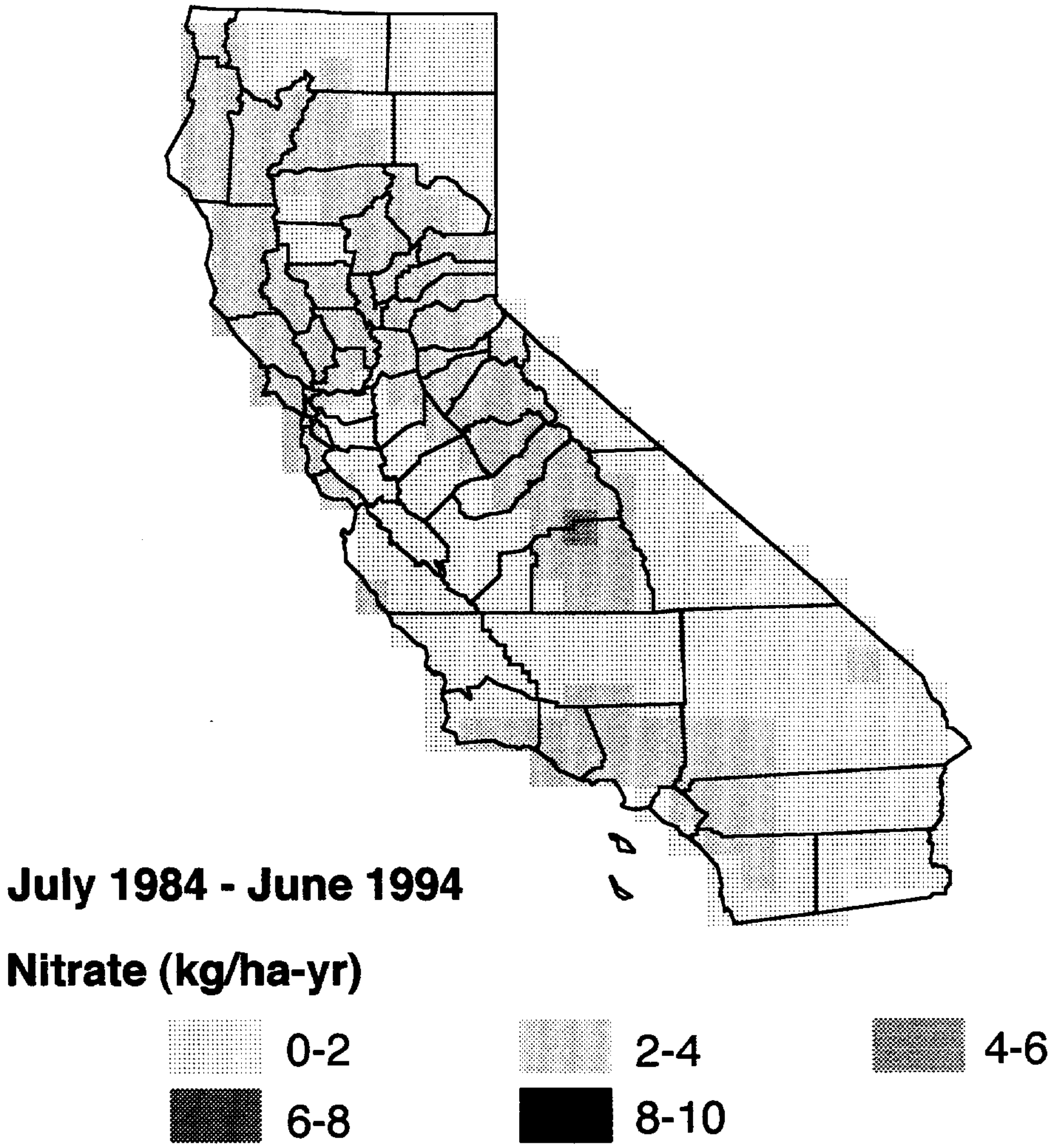

Figure 15. Ten-year average of annual interpolated nitrate deposition, July 1984 through June 1994.

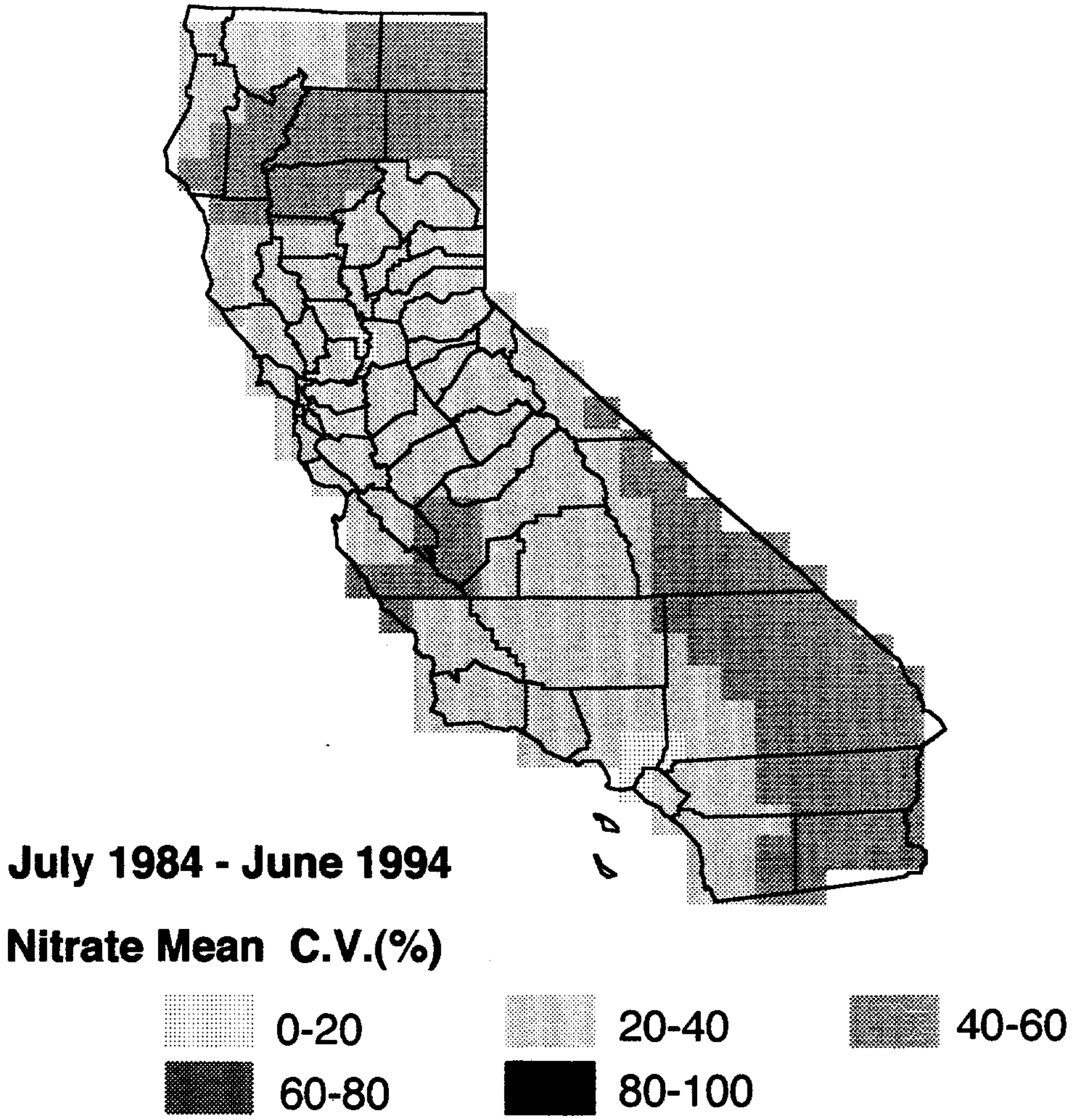

Figure 16. Ten-year average of annual coefficients of variation of interpolated nitrate deposition, July 1984 through June 1994.

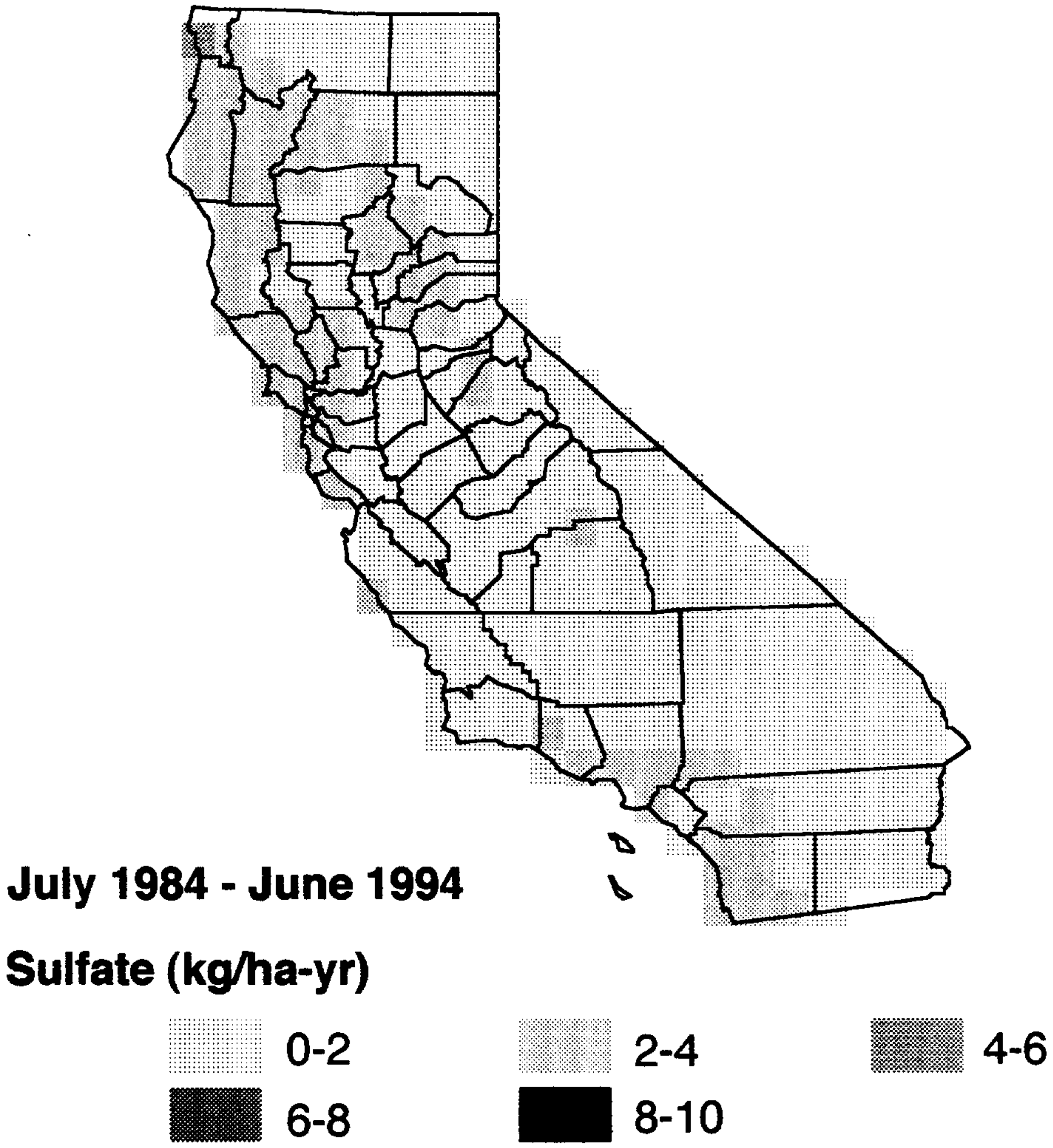

Figure 17. Ten-year average of annual interpolated sulfate deposition, July 1984 through June 1994.

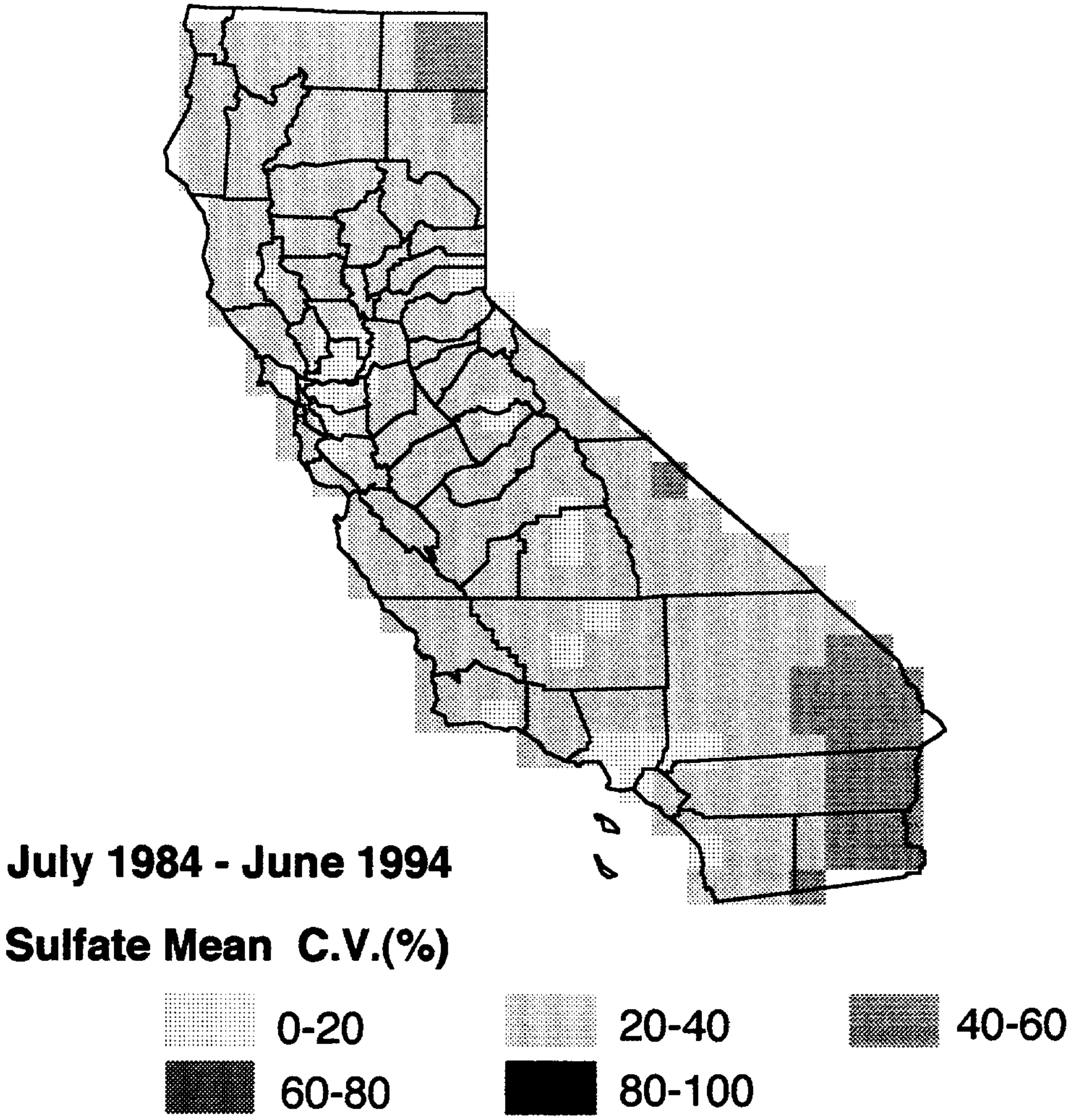

Figure 18. Ten-year average of annual coefficients of variation of interpolated sulfate deposition, July 1984 through June 1994.

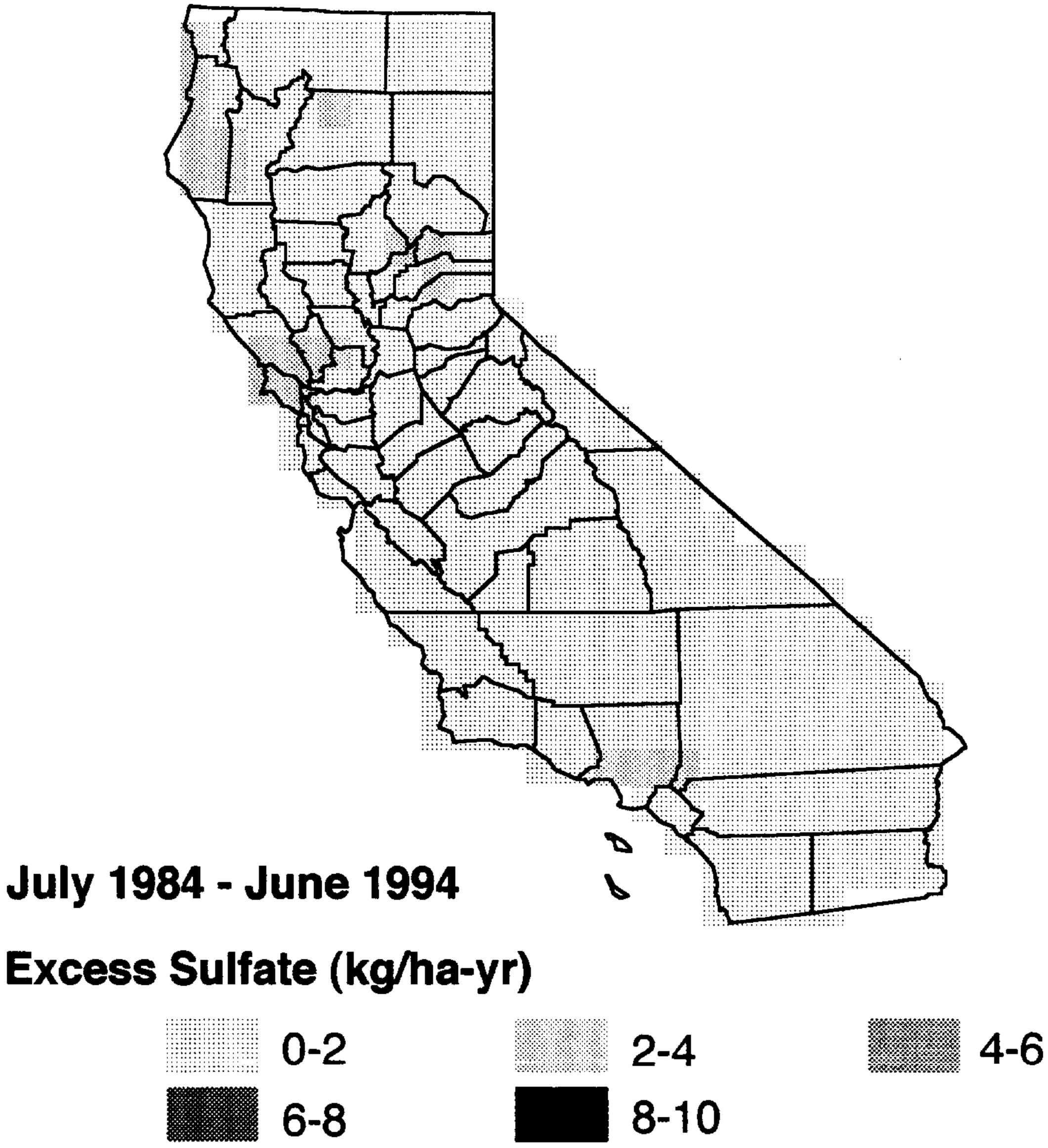

Figure 19. Ten-year average of annual interpolated excess sulfate deposition, July 1984 through June 1994.

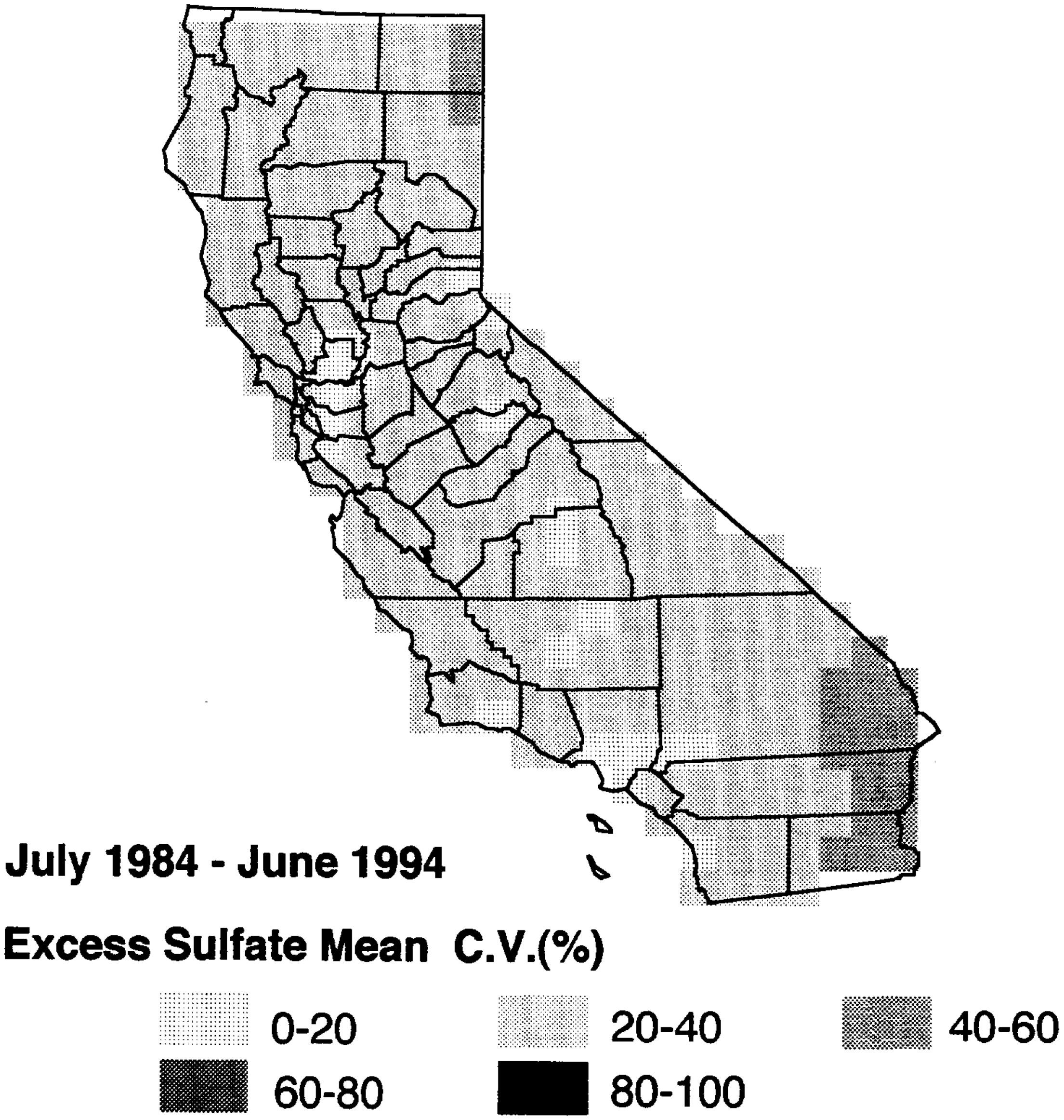

Figure 20. Ten-year average of annual coefficients of variation of interpolated excess sulfate deposition, July 1984 through June 1994.

Table 3. Annual nitrate deposition (kg ha^{-1} yr^{-1}) by site and CARB sample year. Only years in which CI1 and CI3 were at least 75 percent are shown. CADMP and UCSB sites are capitalized. Missing values are shown with periods.

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
ALPINE MDWS	.	.	.	.	.	.	2.65	3.94	3.52	.
ANAHEIM	.	1.74	1.81	2.43	2.75	1.38	0.90	2.05	2.82	1.10
ANGORA LK	.	.	.	.	.	.	3.05	2.17	5.97	.
BAKERSFIELD	1.76	1.02	2.97	2.95	1.59	1.41	1.74	1.73	1.49	1.52
BERKELEY	2.45	3.11	2.18	2.92	.	1.91	1.79	2.88	2.79	.
BETHEL ISL	1.93	2.54	1.72	2.00	1.82	1.37	0.86	1.85	2.47	2.15
Chuchupate Range	4.00	.	2.04	2.23	1.43	0.60	.	.	1.51	.
Davis	3.21	.	1.86	2.95	.	2.21	2.46	3.22	4.38	2.05
EASTRN BRK LK.	.	.	.	.	.	1.43	1.93	2.00	.	
EL MONTE	4.04	4.00	3.07	4.41	2.85	3.43	2.23	3.79	6.30	2.84
EMERALD LK	.	.	.	.	.	.	2.44	3.17	4.40	.
ESCONDIDO	3.27	1.28	2.48	2.64	1.78	1.77	1.26	2.28	1.90	1.86
EUREKA	1.22	1.45	0.95	1.63	.	.	.	.	.	.
GASQUET	1.77	2.38	1.97	2.54	3.11	1.62	.	1.89	3.17	1.24
Hopland	1.83	1.45	2.19	2.73	1.38	1.44	1.83	1.62	2.25	1.47
Hopland Intercom	.	.	.	.	.	.	.	1.80	.	.
KAISER PASS	.	.	.	.	.	.	.	1.69	3.40	.
LAKE ISABELLA	.	1.44	2.54	1.26	1.85	0.66	0.71	.	1.08	.
LAKEPORT	1.96	2.12	1.98	2.57	.	.	.	.	.	.
LINDCOVE	.	4.13	3.36	4.16	.	.	.	.	.	.
LOS ANGELES	.	.	.	.	.	.	1.15	5.33	4.08	2.86
LYNWOOD	3.87	3.46	2.68	2.38	2.03	1.59	0.61	2.61	2.92	1.89
MAMMOTH MTN	.	.	2.81	.	.	.	.	.	.	.
MINERAL KING	.	.	.	.	.	.	4.18	2.95	2.65	.
MMMTH MT/UC	.	.	.	.	.	.	2.83	3.16	3.92	.
MONTAGUE	.	1.26	1.23	1.05	1.57	1.15	1.70	1.35	1.88	1.09
MONTAGUE C	.	.	.	.	.	.	1.71	1.36	1.94	1.18
MT WILSON	5.74	2.52	2.55	6.20	3.38	3.21	1.72	3.89	6.53	3.23
Montague	.	0.98	0.91	1.26	1.18	1.13	1.73	1.25	1.71	1.10
NAPA	.	3.87	2.41	4.02	3.52	2.58	2.95	3.18	4.15	2.63
NIPOMO	1.12	1.16	1.97	1.22	.	.	.	.	.	.
ONION VLLY	.	.	.	.	.	.	2.70	2.24	2.13	.

Table 3, continued

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Organ Pipe Cactu	2.59	1.15	1.12	.	1.95	0.92	3.34	1.60	2.47	0.67
PASADENA	6.68	5.48	4.68	5.23	4.23	4.41	2.79	6.60	6.22	4.45
Palomar Mt	12.12	3.01	2.21	.	.	.	.	.	.	.
QUINCY	.	3.61	2.42	.	.	2.73	2.13	3.13	3.58	2.98
RESEDA	3.79	4.47	3.42	4.79	3.45	1.40	.	.	.	.
Red Rock Canyon	.	.	3.30	1.45	1.62	.	3.48	3.61	.	1.46
SACRAMENTO	3.38	4.94	2.62	3.73	3.84	3.23	1.69	4.46	4.33	2.71
SACRAMENTO C	.	.	.	.	.	.	1.85	3.67	4.31	2.66
SALINAS	1.27	1.18	1.03	1.23	.	.	.	.	.	.
SAN BERNAR	4.22	3.84	2.47	4.90	3.94	4.48	2.53	9.17	4.67	5.17
SAN JOSE	1.40	1.83	1.14	1.61	0.76	0.87	0.86	2.19	1.51	0.94
SAN NICOLAS	1.13	0.56	0.52	0.86	.	.	.	.	.	.
SAN RAFAEL	3.80	.	2.29	5.52	.	.	.	.	.	.
SANTA BARBA	2.89	4.01	2.90	3.05	2.76	0.66	1.62	2.18	3.42	1.89
SEQUOIA ASH	6.76	5.51	4.98	5.76	3.30	6.92	4.58	2.55	4.83	4.22
SEQUOIA GF	.	5.47	5.52	5.11	3.14	5.26	6.32	3.00	6.75	4.96
SEQUOIA GF C	.	.	.	.	.	.	6.32	2.82	.	.
SOUTH LK	.	.	.	.	.	.	1.65	1.67	2.88	.
SODA SPRINGS	.	4.07	4.34	3.03	5.46	4.98	3.90	4.61	5.69	4.31
S. LAKE TAHOE	1.31	2.11	2.08	1.16	2.00	2.67	1.13	1.86	1.73	1.35
SONORA PS	.	.	.	.	.	.	2.13	2.72	2.21	.
Sequoia Nat'l Pa	.	4.37	.	.	.	5.13	6.06	3.64	7.53	5.30
Silver Lake Rang	.	0.99	0.93	0.75	.	0.68	.	0.96	2.01	1.08
Smith Valley	.	0.50	1.36	0.69	1.40	0.76	1.32	.	0.67	.
TANBARK	7.98	5.01	3.49	6.07	6.84	5.35	4.41	5.92	3.91	3.43
TANBARK C	.	.	.	.	.	.	2.60	5.74	4.41	3.53
TIOGA PS	.	.	.	.	.	.	3.12	2.65	4.13	.
Tanbark Flat	6.78	4.33	3.48	6.01	5.66	.	4.27	7.03	5.43	4.86
VICTORVILLE	3.03	1.18	3.34	1.11	.	.	.	.	.	.
YOSEMITE	5.04	.	5.73	3.99	2.49	.	2.38	3.19	3.50	3.11
Yosemite	3.42	.	.	.	.	5.12	.	3.50	.	.

Table 4. Annual sulfate deposition (kg ha^{-1} yr^{-1}) by site and CARB sample year. Only years in which CI1 and CI3 were at least 75 percent are shown. CADMP and UCSB sites are capitalized. Missing values are shown with periods.

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
ALPINE MDWS	.	.	.	.	.	.	1.26	1.80	2.34	.
ANAHEIM	.	2.07	1.42	2.56	1.84	1.49	1.31	2.22	3.15	0.92
ANGORA LK	.	.	.	.	.	.	1.71	1.23	4.42	.
BAKERSFIELD	1.64	1.86	1.76	2.72	2.24	1.33	1.42	1.19	1.81	1.26
BERKELEY	2.65	4.06	2.06	2.48	.	2.93	2.32	3.04	4.59	.
BETHEL ISL	1.06	1.62	0.98	1.13	1.24	1.31	0.77	1.04	2.30	0.91
Chuchupate Range	2.57	.	1.28	1.36	0.86	0.43	.	.	1.06	.
Davis	2.06	.	1.06	1.54	.	1.88	1.53	1.87	3.24	1.00
EASTRN BRK LK	.	.	.	.	.	.	0.77	1.02	1.44	.
EL MONTE	3.09	4.21	2.39	3.56	2.42	2.84	2.50	3.36	6.34	2.10
EMERALD LK	.	.	.	.	.	.	1.34	1.63	3.74	.
ESCONDIDO	3.06	2.00	2.39	2.57	1.72	2.02	2.57	2.43	2.36	2.09
EUREKA	5.80	5.47	3.56	4.90	.	.	.	.	.	.
GASQUET	8.06	7.26	6.42	4.71	7.67	6.07	.	4.16	10.24	3.82
Hopland	2.41	2.78	1.78	1.63	1.47	1.42	1.76	1.44	2.56	0.96
Hopland Intercom	.	.	.	.	.	.	.	1.55	.	.
KAISER PASS	.	.	.	.	.	.	.	0.98	2.56	.
LAKE ISABELLA	.	0.80	1.36	0.56	1.21	0.53	0.56	.	0.71	.
LAKEPORT	1.39	2.28	1.87	1.22	.	.	.	.	.	.
LINDCOVE	.	1.88	1.12	1.80	.	.	.	.	.	.
LOS ANGELES	.	.	.	.	.	.	1.89	5.32	6.85	2.06
LYNWOOD	3.60	4.90	2.88	3.21	2.74	2.72	1.52	3.59	5.47	2.12
MAMMOTH MTN	.	.	2.04	.	.	.	.	.	.	.
MINERAL KING	.	.	.	.	.	.	1.88	1.39	1.78	.
MMMTH MT/UC	.	.	.	.	.	.	1.45	1.94	3.38	.
MONTAGUE	.	0.80	0.59	0.54	0.84	0.74	1.11	0.80	1.04	0.55
MONTAGUE CO	.	.	.	.	.	.	1.12	0.80	1.06	0.67
MT WILSON	2.78	2.50	1.74	3.84	2.23	2.49	1.46	2.31	3.85	1.68
Montague	.	0.85	0.54	0.71	0.63	0.65	0.93	0.77	0.93	0.59
NAPA	.	4.70	2.28	3.36	3.62	3.19	3.60	3.14	5.46	2.60
NIPOMO	1.93	1.80	1.82	1.28	.	.	.	.	.	.
ONION VLLY	.	.	.	.	.	.	1.42	1.46	1.26	.
Organ Pipe Cactu	4.03	1.36	1.47	.	1.46	0.96	2.57	1.90	2.24	0.74

Table 4, continued

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
PASADENA	3.29	4.43	2.68	3.97	3.27	3.23	3.02	4.94	6.43	2.40
Palomar Mt	11.92	3.19	2.72	.	.	.	.	.	.	.
QUINCY	.	2.36	1.49	.	.	2.10	1.52	1.62	2.70	1.34
RESEDA	2.44	3.26	1.41	3.17	2.24	1.27	.	.	.	.
Red Rock Canyon	.	.	1.82	0.97	0.81	.	1.62	2.53	.	0.61
SACRAMENTO	1.97	3.19	1.39	1.81	2.47	2.42	1.23	2.74	3.23	1.30
SACRAMENTO C	.	.	.	.	.	.	1.18	2.20	3.16	1.26
SALINAS	1.56	1.67	1.07	1.15	.	.	.	.	.	.
SAN BERNARD	1.89	2.14	0.97	2.63	2.11	2.65	1.43	3.76	4.53	2.37
SAN JOSE	1.70	2.78	1.30	1.48	1.26	1.13	1.32	1.89	2.56	1.00
SAN NICOLAS	1.06	1.72	0.84	4.22	.	.	.	.	.	.
SAN RAFAEL	5.03	.	3.22	6.74	.	.	.	.	.	.
SANTA BARB	2.21	2.95	1.11	2.26	1.61	1.03	1.27	3.20	3.51	1.89
SEQUOIA ASH	2.30	2.70	2.02	2.13	1.76	2.59	1.63	1.05	2.27	1.46
SEQUOIA GF	.	3.27	2.17	2.39	1.82	2.70	2.19	1.16	3.45	2.06
SEQUOIA GF C	.	.	.	.	.	.	2.09	1.10	.	.
SOUTH LK	.	.	.	.	.	.	1.08	0.78	2.00	.
SODA SPRINGS	.	2.42	2.42	1.57	3.93	3.43	2.66	1.98	4.21	2.12
SO LAKE TAHOE	0.86	1.33	1.30	0.64	1.32	1.60	0.83	1.02	1.15	0.70
SONORA PS	.	.	.	.	.	.	1.71	1.46	1.73	.
Sequoia Nat'l Pa	.	3.02	.	.	.	2.47	2.33	1.48	4.13	1.98
Silver Lake Rang	.	0.79	0.58	0.77	.	0.42	.	0.57	1.20	0.71
Smith Valley	.	0.31	0.98	0.52	0.92	0.36	0.70	.	0.38	.
TANBARK	3.42	3.58	1.58	3.33	3.36	2.92	2.63	3.55	2.29	1.75
TANBARK COL	.	.	.	.	.	.	1.82	3.45	2.58	1.73
TIOGA PS	.	.	.	.	.	.	1.66	1.49	3.23	.
Tanbark Flat	4.06	3.78	1.63	3.82	3.07	.	2.66	4.02	4.90	2.23
VICTORVILLE	1.00	0.58	2.13	0.60	.	.	.	.	.	.
YOSEMITE	2.70	.	2.95	1.54	1.26	.	1.22	1.62	2.03	1.15
Yosemite Nationa	2.86	.	.	.	.	2.73	.	1.81	.	.

Table 5. Annual excess sulfate deposition (kg ha^{-1} yr^{-1}) by site and CARB sample year. Only years in which CI1 and CI3 were at least 75 percent are shown. CADMP and UCSB sites are capitalized. Missing values are shown with periods.

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
ALPINE MDWS	.	.	.	.	.	.	1.16	1.66	2.21	.
ANAHEIM	.	1.59	1.22	2.12	1.54	1.23	0.78	1.59	2.37	0.71
ANGORA LK	.	.	.	.	.	.	1.60	1.12	4.09	.
BAKERSFIELD	1.57	1.75	1.67	2.65	2.12	1.27	1.34	1.15	1.68	1.19
BERKELEY	1.95	2.29	1.60	1.97	.	2.21	1.70	2.16	3.16	.
BETHEL ISL	0.93	1.23	0.85	1.01	1.14	1.24	0.70	0.89	2.06	0.78
Chuchupate Range	2.46	.	1.23	1.29	0.79	0.39	.	.	0.90	.
Davis	1.91	.	0.96	1.41	.	1.75	1.33	1.59	2.75	0.89
EASTRN BRK LK	.	.	.	.	.	.	0.75	0.99	1.40	.
EL MONTE	2.69	3.56	2.21	3.00	2.25	2.56	2.04	2.84	5.31	1.84
EMERALD LK	.	.	.	.	.	.	1.24	1.57	3.49	.
ESCONDIDO	2.03	1.20	1.43	1.69	1.28	1.57	1.17	1.80	1.61	1.34
EUREKA	2.43	2.18	1.37	2.14	.	.	.	.	.	.
GASQUET	3.22	3.06	2.54	1.78	3.25	3.61	.	2.06	4.39	1.52
Hopland	1.93	1.30	1.26	1.22	1.10	1.11	1.31	0.84	1.64	0.68
Hopland Intercom	.	.	.	.	.	.	.	0.90	.	.
KAISER PASS	.	.	.	.	.	.	.	0.92	2.45	.
LAKE ISABELLA	.	0.70	1.29	0.54	1.15	0.48	0.45	.	0.64	.
LAKEPORT	1.13	1.25	1.44	0.98	.	.	.	.	.	.
LINDCOVE	.	1.65	1.01	1.75	.	.	.	.	.	.
LOS ANGELES	.	.	.	.	.	.	1.41	4.57	5.74	1.85
LYNWOOD	3.07	4.08	2.62	2.72	2.49	2.42	1.07	2.91	4.43	1.81
MAMMOTH MTN	.	.	1.96	.	.	.	.	.	.	.
MINERAL KING	.	.	.	.	.	.	1.79	1.34	1.70	.
MMMTH MT/UC	.	.	.	.	.	.	1.37	1.85	3.22	.
MONTAGUE	.	0.75	0.56	0.51	0.81	0.71	1.07	0.77	0.99	0.52
MONTAGUE C	.	.	.	.	.	.	1.09	0.77	1.01	0.64
MT WILSON	2.39	2.11	1.60	3.36	2.07	2.26	1.20	2.05	3.37	1.44
Montague	.	0.81	0.49	0.67	0.59	0.62	0.88	0.73	0.88	0.56
NAPA	.	3.14	1.88	2.82	3.10	2.64	2.84	2.56	4.11	2.09
NIPOMO	1.21	1.01	1.37	0.82	.	.	.	.	.	.
ONION VLLY	.	.	.	.	.	.	1.36	1.41	1.21	.
Organ Pipe Cactu	3.81	1.16	1.27	.	1.39	0.81	2.28	1.70	2.06	0.56

Table 5, continued

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
PASADENA	2.76	3.82	2.47	3.44	3.03	2.87	2.40	4.08	5.38	2.09
Palomar Mountain	9.56	2.27	1.84	.	.	.	.	.	.	.
QUINCY	.	1.92	1.35	.	.	1.99	1.42	1.51	2.47	1.28
RESEDA	2.12	2.88	1.32	2.79	1.94	1.05	.	.	.	.
Red Rock Canyon	.	.	1.76	0.93	0.77	.	1.55	2.47	.	0.58
SACRAMENTO	1.74	2.67	1.22	1.71	2.29	2.28	1.15	2.52	2.88	1.17
SACRAMENTO C	.	.	.	.	.	.	1.11	2.00	2.79	1.13
SALINAS	0.96	0.89	0.69	0.86	.	.	.	.	.	.
SAN BERNARD	1.68	1.82	0.91	2.36	2.02	2.37	1.15	3.52	2.39	2.08
SAN JOSE	1.27	1.79	1.00	1.21	0.92	0.94	1.05	1.36	1.88	0.65
SAN NICOLAS	0.45	0.79	0.27	0.85	.	.	.	.	.	.
SAN RAFAEL	3.51	.	2.24	5.22	.	.	.	.	.	.
SANTA BARB	1.59	1.89	0.93	1.40	1.21	0.65	0.81	1.68	2.00	1.20
SEQUOIA ASH	1.80	2.37	1.90	2.03	1.63	2.45	1.50	0.94	2.08	1.34
SEQUOIA GF	.	2.80	2.09	2.28	1.74	2.56	2.06	1.07	3.29	1.91
SEQUOIA GF C	.	.	.	.	.	.	1.91	1.00	.	.
SOUTH LK	.	.	.	.	.	.	1.04	0.75	1.94	.
SODA SPRINGS	.	1.93	2.20	1.39	3.65	3.27	2.46	1.84	3.77	2.01
SO LAKE TAHOE	0.79	1.20	1.21	0.59	1.15	1.50	0.76	0.95	1.09	0.67
SONORA PS	.	.	.	.	.	.	1.59	1.42	1.66	.
Sequoia Nat'l Pa	.	2.81	.	.	.	2.32	2.13	1.36	3.89	1.82
Silver Lake Rang	.	0.72	0.52	0.70	.	0.39	.	0.54	1.11	0.68
Smith Valley	.	0.30	0.93	0.49	0.86	0.34	0.66	.	0.36	.
TANBARK	2.96	2.90	1.37	2.86	3.14	2.52	2.10	3.00	1.83	1.47
TANBARK COL	.	.	.	.	.	.	1.39	2.92	2.11	1.44
TIOGA PS	.	.	.	.	.	.	1.52	1.43	3.09	.
Tanbark Flat	3.74	3.10	1.46	3.34	2.86	.	2.07	3.43	3.80	1.83
VICTORVILLE	0.91	0.54	2.08	0.56	.	.	.	.	.	.
YOSEMITE	2.42	.	2.79	1.43	1.19	.	1.11	1.54	1.91	1.09
Yosemite Nationa	2.68	.	.	.	.	2.61	.	1.65	.	.

Table 6. Annual ammonium deposition (kg ha^{-1} yr^{-1}) by site and CARB sample year. Only years in which CI1 and CI3 were at least 75 percent are shown. CADMP and UCSB sites are capitalized. Missing values are shown with periods.

	CARB Water Year									
Site	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
ALPINE MDWS	.	.	.	.	.	.	0.73	0.91	1.09	.
ANAHEIM	.	1.02	0.73	1.12	0.86	0.53	0.46	0.96	1.41	0.56
ANGORA LK	.	.	.	.	.	.	0.94	0.67	2.09	.
BAKERSFIELD	0.75	1.03	1.15	1.66	1.17	0.83	1.02	1.35	1.53	1.02
BERKELEY	0.44	0.79	0.53	0.84	.	0.38	0.49	0.90	0.94	.
BETHEL ISL	1.04	1.50	1.10	1.41	0.99	0.85	0.70	1.49	2.22	1.28
Chuchupate Range	0.68	.	0.45	0.32	0.27	0.17	.	.	0.19	.
Davis	1.67	.	1.05	1.52	.	2.01	1.52	2.37	3.42	1.34
EASTRN BRK LK	.	.	.	.	.	.	0.41	0.58	0.52	.
EL MONTE	1.09	1.49	1.11	1.83	1.33	1.18	1.22	2.29	3.21	0.90
EMERALD LK	.	.	.	.	.	.	0.79	1.45	1.36	.
ESCONDIDO	0.62	0.46	0.82	0.84	0.62	0.57	0.55	0.85	0.68	0.58
EUREKA	0.35	0.45	0.57	0.45	.	.	.	.	.	.
GASQUET	0.58	1.07	0.96	0.96	0.65	0.39	.	0.20	0.28	0.13
Hopland	0.42	0.23	0.33	0.53	0.19	0.60	0.52	0.28	0.61	0.44
Hopland Intercom	.	.	.	.	.	.	.	0.35	.	.
KAISER PASS	.	.	.	.	.	.	.	0.79	0.89	.
LAKE ISABELLA	.	0.41	0.70	0.28	0.49	0.15	0.17	.	0.15	.
LAKEPORT	0.49	1.25	1.04	1.03	.	.	.	.	.	.
LINDCOVE	.	1.89	1.53	2.45	.	.	.	.	.	.
LOS ANGELES	.	.	.	.	.	.	0.77	2.87	2.78	1.04
LYNWOOD	0.98	1.35	0.91	1.17	0.96	0.75	0.38	1.50	1.75	0.78
MAMMOTH MTN	.	.	0.89	.	.	.	.	.	.	.
MINERAL KING	.	.	.	.	.	.	1.69	0.99	0.86	.
MMMTH MT/UC	.	.	.	.	.	.	0.93	0.89	1.37	.
MONTAGUE	.	0.55	0.36	0.36	0.44	0.27	0.63	0.39	0.66	0.39
MONTAGUE C	.	.	.	.	.	.	0.64	0.38	0.69	0.49
MT WILSON	1.06	0.59	0.69	1.53	0.76	0.76	0.41	1.05	1.22	0.73
Montague	.	0.23	0.28	0.26	0.32	0.33	0.60	0.33	0.53	0.29
NAPA	.	1.22	0.74	1.19	1.08	0.80	1.07	1.30	1.57	1.03
NIPOMO	0.40	0.49	0.65	0.47	.	.	.	.	.	.
ONION VLLY	.	.	.	.	.	.	0.91	0.57	0.64	.
Organ Pipe Cactu	0.69	0.26	0.22	.	0.38	0.29	1.18	0.37	0.62	0.25

Table 6, continued

Site	CARB Water Year									
	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
PASADENA	1.37	1.28	1.24	1.89	1.22	1.10	1.10	2.41	2.34	1.27
Palomar Mountain	2.68	0.44	0.30	.	.	.	.	.	.	.
QUINCY	.	1.04	0.54	.	.	0.35	0.57	0.70	0.89	0.79
RESEDA	0.81	1.11	0.91	1.33	0.94	0.41	.	.	.	.
Red Rock Canyon	.	.	0.54	0.23	0.33	.	0.73	0.73	.	0.28
SACRAMENTO	1.71	3.26	1.37	2.06	2.24	2.18	1.38	3.24	3.83	1.92
SACRAMENTO C	.	.	.	.	.	.	1.36	2.67	3.87	1.88
SALINAS	0.59	0.76	0.55	0.69	.	.	.	.	.	.
SAN BERNARD	1.71	2.12	0.94	2.64	2.11	2.57	1.54	5.06	4.08	2.62
SAN JOSE	0.48	0.92	0.62	0.81	0.53	0.49	0.51	1.14	1.38	0.74
SAN NICOLAS	0.15	0.17	0.16	0.18	.	.	.	.	.	.
SAN RAFAEL	0.89	.	0.93	2.33	.	.	.	.	.	.
SANTA BARB	0.32	0.61	0.42	0.68	0.48	0.12	0.46	0.52	0.50	0.31
SEQUOIA ASH	1.60	2.20	2.10	2.37	1.43	2.65	2.13	1.19	2.53	2.14
SEQUOIA GF	.	2.05	2.43	2.11	1.00	1.96	2.57	1.09	3.11	2.48
SEQUOIA GF C	.	.	.	.	.	.	2.82	1.09	.	.
SOUTH LK	.	.	.	.	.	.	0.50	0.37	0.70	.
SODA SPRINGS	.	1.26	1.01	1.07	1.08	0.83	0.85	0.69	1.49	1.05
SO LAKE TAHOE	0.23	0.63	0.52	0.30	0.51	0.55	0.32	0.45	0.42	0.37
SONORA PS	.	.	.	.	.	.	0.73	0.66	0.62	.
Sequoia Nat'l Pa	.	1.54	.	.	.	2.04	2.09	1.36	3.50	2.35
Silver Lake Rang	.	0.18	0.15	0.08	.	0.18	.	0.25	0.33	0.19
Smith Valley	.	0.10	0.51	0.19	0.53	0.33	0.59	.	0.25	.
TANBARK	1.69	1.01	0.67	2.00	1.34	1.15	1.09	1.86	0.97	0.87
TANBARK C	.	.	.	.	.	.	0.68	1.88	1.02	0.81
TIOGA PS	.	.	.	.	.	.	0.88	0.77	1.31	.
Tanbark Flat	1.51	0.37	0.43	1.73	0.82	.	0.90	1.90	1.14	1.07
VICTORVILLE	0.75	0.32	0.94	0.56	.	.	.	.	.	.
YOSEMITE	1.53	.	1.69	1.11	0.72	.	0.79	1.01	1.00	1.01
Yosemite Nationa	0.80	.	.	.	.	1.61	.	0.77	.	.

Table 7. Multi-year mean annual wet deposition of nitrate, sulfate (not adjusted for sea salt), excess sulfate (adjusted for sea salt), and ammonium by site (kg ha^{-1} yr^{-1}). Years were included if CI1 and CI3 were at least 75 percent. CADMP and UCSB sites are capitalized. Missing values are shown with periods.

			Species			
Site	Network	No. yrs.	SO_4^{-2}	Excess SO_4^{-2}	NO_3^-	NH_4^+
ALPINE MDWS	UCSB	3	1.80	1.68	3.37	0.91
ANAHEIM	CADMP	9	1.89	1.46	1.89	0.85
ANGORA LK	UCSB	3	2.45	2.27	3.73	1.23
BAKERSFIELD	CADMP	10	1.72	1.64	1.82	1.15
BERKELEY	CADMP	8	3.02	2.13	2.50	0.67
BETHEL ISL	CADMP	10	1.24	1.08	1.87	1.26
Bishop	NADP	1	1.05	1.01	0.72	0.27
Chuchupate Ranger Station	NADP	7	1.22	1.14	1.78	0.31
Davis	NADP	10	2.17	1.92	3.29	2.05
EASTRN BRK LK	UCSB	3	1.08	1.05	1.79	0.50
EL MONTE	CADMP	10	3.28	2.83	3.69	1.57
EMERALD LK	UCSB	3	2.24	2.10	3.34	1.20
ESCONDIDO	CADMP	10	2.32	1.51	2.05	0.66
EUREKA	CADMP	4	4.93	2.03	1.31	0.46
GASQUET	CADMP	9	6.49	2.82	2.19	0.58
Hopland	NADP	14	2.37	1.64	2.15	0.48
Hopland Intercomparison	NADP	1	1.55	0.90	1.80	0.35
KAISER PASS	UCSB	2	1.77	1.68	2.55	0.84
LAKE ISABELLA	CADMP	7	0.82	0.75	1.36	0.34
LAKEPORT	CADMP	4	1.69	1.20	2.16	0.95
LINDCOVE	CADMP	3	1.60	1.47	3.89	1.96
LOS ANGELES	CADMP	4	4.03	3.39	3.36	1.86
LYNWOOD	CADMP	10	3.28	2.76	2.40	1.05
MAMMOTH MTN	CADMP	1	2.04	1.96	2.81	0.89
MINERAL KING	UCSB	3	1.68	1.61	3.26	1.18
MMMTH MT/UC	UCSB	3	2.26	2.15	3.30	1.06
MONTAGUE	CADMP	9	0.78	0.74	1.36	0.45
MONTAGUE COL	CADMP	4	0.91	0.88	1.55	0.55
MT WILSON	CADMP	10	2.49	2.19	3.90	0.88
Montague	NADP	9	0.73	0.69	1.25	0.35
NAPA	CADMP	9	3.55	2.80	3.26	1.11
NIPOMO	CADMP	4	1.71	1.10	1.37	0.50

Table 7, continued

Site	Network	No. yrs.	Species			
			SO_4^{-2}	Excess SO_4^{-2}	NO_3^-	NH_4^+
ONION VLLY	UCSB	3	1.38	1.33	2.36	0.71
Organ Pipe Cactus Nat'l Mon.	NADP	13	2.12	1.91	1.78	0.47
PASADENA	CADMP	10	3.77	3.23	5.08	1.52
Palomar Mountain	NADP	4	5.42	4.28	5.14	1.01
QUINCY	CADMP	7	1.88	1.71	2.94	0.70
RESEDA	CADMP	6	2.30	2.02	3.55	0.92
Re Rock Canyon	NADP	6	1.39	1.34	2.49	0.47
SACRAMENTO	CADMP	10	2.18	1.96	3.49	2.32
SACRAMENTO COL	CADMP	4	1.95	1.76	3.12	2.45
SALINAS	CADMP	4	1.36	0.85	1.18	0.65
SAN BERNARDINO	CADMP	10	2.45	2.03	4.54	2.54
SAN JOSE	CADMP	10	1.64	1.20	1.31	0.76
SAN NICOLAS	CADMP	4	1.96	0.59	0.77	0.16
SAN RAFAEL	CADMP	3	5.00	3.65	3.87	1.38
SANTA BARBARA	CADMP	10	2.11	1.33	2.54	0.44
SEQUOIA ASH MTN	CADMP	10	1.99	1.80	4.94	2.03
SEQUOIA GF	CADMP	9	2.36	2.20	5.06	2.09
SEQUOIA GF COL	CADMP	2	1.59	1.46	4.57	1.95
SOUTH LK	UCSB	3	1.28	1.25	2.07	0.52
SODA SPRINGS	CADMP	9	2.75	2.50	4.49	1.04
SOUTH LAKE TAHOE	CADMP	10	1.07	0.99	1.74	0.43
SONORA PS	UCSB	3	1.64	1.56	2.35	0.67
Sequoia Nat'l Park-Giant Forest	NADP	10	3.35	3.15	4.91	1.82
Silver Lake Ranger Station	NADP	7	0.72	0.67	1.06	0.19
Smith Valley	NADP	7	0.59	0.56	0.96	0.36
TANBARK	CADMP	10	2.84	2.42	5.24	1.27
TANBARK COL	CADMP	4	2.39	1.97	4.07	1.10
TIOGA PS	UCSB	3	2.12	2.02	3.30	0.99
Tanbark Flat	NADP	11	3.74	3.22	5.74	1.17
VICTORVILLE	CADMP	4	1.08	1.02	2.17	0.65
YOSEMITE	CADMP	8	1.81	1.68	3.68	1.11
Yosemite National Park	NADP	5	3.42	3.17	4.63	1.24

PART II: DRY DEPOSITION

INTRODUCTION

Objectives

The specific objectives of this part of the project are to

1. Evaluate the quality of the CADMP dry-deposition data;
2. Compute estimates of the dry deposition of each species of interest at each monitoring site having sufficient data;

Overview of Part II

We first summarize the methods used. We describe the approach for calculating deposition fluxes (the inferential method) in some detail. We then briefly describe the data that are available and discuss the quality of these data. We discuss the structure of the program that is used for calculating deposition. Following the description of the methods, we present sensitivity analyses and summary results.

METHODS

Use of the Inferential Method

Description. The CADMP dry-deposition network was designed with the intent of implementing the inferential method. In this approach, the flux of a particular species is calculated as the product of its ambient concentration and its deposition velocity, V_d (Hicks et al., 1987). Deposition velocity generally depends on both the nature of the pollutant and the surface. The inferential method is strictly applicable to cases in which the flux is unidirectionally toward the surface, i.e., no surface source exists. This assumption might prove questionable for ammonia gas at some sites (e.g., in rural locations) or NO_x at some urban locations.

At the CADMP monitors, deposition of a particular species *i* to surface *j* during a specified time interval (e.g., one hour) is computed as

$$F_{ij} = C_i \, V_{d_{ij}} \quad , \tag{4}$$

where C is concentration and V_d is deposition velocity. (Actually, we have 12-hour concentration averages and 1-hour averages of the meteorological parameters from which V_d is calculated).

The flux of pollutant *i* over an area that includes several different types of plants or surfaces is

$$F_i = \sum_j C_i V_{ij} A_j \quad , \qquad (5)$$

where A_j is the portion of the area covered by surface type *j*. The fact that most surface types have a true surface area larger than the horizontal plane they cover is included in V_d by the use of adjustment factors such as leaf area index (LAI). The LAI is the ratio of the area of one side of all the leaves to the area of the ground underneath the plant.

Deposition velocity for gases is calculated as the inverse of total resistance to deposition, $V_d = 1/R_T$, where R_T is calculated as a combination of resistances to dry deposition:

$$V_d = \frac{1}{R_a + R_b + R_t} \quad , \qquad (6)$$

where R_a = aerodynamic resistance (determined by turbulent exchange), R_b = quasi-laminar boundary resistance (determined by molecular diffusivity of the pollutant and the thickness of the quasi-laminar boundary layer in contact with receptor surfaces), and R_t = transfer, or canopy resistance (determined by the uptake processes of a given surface for the species in question).

Aerodynamic resistance, R_a, is species-independent and reflects turbulent transport through the atmospheric surface layer. Quasi-laminar boundary layer resistance, R_b, is both species- and turbulence-dependent and reflects the importance of molecular diffusivity within about a millimeter (mm) or less of the surface. Transfer resistance, R_t, depends on both the species and the surface and reflects adsorption and uptake mechanisms of all types.

In calculating deposition velocity for large particles, settling velocity becomes important and requires the inclusion of another term in addition to the inverse resistance.

The terms R_a and R_b can be determined as described by Hicks et al. (1987) and Meyers and Yuen (1987) from the meteorological measurements taken at each of the CADMP sites (Watson et al., 1991). In brief, the resistance R_a can be approximated from field measurements as

$$R_a \approx \frac{4}{u\,\sigma_\theta^2} \quad \textit{(neutral and stable conditions)} \quad ,$$
$$R_a \approx \frac{9}{u\,\sigma_\theta^2} \quad \textit{(unstable conditions)} \quad , \tag{7}$$

where u = mean wind speed and σ_Θ = standard deviation of horizontal wind direction. The standard deviation of the horizontal wind direction contains information related to both stability and surface roughness. If net radiation is positive and σ_Θ exceeds some critical value, conditions are unstable. Although the critical value is site-specific, it is presently assumed by the EPA to be $\sigma_\Theta = 10^\circ$ (Hicks et al., 1987).

R_b is obtained from (Hicks et al., 1987):

$$R_b = \frac{2}{k\,u_*}\left(\frac{Sc}{Pr}\right)^{2/3} \quad , \tag{8}$$

where k = von Karman's constant (0.4), u_* = friction velocity, Sc = Schmidt number (for gases or particles), and Pr = Prandtl number for air (≈ 0.72). Once R_a has been determined, it is possible to determine R_b because u_* can be determined from the approximation (Hicks et al., 1987):

$$R_a \approx u\,u_*^{-2} \quad , \tag{9}$$

In the computer programs developed by Oak Ridge Laboratory for carrying out the calculations of deposition, the ratio of the Schmidt to Prandtl numbers is approximated by the ratio of the molecular diffusivity of water in air to that of the gaseous pollutant in air. Thus R_b is calculated as

$$R_b = \frac{2}{ku_*}\left(\frac{D_{H2O}}{D_{pollutant}}\right)^{2/3} \quad . \tag{10}$$

In the current version of the program from Oak Ridge, which has a 21-layer canopy, a separate R_b is calculated for each layer, on the basis of the work of Cionco (1972, 1978) and of Shaw and Pereira (1982). The resistance at the top of the canopy is slightly greater than that calculated by the preceding equation. This outcome is expected because areas within the canopy are more protected than is the top and because one factor damping canopy turbulence is the flexibility of leaves.

R_t is specific to particular species-surface combinations. For some reactive species, such as nitric acid, R_t can be assumed to be zero (Hicks et al., 1987). For other species, R_t

is nonzero. In general, R_t consists of parallel resistance terms for water, soil, leaf, and other surfaces. The leaf surface resistance, in turn, consists of resistances for stomata, cuticle, and mesophyll.

Limitations. The method described here represents a model of deposition processes. As is the case with any model, it is important to recognize key limitations. For example, the surface resistance terms are highly simplified parameterizations of complex physical processes. Moreover, for NH_3, which can be emitted from the surface, and possibly for NO_2, which can be produced from NO below the height of the monitoring instruments, the assumption of strictly downward transfer is not always correct (Hicks et al., 1991). Few comparisons of the results from the inferential method to micrometeorological estimates of deposition are available. Uncertainties in the deposition velocities of SO_2 and ozone (O_3) calculated by the inferential method at sites located away from major emission sources, having uniform vegetation, and located in uncomplicated terrain, are thought to be about 30 percent (McMillen, 1990; Hicks et al., 1991; Clarke et al., 1992). Uncertainties for HNO_3 and particulate nitrate or sulfate are thought to be in the range of 30 to 50 percent (McMillen, 1990; Clarke et al., 1992).

Data Availability

The CADMP dry-deposition network consists of 10 sites (see Figure 21); a collocated sampler was situated at the Sacramento site until July 1993, when it was moved to Azusa. Two measurements are made every sixth day: one from 6:00 a.m. to 6:00 p.m. and one from 6:00 p.m. to 6:00 a.m. Sampling methods, species monitored, and initial results are described in Watson et al. (1991).

Briefly, the CADMP dry-deposition data base includes gases (sulfur dioxide, nitrogen dioxide, ammonia, ozone, and nitric acid) and total mass for particles (PM) in the PM2.5 and PM10 size ranges. The particle mass has been further analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, potassium and calcium.

Previously, we were provided with data from the program's inception (early 1988) through September 1991. This report uses CADMP data from October 1991 through April 1994.

In addition to the CADMP data, CARB aerometric data are available for a limited number of species at more monitoring sites. These measurements consist of O_3, NO_2, SO_2, PM10-nitrate, PM10-sulfate, PM10-ammonium, and PM10-chloride (HNO_3 is not measured at CARB aerometric sites). The CARB's routine PM10 samples are collected every sixth day (on the same schedule as the CADMP samples); however, samples are collected as 24-hour averages (from midnight to midnight). We obtained hourly NO_2 and SO_2 data, PM10 data (speciated), and 12-hour O_3 data from all monitors in California from 1989 through 1994.

Figure 21. Locations of CADMP dry-deposition monitoring sites.

Data Quality

Evaluation of the quality of the earlier data base is described in Blanchard and Michaels (1994). Here, we summarize some of the earlier findings and describe new analyses.

Comparison of CADMP data to other data bases. In the March 1994 report, we made a considerable number of comparisons of CADMP to other data: (1) collocated routine PM10 measurements, (2) O_3 measurements (for correlation with HNO_3), and (3) the 1986 CalTech study (Solomon et al., 1988). Six CADMP sites are collocated with a routine PM10 monitor: Azusa, Bakersfield, Fremont, Los Angeles, Long Beach, and Sacramento. The CADMP and routine samples are not simultaneous (they overlap for 18 of 24 hours). We therefore did not expect exact agreement. Most comparisons showed a good level of agreement, though. There is no evidence of a bias in the CADMP sampler's particulate measurements relative to those of the routine samplers.

Potential biases in nitric acid measurements. Unresolved questions still remain regarding the accuracy of the HNO_3 data (see Tuazon et al., 1995).

From our previous report, it is clear that the denuder-difference HNO_3 measurements at Azusa and Los Angeles are incorrect beginning as early as the spring of 1989, possibly as a result of diminution of denuder efficiency. Although the CADMP samplers were tested when prototypes were developed, after years of operation in the field, the samplers at Azusa and Los Angeles showed evidence of inaccuracies in the HNO_3 measurements.

To test the reproducibility of the HNO_3 measurements, the CARB first collocated a relatively new sampler at Azusa in July 1993 (the collocated sampler had been tested and operated at the Sacramento site for one year prior to its relocation). With the availability of the collocated measurements, it thus became possible to check the replicability of the Azusa measurements. Later, during October 1993, the CARB carried out a series of comparisons of the CADMP measurements to HNO_3 measurements made using a tunable diode laser absorption spectrophotometer (TDLAS) system (see Tuazon et al., 1995).

During the period July 30 through September 30 (11 sampling days), the daytime (6:00 a.m. to 6:00 p.m.) denuded particulate nitrate measurements from the CADMP primary sampler at Azusa exceeded those obtained from the secondary sampler by about 2 to 10 $\mu g\ m^{-3}$ (or 20 to 100 percent) (see Figure 22). The nighttime measurements, which ranged from about 2.5 to 5.5 $\mu g\ m^{-3}$, agreed to within 1 $\mu g\ m^{-3}$. Consequently, the daytime denuder difference HNO_3 measurements from the secondary sampler were up to about 10 $\mu g\ m^{-3}$ higher than those from the primary sampler (see Figure 23). In contrast, the filter-pack HNO_3 measurements, which were obtained from the sampler channels that were <u>not</u> downstream from the denuder, replicated well (see Figure 24). These results indicate that the denuder in the primary sampler, which had not been serviced in several years, was not removing nitric acid with 100 percent efficiency. Possible causes include deterioration of the denuder, leakage between the denuder and its filter, or artifacts associated with sample collection, shipment, or storage. Meteorological data for that time period were examined but no obvious relationships of sampler replicability to either ambient temperature or humidity were found.

To further check the nitric acid measurements, we carried out a series of linear regressions between the CADMP HNO_3 and collocated ozone measurements (see Table 8). As described in Tuazon et al. (1995), the secondary sampler exhibited a ratio (and regression slope) of HNO_3 to ozone of about 0.1 during the period July through September 1993, which is a value consistent with those found in several earlier studies (Tuazon et al., 1995). In contrast, the ratio and regression slope for the primary sampler were both less than 0.05, or roughly one-half the value occurring in earlier studies and for the secondary sampler. These comparisons with collocated ozone concentrations again indicate that the HNO_3 measurements from the primary CADMP sampler at Azusa were too low.

Table 8. Regression of daytime nitric acid concentrations against ozone concentrations at Azusa.

Site/ sampler	Measurement Period	Intercept	Slope	r^2	N	Mean (HNO_3/ O_3)
CADMP/ AZUSA/ Primary	7/1/93- 9/30/93 12-hr ave 6 am - 6 pm	0.257 (± 0.700)	0.0462 (± 0.0094)	0.686	13	0.0487
CADMP/ AZUSA/ Secondary	7/1/93- 9/30/93 12-hr ave 6 am - 6 pm	-0.117 (± 0.953)	0.100 (± 0.013)	0.877	10	0.0972

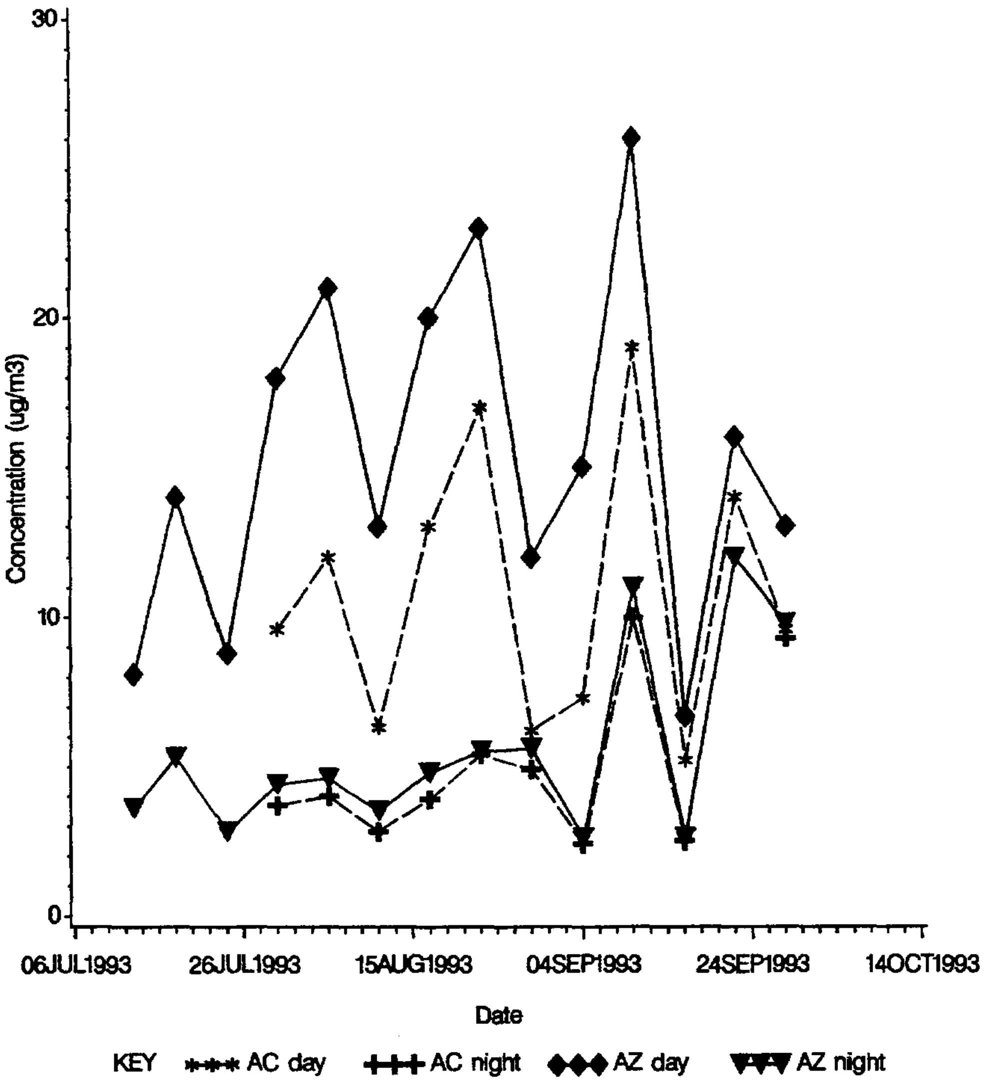

Figure 22. Denuded particulate nitrate versus date for CADMP Azusa primary (AZ) and collocated (AC) samplers.

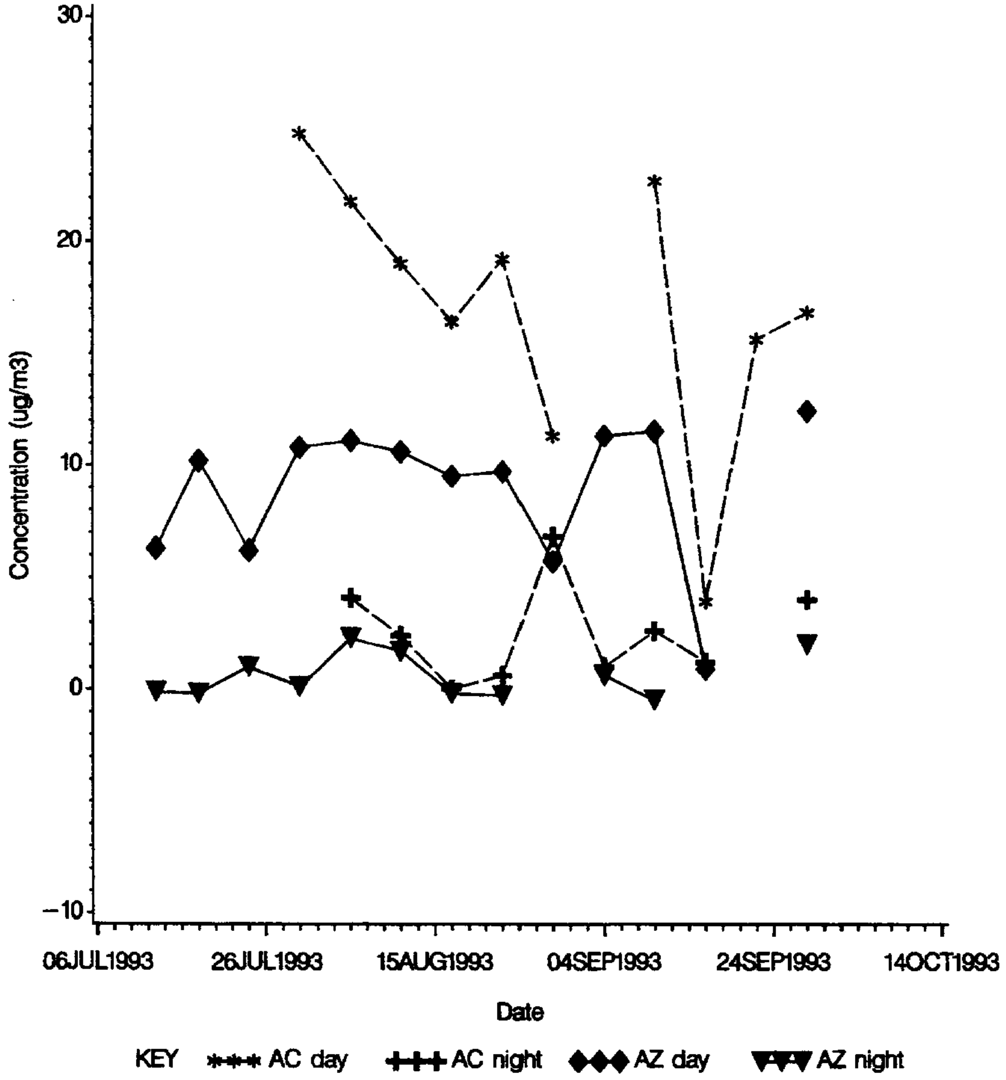

Figure 23. Denuder difference nitric acid versus date for CADMP Azusa primary (AZ) and collocated (AC) samplers.

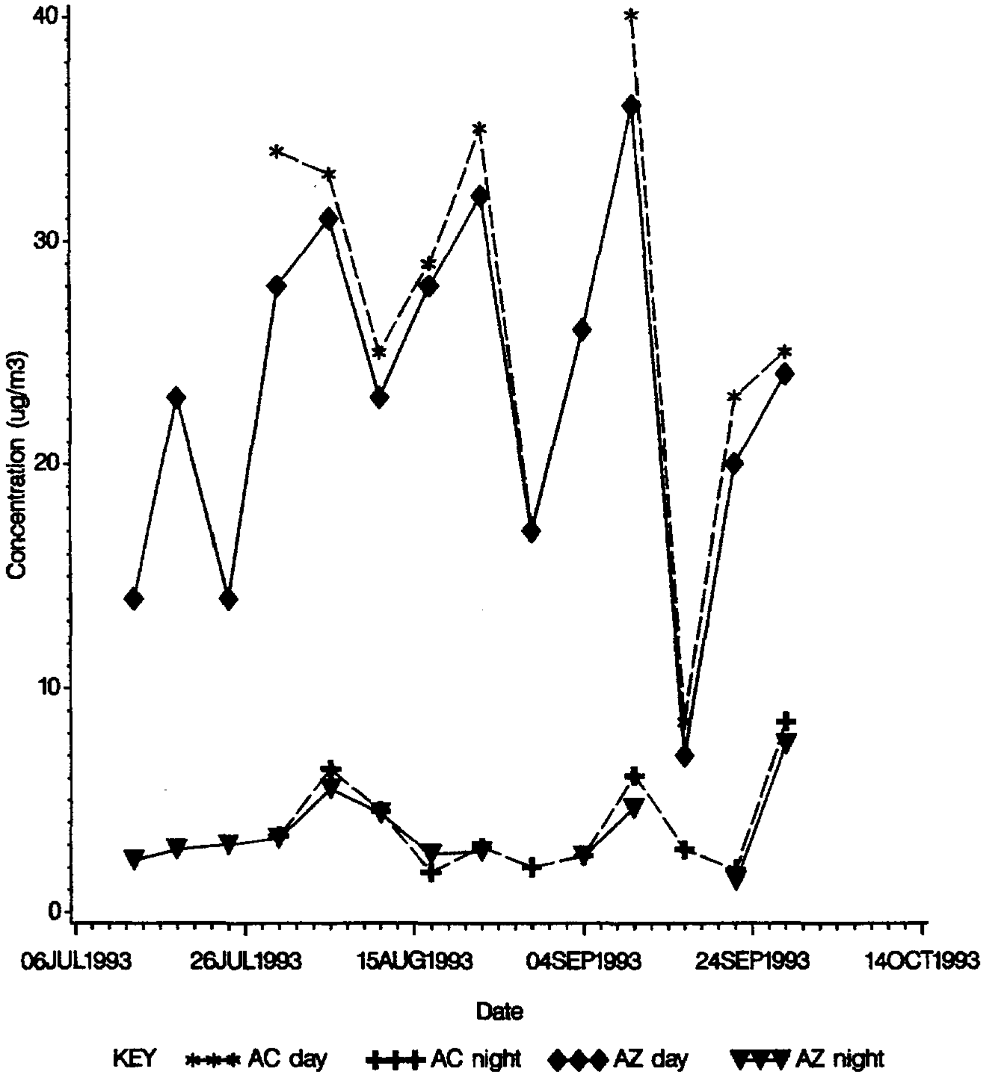

Figure 24. Filter-pack nitric acid versus date for CADMP Azusa primary (AZ) and collocated (AC) samplers.

Data validation procedure. After examining the data for systematic biases, as described above, we carried out a series of internal consistency checks:

1. Charge balance for PM2.5 species.

2. Charge balance for PM10 species.

3. Comparison of the sum of PM2.5 species concentrations to the PM2.5 mass.

4. Comparison of the sum of PM10 species concentrations to the PM10 mass.

5. Comparison of PM2.5 to PM10 mass.

6. Comparison of actual to nominal sample volumes.

In the previous report, we added four flags to the data base (one for each of the four filter packs). These flags take on values of "I" (invalid), "i" (some species invalid), "S" (suspect), "s" (some species suspect), "V" (valid), or "C" (charge balance failed). We used the flags initially in the data base and we incorporated the information from our consistency checks. For the earlier data, we:

1. Invalidated samples in which the following ratios exceeded $1+2*\sigma_R$, where σ_R represents the standard deviation of the ratios: (a) sum of PM2.5 species to PM2.5 mass, (b) sum of PM10 species to PM10 mass, and (c) PM2.5 mass to PM10 mass. (Note: σ_R is a function of the uncertainties associated with both the numerator and denominator of each ratio, which, in turn, are functions of the magnitudes of the concentrations). Failure to satisfy one or more of these ratio tests violates physical principles, so samples should be excluded. This criterion eliminated very few samples (generally because PM2.5 mass was greater than PM10 mass).

2. Invalidated measurements from any filter showing a deviation of sample volume in excess of 15 percent from nominal. This percentage represents a compromise between possible inaccuracy caused by incorrect sampling volume and loss of too much data. Failure to satisfy this criterion does not actually violate physical principles. At most sites, this rule eliminated about 5-7 percent of the total samples; some of these samples were void anyway and had no measurements. Thus, at most sites, about 2-3 percent of the actual data (i.e., samples having volumes greater than zero) were lost. This criterion eliminated all samples exhibiting grossly incorrect volumes. Application of this criterion to the earlier data base helped us identify a systematic error in the calculation of sample volumes (which has since been corrected).

3. Flagged as suspect all samples that failed charge balance for either the PM2.5 or

PM10 size fractions (i.e., if $|\Sigma(\text{Cations - Anions})| > 2^*\sigma_\Sigma$, where σ_Σ is the standard deviation of the sum). Failure to meet this criterion does not violate physical principles because some chemical species may not have been measured. Many samples failed to meet either (or both) the criteria for charge balance for PM2.5 and PM10. Violations involved excesses of both cations and anions in roughly equal numbers (except at Bakersfield, where most violations involved an excess of cations).

In contrast to the CADMP data from March 1988 through September 1991, the more recent data base does not include validation flags or estimated measurement uncertainties. Therefore, the validation procedure used here differs from the earlier one.

We determined mean measurement uncertainties using the earlier data base. The resulting values were:

- Σ(Cations - Anions)(PM2.5 and PM10): 0.04 $\mu g\ m^{-3}$
- ratio of ΣPM2.5 species to PM2.5 mass: 0.12
- ratio of ΣPM10 species to PM10 mass: 0.10
- ratio of PM2.5 mass to PM10 mass: 0.15

The flag values were:

- C $|\Sigma(\text{Cations - Anions})| > 2^*\sigma_\Sigma$, where σ_Σ is the standard deviation of the sum ($\sigma_\Sigma = 0.04\ \mu g\ m^{-3}$)
- F flow rate shows more than a 15 percent deviation from nominal
- I sample determined to be invalid after investigation
- M ratio of PM2.5 mass to PM10 mass exceeds $1+2^*\sigma_R$ ($\sigma_R = 0.15$)
- R ratio of ΣPM2.5 species to PM2.5 mass exceeds $1+2^*\sigma_R$ ($\sigma_R = 0.12$) or ratio of ΣPM10 species to PM10 mass exceeds $1+2^*\sigma_R$ ($\sigma_R = 0.10$)
- S indicates measurements that are suspect for other reasons
- V valid according to the preceding tests

Multiple flag values were assigned, if needed. Some flag values are not applicable to all four of the flag variables. The C value is applicable to FLG_TN and FLG_TCK, the F value is applicable to all four flags, the M value is assigned to both FLG_TN and FLG_TCK when the specified condition occurs, and the R value is applicable to FLG_TN and FLG_TCK. Conversely, it is possible for a sample to carry a flag value of, e.g., F for one flag variable and different values, e.g., V, for the other flag variables.

The validity of the different measurements may be evaluated by considering the different flag codes, as follows:

- DDNO3: validity indicated by FLG_DN and FLG_TN
- NO_2: validity indicated by FLG_GT
- PM10 mass, chemical concentrations, SO2, and NH3: validity indicated by

FLG_TCK

- PM2.5 mass, chemical concentrations, and FPNO3: validity indicated by FLG_TN

In summary, for both the earlier and more recent data, we invalidated only those measurements that were clearly incorrect on the basis of (1) comparisons with other data, (2) violation of criteria that must be met to satisfy physical principles (e.g., ratio of PM2.5 to PM10 mass), or (3) violation of sampling/analytical protocols. Measurements that were determined invalid or suspect were flagged without deleting them from the data base. If a filter pack carried more than one flag, the most serious was retained (e.g., if it earned an "S" for one reason and an "I" for another, the "I" was used).

In the updated data base, we flagged denuder difference nitrate and filter-pack nitrate measurements at Azusa from 10/91-9/93 as S (suspect) (due to suspected problems in the denuder channel; the sampler was cleaned 10/93). We also flagged denuder difference nitrate and filter-pack nitrate measurements at Los Angeles from 10/91-4/94 as S (suspect).

The Santa Barbara sampler volumes for all but the GT filter-pack deviated by more than 15 percent from nominal through the end of 1991 (these deviations also appeared in the earlier data base). Some recalibration appears to have occurred in January 1992, when the actual and nominal volumes came within ± 15 percent.

Selecting Samples for Flux Calculations

Samples were selected or excluded according to the following rules:

1. Samples with flags of V or C are usable.

2. Measurements related to flag variables that carry values of I, M, R, or S will not be used unless further investigation reveals that one or more of the affected measurements are valid.

Failure to satisfy one or more of the ratio tests (flags M or R) violates physical principles, so measurements should be excluded. Failure to satisfy the volume criterion does not actually violate physical principles; however, application of the criterion does eliminates all samples exhibiting grossly incorrect volumes. Failure to meet the charge balance criteria also does not violate physical principles because some chemical species may not have been measured. However, a C flag does suggest that one or more measurements could be inaccurate.

Substituting Alternative Measurements for Suspect Measurements

Because the CADMP sampler measures many species, it is possible to substitute some values for missing or invalid measurements. We used the variables listed in Table 9.

Table 9. List of alternative species used in flux calculations.

Species	Measured variable
HNO_3	denuder difference or filter-pack nitrate
particulate nitrate	denuded, PM2.5, or PM10 nitrate
particulate sulfate	PM2.5 or PM10 sulfate
particulate ammonium	PM2.5 or PM10 ammonium
SO_2	SO_2
NO_2	NO_2
NH_3	NH_3

Characterizing Sampling Completeness

Because the CADMP sampler collects samples once every six days, 60 to 61 samples per year would be collected each year by a sampler that operated every sampling day. Approximately 15 samples per quarter would be obtained. We initially attempted to require 75 percent sampling completeness (11 of 15 samples) per quarter, but found that many quarters of data would be designated incomplete by this criterion (the average number of valid samples per quarter generally ranged from about 8 to 12 for most sites and species). We therefore reduced the completeness requirement to 50 percent (8 of 15 samples), which generally yielded similar quarterly average flux rates and far fewer incomplete quarters. Table 10 lists the number of complete quarters obtained for each site and for eight chemical species; the table is based upon the 50 percent completeness requirement.

Samples falling below detection or quantification limits. Many measurements fall below the detection limits or limits of quantification that are reported by Watson et al. (1991); the March 1994 report list the numbers of these samples. Sample values falling below the limits of detection and quantification appear in the data base; they have not been censored. Censoring raises a number of difficulties with respect to most statistical analyses, and procedures are available for treating censored data (e.g., El-Shaarawi, 1989; Gilliom and Helsel, 1986). We neither censor nor exclude measurements that fall below detection or quantification limits. Such measurements will contribute little to total deposition over quarterly or annual time scales.

Table 10. Summary of data completeness for flux calculations.

		Number of Complete Quarters (n > 7 Sampling Days)								
Site	Qtr	Max*	SO_2	O_3	HNO_3	NO_2	NH_3	pNO_3	pSO_4	pNH_4
AZ	1	5	2	3	2	1	2	3	3	3
AZ	2	5	4	3	5	3	5	5	5	5
AZ	3	5	5	3	5	4	5	5	5	5
AZ	4	5	4	1	4	2	4	4	4	4
BA	1	4	2	3	3	1	3	3	3	3
BA	2	4	3	2	3	1	3	4	3	3
BA	3	4	3	2	3	2	3	3	3	3
BA	4	4	4	2	3	1	4	4	4	4
FR	1	6	6	3	6	4	6	6	6	6
FR	2	6	5	3	5	4	5	5	5	5
FR	3	6	5	3	5	4	5	5	5	5
FR	4	6	5	3	6	4	6	6	6	6
GA	1	4	3	1	2	1	3	3	3	3
GA	2	4	2	0	2	1	2	2	2	2
GA	3	4	3	1	3	2	3	3	3	3
GA	4	3	2	0	2	1	1	2	2	2
LA	1	5	3	3	3	1	4	4	4	4
LA	2	5	3	3	3	2	3	3	3	3
LA	3	5	4	3	4	3	4	4	4	4
LA	4	5	4	2	4	2	4	4	4	4
LB	1	5	2	3	3	0	3	3	2	2
LB	2	5	4	3	5	3	5	5	5	5
LB	3	4	4	3	4	3	4	4	3	4
LB	4	4	4	2	4	2	4	4	4	4
SA	1	3	2	2	1	0	2	2	2	2
SA	2	3	0	1	1	1	1	1	1	1
SA	3	2	2	2	2	2	2	2	2	2
SA	4	3	2	1	2	1	1	2	2	2

Table 10, continued

SB	1	4	1	2	1	1	1	3	1	1
SB	2	5	2	2	2	3	2	4	2	2
SB	3	5	1	3	1	3	1	2	1	1
SB	4	5	1	2	2	2	1	4	2	2
SC	1	3	2	2	1	0	2	2	2	2
SC	2	3	0	1	1	1	1	1	1	1
SC	3	2	2	2	2	2	2	2	2	2
SC	4	3	2	1	2	1	1	2	2	2
SE	1	3	1	1	1	1	1	1	1	1
SE	2	3	2	3	3	1	2	3	3	3
SE	3	3	3	3	2	2	3	3	2	3
SE	4	2	1	1	1	0	1	1	1	1
YO	1	4	0	0	0	0	0	0	0	0
YO	2	5	2	0	1	2	3	4	3	3
YO	3	4	3	1	2	2	3	3	3	3
YO	4	4	0	0	0	0	0	0	0	0

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*Max denotes the maximum possible quarters given the length of monitoring.

Specification of Variables of Interest

The variables of interest include the following species, which were treated in the Oak Ridge/EPA dry-deposition program (described in the next section):

- O_3 (g);
- SO_2 (g);
- HNO_3 (g);
- particulate sulfate;
- particulate nitrate.

The following species are also of interest, but were not treated in the Oak Ridge/EPA program:

- NH_3 (g);
- NO_2 (g);
- particulate ammonium.

Because particulates are differentiated by size only for deposition velocity calculations, particulate ammonium is treated identically to particulate sulfate and nitrate. Rough estimates of transfer resistances for ammonia and nitrogen dioxide gases were obtained by applying the algorithms of Wesely (1989). The resistance values we used [seconds per meter (s/m)] are shown in the tabulation below:

	NO_2	NH_3
Mesophyll	0	0
Cuticle	20,000	10,000
Soil	2000	2000

Modifications to the Oak Ridge/EPA Algorithm

Our philosophy has been to simplify the EPA algorithm where our data do not justify higher levels of detail. The more detailed formulation can be used in sensitivity and uncertainty analyses.

In making point estimates, we use the values of u and u_* determined at the site and do not routinely adjust them for different surrounding surfaces. However, the adjustments for different surfaces have been used to explore the uncertainties inherent in the estimates of u and u_*.

The second simplification is not adjusting for temporal variation in LAI. The

California sites are either urban, where plant type and LAI data are not available, or in predominantly non-deciduous plant communities, where LAI does not vary seasonally.

We do not have the information needed to make use of the 21-layer canopy subroutine. We have simplified to the case of a single layer.

We expanded the number of gaseous species considered to include nitrogen dioxide and ammonia, which required determining appropriate values for cuticular and soil resistance.

The program deals only with submicron particles, for which settling velocity may be ignored. The CADMP data suggest that species formed primarily from condensation processes, such as sulfate, nitrate, and ammonium, are primarily submicron (PM2.5 concentrations are typically a large fraction of PM10 concentrations for these three species). The program deals only with sulfate and nitrate particles, but adding others is straightforward since canopy or transfer resistance is absent (i.e., deposition velocity does not depend on the adsorptive or chemical interaction of the species and surface) (Seinfeld, 1986).

It is possible to determine deposition velocities for larger particles, for which settling velocity is important or even dominant. The expression would be (Hicks et al. 1987):

$$V_d = V_s + \frac{1}{R_a + R_b + R_a R_b V_s} \tag{11}$$

The only new term is settling velocity, V_s, which depends critically on particle size. However, since the CADMP data do not include a complete size distribution, one must either postulate a distribution or simply generate only upper and lower bounds for fluxes of large particles.

RESULTS

Compiling Flux Rates and Amounts

We first compiled quarterly flux rates for the entire duration of CADMP sampling (1988 - 1994) (not all sites had data for the entire period). From the quarterly flux rates, annual average flux rates were compiled for each year that had four complete quarters (see Table 11). Note that the years 1993 and 1994 are not listed for some sites because the meteorological measurements were not carried out at all locations during those two years. Many missing values appear in Table 11 because many species at most sites failed to have four complete samples per year. The variables "Low" and "High" denote the minimum and maximum number of complete quarters per year, which vary among chemical species.

Long-term seasonal average flux rates (expressed as annual-equivalent rates) were compiled from the quarterly flux rates by averaging over all years (see Table 12). For example, all January through March periods at Azusa were averaged to form a mean January through March flux rate. The variables "Low" and "High" denote the minimum and maximum number of years data contained within each seasonal average (the number varies among chemical species).

Long-term flux rates (expressed as average annual rates, see Table 13) were compiled by averaging the long-term quarterly average flux rates previously shown in Table 12. The averaging was carried out in this manner so as to weight each of the four seasons equally. However, for some species at some sites, not all four seasons were represented (see "Low" and "High" variables in Table 13).

Summary Results

The fluxes of HNO_3 are of particular interest because of their magnitude. Estimated deposition of HNO_3 ranges from 1 to 86 kg ha^{-1} yr^{-1}. A distinct gradient of HNO_3 deposition exists in the SoCAB, from Long Beach (22 kg ha^{-1} yr^{-1}) to downtown Los Angeles (68 kg ha^{-1} yr^{-1}) to Azusa (86 kg ha^{-1} yr^{-1}) At Azusa, Bakersfield, Los Angeles, and Sacramento, HNO_3 accounts for approximately 60 to 70 percent of the deposition of oxidized nitrogen species. At Fremont, Long Beach, and Santa Barbara, HNO_3 accounts for approximately 30 to 50 percent of the deposition of oxidized nitrogen species.

Sensitivity Analyses

A detailed discussion of sensitivity analyses can be found in our March 1994 report. However, the sensitivity analyses that we carried out do not encompass the full range of uncertainties associated with the inferential method and with the data. As noted previously, the accuracy of the inferential method is considered to be no better than about 30 to 50 percent, depending upon the chemical species involved, for stations located in uncomplicated terrain and having uniform surroundings.

Table 11. Calculated dry deposition fluxes by site and year. Units are kg ha^{-1} yr^{-1} (periods indicate missing data).

		Gas-Phase Species					Particulate			No. Qtrs.	
Site	Year	SO_2	O_3	HNO_3	NO_2	NH_3	NO_3	SO_4	NH_4	Low	High
AZ	1989	.	24.05	.	.	.	.	.	.	2	4
AZ	1990	2.25	.	72.17	.	1.70	1.02	1.28	0.57	0	4
AZ	1991	.	.	97.43	.	1.85	1.85	2.02	0.98	2	4
AZ	1992	.	.	.	.	.	.	.	.	0	3
AZ	1993	.	.	.	.	.	.	.	.	0	3
BA	1988	.	.	.	.	.	.	.	.	0	1
BA	1989	.	18.59	39.68	.	4.80	3.44	1.20	0.85	3	4
BA	1990	2.54	.	22.70	.	3.10	2.40	1.00	0.59	0	4
BA	1991	2.58	.	34.29	.	3.30	2.51	1.09	0.68	1	4
BA	1992	.	.	.	.	.	.	.	.	0	1
FR	1988	.	.	.	.	.	.	.	.	0	1
FR	1989	0.68	12.32	7.63	.	1.65	1.82	0.67	0.27	3	4
FR	1990	0.79	10.57	4.78	.	0.92	0.96	0.61	0.20	0	4
FR	1991	1.08	.	5.66	.	1.03	0.71	0.36	0.16	3	4
FR	1992	0.73	.	4.83	9.97	1.22	0.70	0.35	0.14	0	4
FR	1993	0.69	.	4.82	10.00	0.94	0.66	0.29	0.09	0	4
FR	1994	.	.	.	.	.	.	.	.	0	1
GA	1988	.	.	.	.	.	.	.	.	0	0
GA	1989	.	.	.	.	.	.	.	.	0	3
GA	1990	.	.	.	.	.	.	.	.	0	3
GA	1991	.	.	.	.	.	.	.	.	1	3
GA	1992	.	.	.	.	.	.	.	.	0	1
LA	1989	.	12.42	79.36	.	2.73	1.21	1.61	0.80	3	4
LA	1990	1.94	9.86	34.86	.	1.77	0.88	0.94	0.53	0	4
LA	1991	.	.	.	.	.	.	.	.	0	3
LA	1992	.	.	.	.	.	.	.	.	0	2
LA	1993	1.63	.	84.69	.	2.84	1.10	1.77	0.56	0	4
LA	1994	.	.	.	.	.	.	.	.	0	0

Table 11, continued

		Gas-Phase Species					Particulate			No. Qtrs.	
Site	Year	SO_2	O_3	HNO_3	NO_2	NH_3	NO_3	SO_4	NH_4	Low	High
LB	1989	.	13.58	31.70	.	2.79	2.43	.	.	2	4
LB	1990	3.09	6.84	7.92	.	1.49	1.82	0.97	0.55	0	4
LB	1991	.	.	21.26	.	1.64	1.71	.	0.65	2	4
LB	1992	.	.	.	.	.	.	.	.	0	3
LB	1993	.	.	.	.	.	.	.	.	0	1
SA	1989	.	.	.	.	.	.	.	.	1	2
SA	1990	.	.	.	.	.	.	.	.	0	1
SA	1991	.	.	.	.	3.01	1.24	0.51	0.35	3	4
SA	1992	.	.	.	.	.	.	.	.	0	0
SB	1989	.	.	.	.	.	.	.	.	0	2
SB	1990	.	15.94	.	.	.	0.38	.	.	0	4
SB	1991	.	.	.	.	.	.	.	.	0	3
SB	1992	0.19	.	7.64	7.04	0.95	0.73	0.88	0.26	0	4
SB	1993	.	.	.	.	.	.	.	.	0	1
SC	1989	.	.	.	.	.	.	.	.	1	2
SC	1990	.	.	.	.	.	.	.	.	0	1
SC	1991	.	.	.	.	2.80	1.18	0.53	0.37	3	4
SC	1992	.	.	.	.	.	.	.	.	0	0
SE	1989	.	28.82	3.61	.	.	0.28	0.34	0.16	2	4
SE	1990	.	.	.	.	.	.	.	.	0	2
SE	1991	.	.	.	.	.	.	.	.	1	2
YO	1989	.	.	.	.	.	.	.	.	0	2
YO	1990	.	.	.	.	.	.	.	.	0	2
YO	1991	.	.	.	.	.	.	.	.	0	2
YO	1992	.	.	.	.	.	.	.	.	0	1
YO	1993	.	.	.	.	.	.	.	.	0	0

Table 12. Long-term seasonal averages of calculated dry deposition fluxes by site using variable length records from 1988-94. Units are kg ha^{-1} yr^{-1} (periods indicate missing data).

		Gas-Phase Species					Particulate			No. Years	
Site	Qtr	SO_2	O_3	HNO_3	NO_2	NH_3	NO_3	SO_4	NH_4	Low	High
AZ	1	1.47	15.18	37.70	18.74	1.77	1.73	0.54	0.57	1	3
AZ	2	1.76	26.62	107.11	16.83	2.11	1.08	1.90	0.72	3	5
AZ	3	2.49	29.59	142.81	24.32	2.34	0.68	2.45	0.76	3	5
AZ	4	1.46	14.94	55.43	21.01	1.54	1.78	0.75	0.63	1	4
BA	1	1.72	13.01	7.60	7.15	3.83	3.13	0.64	0.85	1	3
BA	2	2.97	23.98	44.59	9.09	3.46	1.70	1.24	0.38	1	4
BA	3	3.27	25.63	56.90	9.70	3.92	1.80	1.48	0.46	2	3
BA	4	2.92	13.85	19.81	11.86	3.99	4.55	1.07	1.31	1	4
FR	1	0.53	7.02	3.22	9.01	1.11	0.74	0.20	0.16	3	6
FR	2	0.62	17.30	5.94	7.79	1.01	0.73	0.58	0.10	3	5
FR	3	0.96	14.27	10.77	9.29	1.20	0.86	0.74	0.17	3	5
FR	4	1.03	5.63	2.82	11.60	1.11	1.35	0.27	0.23	3	6
GA	1	0.23	18.41	0.95	2.18	0.26	0.07	0.10	0.01	1	3
GA	2	0.41	.	0.35	1.71	2.93	0.14	0.43	0.06	0	2
GA	3	0.17	22.73	1.70	0.69	0.21	0.13	0.47	0.12	1	3
GA	4	0.19	.	1.11	3.01	0.19	0.10	0.18	0.05	0	2
LA	1	1.54	5.50	19.97	9.77	2.37	0.94	0.53	0.45	1	4
LA	2	2.29	16.36	95.37	19.58	2.56	0.93	1.86	0.64	2	3
LA	3	1.90	18.39	108.71	25.47	2.69	0.50	2.41	0.76	3	4
LA	4	1.85	9.10	47.41	21.80	2.31	1.79	0.94	0.63	2	4
LB	1	3.10	8.67	10.09	.	2.54	2.37	0.81	0.55	0	3
LB	2	2.80	13.65	24.26	16.10	1.63	1.62	1.68	0.54	3	5
LB	3	3.63	14.02	37.37	17.37	1.68	1.94	2.63	0.93	3	4
LB	4	2.93	6.07	14.73	25.10	2.42	2.63	1.06	0.68	2	4

Table 12, continued

		Gas-Phase Species					Particulate			No. Years	
Site	Qtr	SO_2	O_3	HNO_3	NO_2	NH_3	NO_3	SO_4	NH_4	Low	High
SA	1	0.91	10.82	14.64	.	3.09	1.97	0.48	0.58	0	2
SA	2	.	21.80	15.61	9.00	2.87	0.74	0.65	0.15	0	1
SA	3	1.82	16.32	23.28	8.35	2.96	0.75	0.73	0.22	2	2
SA	4	1.56	3.04	13.67	17.99	3.85	1.88	0.39	0.52	1	2
SB	1	0.15	14.67	7.36	6.89	0.72	0.32	0.39	0.14	1	3
SB	2	0.24	18.68	9.09	5.70	1.07	0.90	1.64	0.28	2	4
SB	3	0.23	20.42	9.29	5.96	1.02	0.62	1.65	0.42	1	3
SB	4	0.13	14.16	9.11	7.78	0.83	0.71	0.70	0.27	1	4
SC	1	0.96	10.82	11.92	.	2.99	1.72	0.44	0.52	0	2
SC	2	.	21.80	17.06	7.72	2.41	0.54	0.56	0.13	0	1
SC	3	1.63	16.27	25.82	7.52	3.00	0.69	0.83	0.33	2	2
SC	4	1.61	2.96	13.73	18.78	3.66	1.87	0.46	0.58	1	2
SE	1	0.03	15.77	0.01	0.00	0.25	0.35	0.10	0.08	1	1
SE	2	0.47	36.93	3.74	0.06	0.55	0.29	0.49	0.19	1	3
SE	3	0.66	41.02	6.74	0.09	0.92	0.27	0.52	0.18	2	3
SE	4	0.06	18.58	0.55	.	0.24	0.51	0.10	0.13	0	1
YO	1	.	.	.	.	.	.	.	.	0	0
YO	2	0.23	.	2.08	0.28	0.29	0.16	0.31	0.08	0	4
YO	3	0.33	46.82	4.64	0.01	0.45	0.14	0.50	0.13	1	3
YO	4	.	.	.	.	.	.	.	.	0	0

Table 13. Long-term annual averages of calculated dry deposition fluxes by site using variable length records from 1988-94. Units are kg ha^{-1} yr^{-1} (periods indicate missing data).

	Gas-Phase Species					Particulate			No. Seasons	
Site	SO_2	O_3	HNO_3	NO_2	NH_3	NO_3	SO_4	NH_4	Low	High
AZ	1.80	21.58	85.76	20.22	1.94	1.32	1.41	0.67	4	4
BA	2.72	19.12	32.22	9.45	3.80	2.80	1.11	0.75	4	4
FR	0.78	11.05	5.69	9.42	1.11	0.92	0.45	0.16	4	4
GA	0.25	20.57	1.03	1.90	0.90	0.11	0.29	0.06	2	4
LA	1.89	12.34	67.87	19.16	2.48	1.04	1.44	0.62	4	4
LB	3.11	10.60	21.61	19.52	2.07	2.14	1.55	0.68	3	4
SA	1.43	12.99	16.80	11.78	3.20	1.34	0.56	0.37	3	4
SB	0.19	16.98	8.71	6.58	0.91	0.64	1.10	0.28	4	4
SC	1.40	12.96	17.13	11.34	3.01	1.21	0.57	0.39	3	4
SE	0.30	28.07	2.76	0.05	0.49	0.35	0.30	0.14	3	4
YO	0.28	46.82	3.36	0.14	0.37	0.15	0.41	0.10	1	2