

# *Atmospheric Acidity Protection Program:*

Final Assessment

October 2000

California Environmental Protection Agency

 **Air Resources Board**

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## *Acknowledgements*

The final assessment was written under the direction of the Scientific Advisory Committee on Acid Deposition (listed below) and the Research Division management in 1999 (John R. Holmes, Ph.D. and Robert D. Barham, Ph.D.). Staff of the Research Division prepared the assessment report.

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## *Preface & Disclaimer*

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## *Abbreviations and Symbols*

AAPP	Atmospheric Acidity Protection Program
ANC	Acid Neutralizing Capacity
ARB	Air Resources Board
Base Cation	Selected positively charged ions other than H <sup>+</sup> (e.g., Ca <sup>2+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> )
CADMP	California Acid Deposition Monitoring Program
CMB	Chemical Mass Balance Receptor Model
eq	Equivalent
FCAAA	Federal Clean Air Act Amendments of 1990
H <sup>+</sup>	Hydrogen Ion
ha	Hectare (10,000 m <sup>2</sup> = 2.47 acres)
hr	Hour (60 minutes)
KADP	Kapiloff Acid Deposition Program
kg	Kilogram (1000 grams = 2.205 pounds)
L	Liter (1000 mL = 1.057 quarts)
m <sup>3</sup>	Cubic Meter
N	Nitrogen (atomic number 7; atomic weight = 14.01)
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NAPAP	National Acid Precipitation Assessment Program
N-Deposition	The deposition of nitrogen-containing compounds to surface receptors
nmol	Nanomole (10 <sup>-9</sup> mole)
NO <sub>x</sub>	Nitrogen Oxides
N-Saturation	An ecosystem-level condition in which the amount of nitrogen available is in excess of that needed for plant and microbial growth
pH	The negative common logarithm of the free hydrogen ion concentration of a solution (e.g., pH 3.0 corresponds to [H <sup>+</sup> ] of 0.001 mole H <sup>+</sup> per liter).
PM	Particulate Matter
PM2.5	Particulate Matter with a Diameter ≤ 2.5 μm (a.k.a. fine PM)
PM10	Particulate Matter with a Diameter 2.5 to 10 μm (a.k.a. coarse PM)
S	Sulfur (atomic number 16; atomic weight = 32.064)
SoCAB	South Coast Air Basin (a.k.a. Los Angeles Basin)
USEPA	U.S. Environmental Protection Agency
μeq	Microequivalent (10 <sup>-6</sup> equivalents)
μm	Micrometer (10 <sup>-6</sup> meters)

## *Executive Summary*

Scientific evidence in other parts of the world has shown that atmospheric deposition of sulfur and nitrogen compounds can cause harm to the environment and, thus, may present a threat to California's ecosystems and the health of its citizens. To adequately address this serious concern, the causes and effects of acid deposition in California were studied in two comprehensive State-funded research programs. These studies examined the atmospheric processes associated with acid deposition and its effects on human health, aquatic ecosystems, forest ecosystems, agricultural crops, and man-made materials. Statewide networks to monitor pollutant concentrations in wet and dry deposition were established to measure conditions in both urban and rural areas.

Nitrogen-containing gases and particles proved to be an important source of airborne acidity in California. In contrast to the eastern United States (U.S.), where precipitation chemistry is dominated by sulfur-containing acids, nitrogen-containing acids are responsible for a major portion of acidity in precipitation, fogs and clouds, dry deposited gases, and particles within the state. Although annual precipitation acidity is ten-fold lower in California than in the eastern U.S., summertime concentrations and deposition of nitric acid vapor and particle nitrate are among the highest in the nation. Adverse effects on human lung function have not been observed after acute exposures to acidity, but long-term exposures may pose a chronic health risk, alone or in combination with other airborne pollutants. Results from the Children's Health Study showed an association between nitrogen oxides, particulate matter, and nitric acid and decreased rates of lung function growth in children living in the most polluted communities of Southern California. While acute, short-term effects on human health and welfare (i.e., agricultural crops and man-made materials) are projected to be minor, long-term effects on human health, as well as aquatic and forest ecosystems, are of potential concern.

The long-term effects of episodic acidification are largely unknown, and monitoring programs to detect changes in surface water chemistry and precipitation chemistry may be needed to assess ecosystem-level alterations in the high elevation watersheds of the Sierra Nevada. Chronic acidification of high elevation surface waters in the Sierra Nevada has not been found, but episodic depressions in acid neutralizing capacity do occur. While no large-scale or widespread adverse ecological impacts have been detected, many high elevation aquatic ecosystems are nitrogen-limited and potentially at risk from current levels of atmospheric nitrogen deposition. In Lake Tahoe, studies indicate that phytoplankton growth is not co-limited by the availability of nitrogen and phosphorus; rather, growth is limited by phosphorus alone, due to the deposition of atmospheric nitrogen. Nitrogen saturation has occurred in forested watersheds in the San Bernardino Mountains, and nitrate contamination of groundwater is of near-term concern. In future years, atmospheric nitrogen deposition could lead to forest soil nitrogen saturation in other areas such as the

San Gabriel Mountains and southern Sierra Nevada. Ozone is the primary air pollution stressor of forests, and there is the potential for interactive effects with atmospheric nitrogen. Monitoring of tree health and air quality in forests surrounding the South Coast Air Basin and on the western slope of the Sierra Nevada may be needed to detect air pollution-caused changes in forest conditions. The impacts from current levels of acidic deposition on agricultural crops, soils, and man-made materials were found to be minor.

Atmospheric nitrogen levels (i.e., concentrations of gaseous nitrogen oxides and particulate nitrate) have declined in response to control measures adopted to reduce ambient ozone and particulate matter. Consequently, until further evidence indicates otherwise, there does not appear to be an immediate need to set an ambient air quality standard for acidity to protect human health or an acid deposition standard for welfare protection. However, as air pollution-caused alterations in ecosystems are known to occur over multi-decade time periods, consideration should be given to monitoring long-term responses in forests and high elevation watersheds at two-to three-year intervals. In forests, surveys of ozone damage to pine tree needles and regional-scale monitoring of ozone and nitrogen gases using passive samplers could be conducted on a triennial basis to assess changes in forest conditions. Similarly, in high elevation watersheds, biennial measurements of snow and lake-water chemistry could be performed to track long-term impacts in habitat quality. In this regard, since air quality improvements are projected to occur across the state through 2010 and beyond, the prevention and/or remediation of forest and aquatic ecosystem deterioration could be concurrently documented.

## *I. Introduction*

In 1980, the National Acid Precipitation Assessment Program (NAPAP) was established to investigate the causes and effects of acidic deposition in the U.S. While the cause of acidic precipitation is largely due to the dissolution of sulfur and nitrogen oxides in rain, the impacts of sulfur-derived acids were of principal concern in the eastern U.S., and the effects of nitrogen-derived acids were of primary interest in the western U.S. In consideration of the nitrogen-dominated rain chemistry of California, and the potential for distinct health and welfare effects from the eastern U.S., two five-year programs of monitoring and research were enacted by the California Legislature: the Kapiloff Acid Deposition Program (KADP) and the Atmospheric Acidity Protection Program (AAPP). Concentrations of acidic air pollutants in precipitation, fog, and dry-deposited particles and gases were measured in support of the KADP and AAPP by the Air Resources Board's (ARB) California Acid Deposition Monitoring Program (CADMP). Analyte levels in rain/snow and dry deposition have been reported in data summaries (Takemoto et al., 1996), final reports (Watson et al., 1991; Blanchard and Michaels, 1994), and the open literature (Blanchard and Tonnessen, 1993; Melack and Sickman, 1997). The major findings from the KADP and AAPP have also been documented in final reports, Annual Reports to the Governor and the Legislature (ARB, 1983-1986; 1988; 1991-1994a), a technical assessment (ARB, 1989), and the open literature (e.g., Takemoto et al., 1995).

With the adoption of the Federal Clean Air Act Amendments of 1990 (FCAAA), reductions in sulfur and nitrogen oxide emissions were mandated to reduce acidic deposition, and projected to provide significant health and welfare benefits to the U.S. and Canada. The benefits include: decreases in the acidity of lakes and streams, concomitant improvements in aquatic wildlife health, decreases in soil degradation and forest stress, improvements in visibility, decreases in damage to man-made materials and cultural resources, and reduced stress on human health. In its report on the need for an acidic deposition standard to protect critically sensitive aquatic and terrestrial resources, the U.S. EPA concluded that establishing standards for sulfur (S) and nitrogen (N) deposition were technically feasible, but two key uncertainties precluded them from developing standards (USEPA, 1995). From a policy perspective, there is uncertainty insofar as the appropriate or desired environmental protection goals for an acidic deposition standard, and from a scientific standpoint, the processes leading to and time scales for achieving watershed N saturation were deemed to be highly speculative.

In the following report, the major findings from six research programs sponsored under the KADP and AAPP are summarized, and recommendations as to future research, monitoring, or ambient air quality standard setting are provided. Funding for this effort was allocated over an 11-year period from 1983-1993, in which \$25 million of research was sponsored under the

direction of the Scientific Advisory Committee on Acid Deposition and the ARB (Table 1).

Table 1. Allocation of Research Funds in the Kapiloff Acid Deposition and Atmospheric Acidity Protection Programs: 1983-1993						
Year	----- Research Area -----					
	Atmospheric Processes	Aquatic Ecosystems	Human Health	Man-made Materials	Forests & Crops	Summary Workshop
1983	\$386,342	\$1,114,948	-----	-----	-----	-----
1984	\$1,376,009	\$835,858	\$600,000	\$306,757	-----	-----
1985	\$1,079,098	\$748,591	\$725,609	\$454,184	\$153,518	-----
1986	\$1,595,637	\$703,974	\$457,909	\$280,000	\$123,480	-----
1987	\$1,554,843	\$1,022,682	\$354,978	\$228,497	-----	-----
1989	\$832,285	\$749,129	\$561,635	\$18,951	-----	-----
1990	\$215,817	\$641,683	\$741,846	\$94,516	\$478,680	-----
1991	\$155,475	\$794,442	\$815,485	-----	\$290,303	-----
1992	\$426,715	\$256,196	\$1,452,442	-----	\$212,400	-----
1993	\$1,118,068	\$60,797	\$861,320	-----	\$75,339	-----
Total	\$8,740,289	\$6,928,300	\$6,571,224	\$1,382,905	\$1,333,720	\$46,476
%	35.0	27.7	26.3	5.5	5.3	0.2

## II. Research Area Summaries

### A. Atmospheric Processes

In the KADP, the primary research focus was the development of new techniques for measuring concentrations of acidic air pollutants and their rates of deposition. In the AAPP, the newly developed methods were used to generate databases on selected acidic air pollutants, and source-receptor relationships were investigated. The research objectives were: (1) to improve our understanding of nitrate and sulfate chemistry, (2) to clarify the relationships among emissions and rates of deposition, (3) to determine trends in particulate matter (PM) concentrations, (4) to characterize fog chemistry across the state, and (5) to project future source-receptor relationships.

#### 1.a. Nitrate Chemistry (cf. Pandis and Seinfeld, 1989)

Emissions of nitrogen oxides (NO<sub>x</sub>) consist primarily of nitric oxide (NO), which can be oxidized by ozone and/or peroxy radicals to form nitrogen dioxide (NO<sub>2</sub>). During the day, NO<sub>2</sub> reacts with hydroxyl radical to form nitric acid, which is the principal means of nitric acid formation. Conversion rates for NO<sub>2</sub> to nitric acid range from <1 to 90 percent/hour. The second major pathway for nitric acid formation is the reaction of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) with water, which is significant when the liquid water content of the atmosphere is high (i.e., when clouds and fog are present). The principal loss process for nitric acid is the formation of particulate nitrate. In the presence of ammonia gas, nitric acid vapor reacts to form ammonium nitrate, which is believed to be the primary

source of fine particle nitrate (<2.5  $\mu\text{m}$  diameter) in urban air. The formation of ammonium nitrate is favored under conditions of high humidity and low temperature. Particle nitrate is also formed during the conversion of nitric acid to hydrochloric acid. In this process, sodium nitrate and/or calcium nitrate is produced, and may be the principal source of coarse particle nitrate (2.5-10  $\mu\text{m}$  diameter). Significant amounts of  $\text{NO}_x$  can also be converted to organic nitrates such as peroxyacetyl nitrate (PAN), which is the most abundant organic nitrate in urban air.

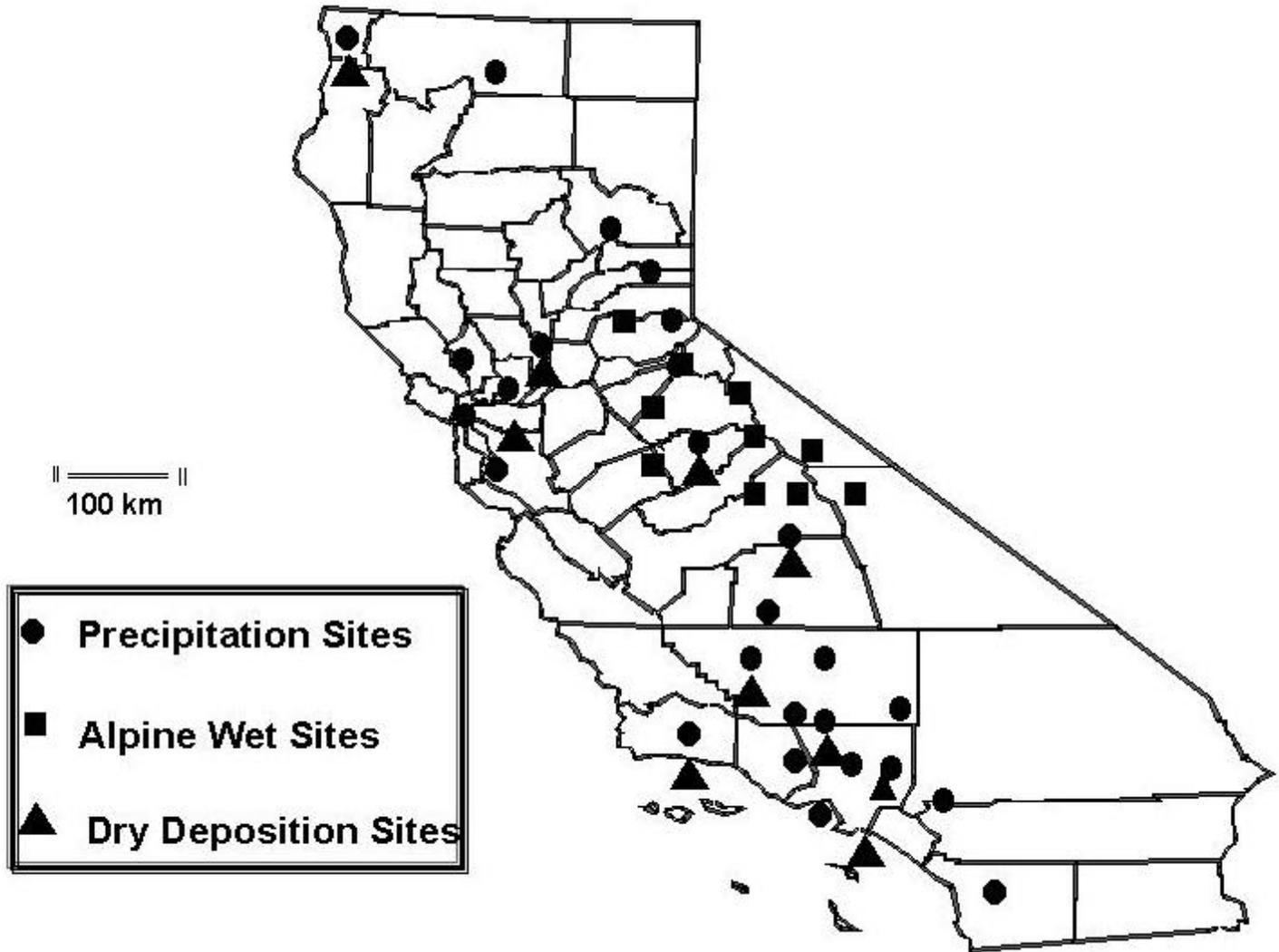
#### 1.b. Sulfate Chemistry (cf. Seinfeld and Pandis, 1998)

Emissions of sulfur dioxide are chemically transformed to sulfuric acid, which can be partially or completely neutralized by ammonia and other alkaline substances to form sulfate salts. The oxidation of sulfur dioxide to sulfuric acid can occur in the gasphase, the aqueous phase (i.e., in rain, cloud, or fog), and the particle phase. In daytime gas-phase reactions, sulfur dioxide is converted to sulfuric acid primarily by reaction with hydroxyl radical. In the aqueous phase ozone is an important oxidant for sulfur dioxide at high pH, but its effect becomes negligible at pH levels more acidic than 4.0. Because of its extremely low vapor pressure, sulfuric acid quickly adheres to existing particles. Reaction with ammonia leads to the formation of ammonium bisulfate and ammonium sulfate salts. These submicron particles have a very low sedimentation velocity and can be transported long distances. In the absence of precipitation or fog, the atmospheric lifetime of fine particle sulfate is several days.

#### 2. Annual Deposition Rates and Relationship to Emissions

Across the state the deposition of N-derived acidic gases and particles provides most of the atmospheric acidity and N to urban landscapes, and to mid-elevation forests in southern California. Blanchard et al. (1996) used precipitation chemistry data from the CADMP, the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), and an alpine precipitation sampling network in the Sierra Nevada Mountains to estimate regional-scale rates of wet-deposited nitrate, sulfate, ammonium, calcium, and  $\text{H}^+$  from 1985 through 1994 (Figure 1). Rates of wet sulfate, nitrate, and ammonium deposition were found to be <4, <3, and <4 kg S or N/ha/yr in at all sites, respectively (Blanchard et al., 1996). In comparison, rates of wet sulfate and nitrate deposition in eastern North America exceed 8.3 and 3.4 kg S or N/ha/yr, respectively, and deposition rates of ammonium are <3.1 kg N/ha/yr (Sisterson, 1991). In most years, wet nitrate deposition was estimated to be greater in urban areas of the South Coast Air Basin (SoCAB) and the southern Sierra Nevada, than in other parts of California. Along the northwest coast where wet sulfate deposition is highest, much of the sulfate is derived from sea salt. Uncertainties in the wet deposition estimates are  $\leq 20$  percent in the SoCAB, which has a large number of monitors, but are two to three fold higher in other parts of the state.

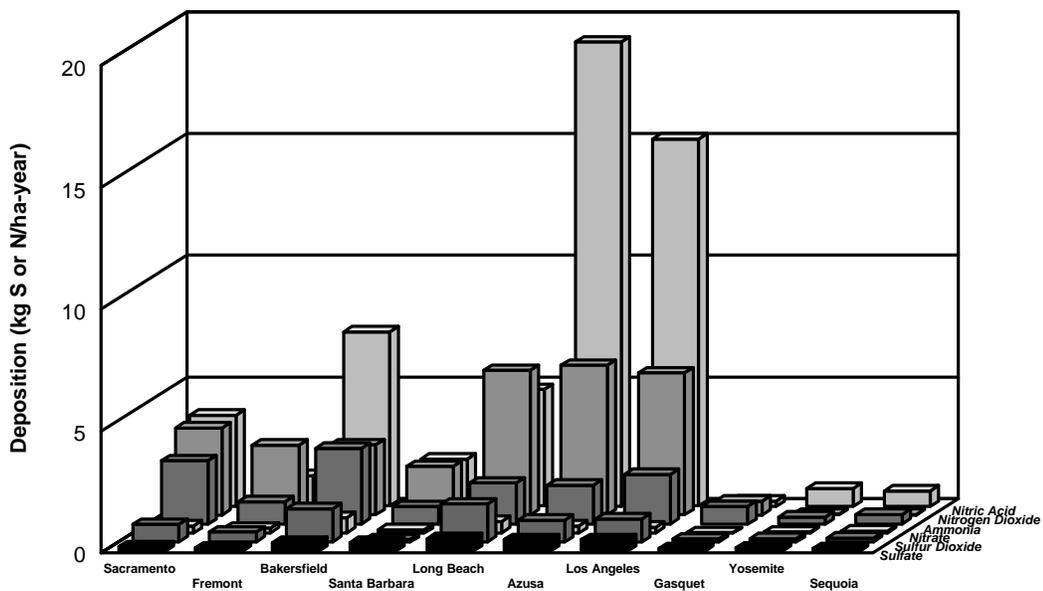
Figure 1. Location of CADMP, NADP/NTN, and Sierra Nevada Alpine  
Wet Deposition Monitoring Sites



From 1995-1998, rates of wet N deposition continued to be measured at ten sites. Relative to the multi-year average for 1985-1994, wet N deposition rates at urban sites were 10-40 percent higher, while rates at rural sites were 20-40 percent lower. Across the ten sites, annual rates of wet N deposition were within 20 percent of previously measured ten-year averages.

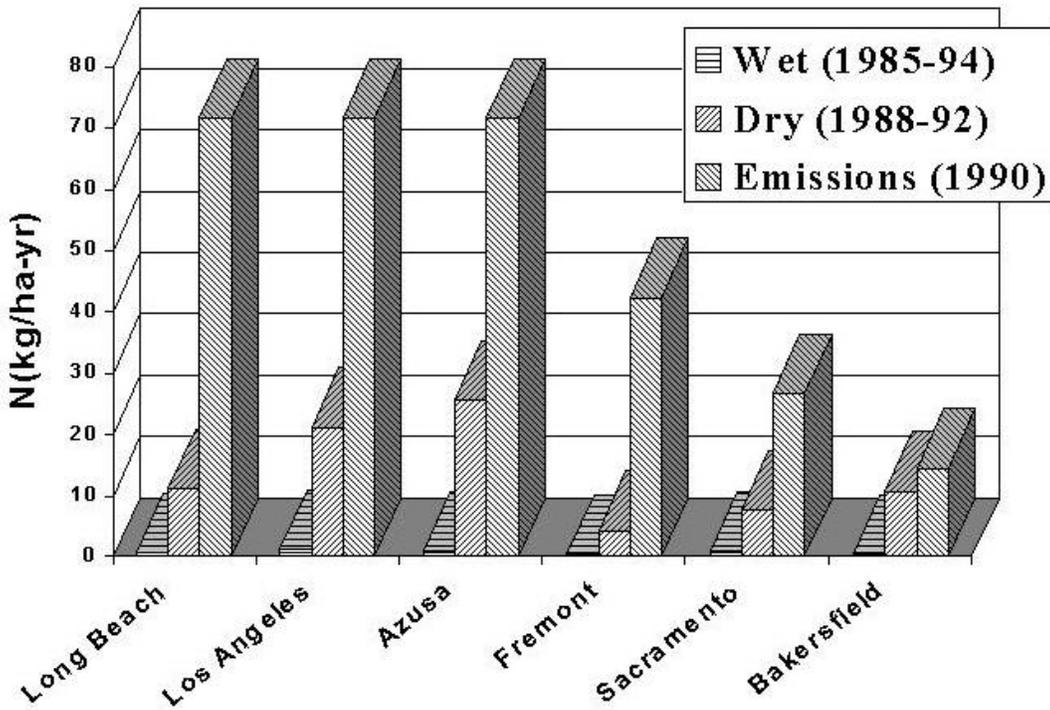
For dry deposition, data from the CADMP were used to calculate deposition rates for particle sulfate, sulfur dioxide, particle nitrate, ammonia, nitrogen dioxide, and nitric acid vapor from 1988 through 1992 (Figure 2). Regional-scale estimates of dry nitrate deposition ranged from 1 to 86 kg/ha/yr (Blanchard et al., 1996). At urban sites, nitric acid deposition accounts for 30-80 percent of the dry deposition of oxidized N species, and 20-70 percent of total dry N deposition. Annual rates of oxidized N deposition at the three rural sites (Gasquet, Sequoia, and Yosemite) were about one-tenth to one-half as great as values in the eastern U.S. (Meyers et al., 1991). The deposition rates calculated for the rural CADMP sites are quite uncertain because many of the measurements were below the limits of analytical detection. The rates of total N deposition at Azusa, Bakersfield, Long Beach, and Los Angeles exceed eastern U.S. values by 2 to 17 fold. Compared to wet deposition, annual inputs of N and S from dry deposition are much greater at urban sites, but are of similar magnitude at forest sites (e.g., Gasquet).

Figure 2. Annual Average Rates of Dry Particle and Gas Deposition at CADMP sites from 1988-1993 (cf. Blanchard et al., 1996)



Comparisons of estimated NO<sub>x</sub> emission and total N deposition rates (wet and dry) show that the deposition of oxidized N in the SoCAB accounts for 16-37 percent of the NO<sub>x</sub> emitted in the Basin (Figure 3; Blanchard et al., 1996). The total N deposition at Fremont was about 11 percent of the NO<sub>x</sub> emission rate in San Francisco Bay Area. Total N deposition rates at Bakersfield and Sacramento are about 76 and 32 percent of the NO<sub>x</sub> emission rates in Kern and Sacramento County, respectively. Transport of NO<sub>x</sub> from upwind areas could account in part for the relatively large deposition-to-emissions ratio at Bakersfield (Tracer Technologies, 1992).

Figure 3. Rates of Oxidized N Emissions, and Wet and Dry N Deposition at Urban CADMP Sites (cf. Blanchard et al., 1996)



### 3. Trends in Particulate Matter Concentrations

The CADMP dry deposition monitoring program was established in 1988 to determine spatial and temporal patterns of acidic pollutant concentrations in the state. Daytime and nighttime dry particle and gas concentrations were measured once every six days (Watson et al., 1991). Initially, the network consisted of ten sites located in Azusa, Bakersfield, Fremont, Gasquet, Long Beach, Los Angeles, Sacramento, Santa Barbara, Sequoia National Park, and

Yosemite National Park. Over the years, data analyses indicated that acidic pollutants were a moderate-to-minor problem in California, and the number of monitoring sites was reduced, as well as the frequency and range of pollutants sampled. In September 1995, the CADMP dry deposition network was reduced to five sites (Azusa, Bakersfield, Long Beach, Los Angeles, and Sacramento) in urban areas. Also, instead of collecting daytime and nighttime samples of PM10 and PM2.5, only one 24-hour-average sample of PM2.5 was collected.

From 1989-1994, annual-average PM10 and PM2.5 concentrations declined at all ten sites. Representative data from five sites are shown in Figures 4 and 5. Most areas with high PM10 levels also have high PM2.5 concentrations. At rural sites (Gasquet, Yosemite, and Sequoia National Parks), annual average concentrations of PM2.5 were 4-6  $\mu\text{g}/\text{m}^3$ . Near to Redwood National Park, Gasquet is far removed from most anthropogenic emissions sources, and provides an estimate of background ambient PM concentrations in California. On the western slope of the Sierra Nevada, Sequoia and Yosemite National Parks receive pollutants transported from the San Joaquin Valley by upslope flows. Compared to these rural sites, annual-average concentrations of PM2.5 are two to five times greater at urban locations.

Figure 4. Annual Geometric Mean PM10 Mass at CADMP Sites

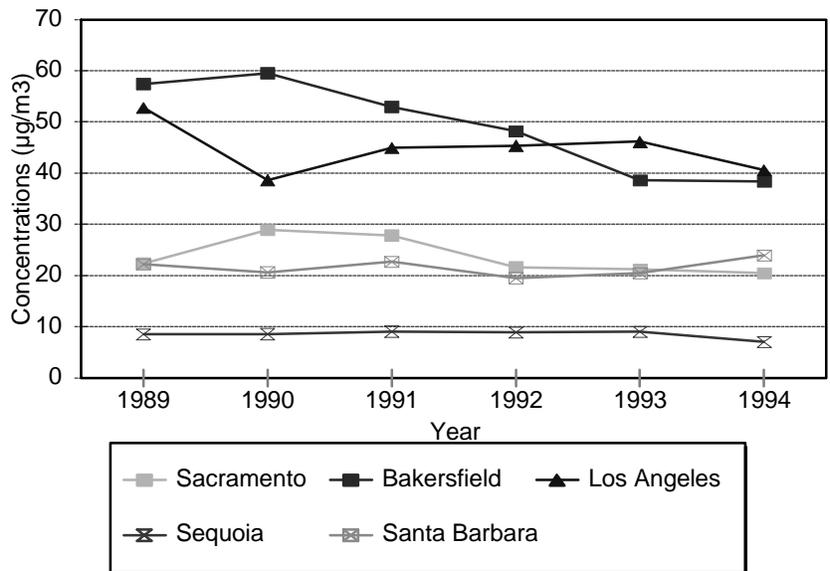
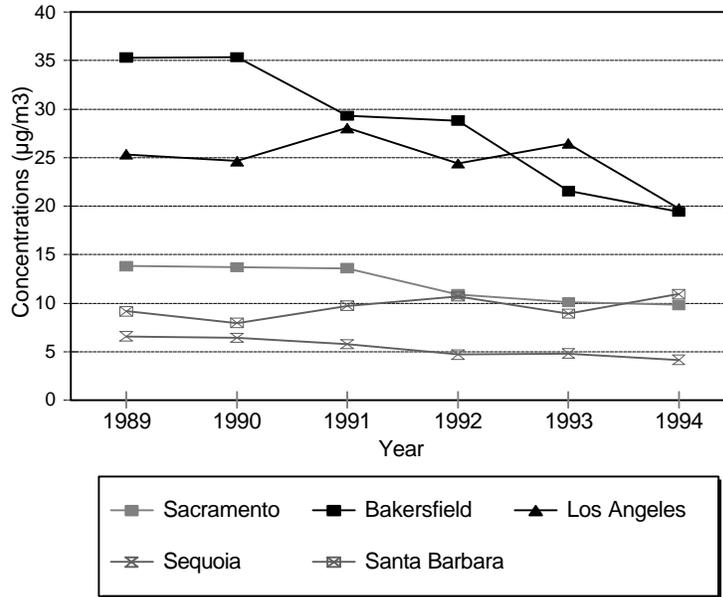
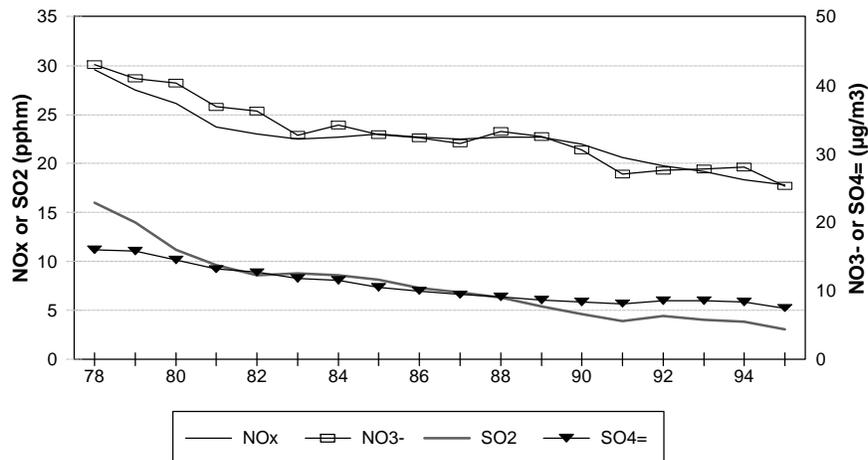


Figure 5. Annual Geometric Mean PM<sub>2.5</sub> Mass at CADMP Sites



The trends of particle nitrate and sulfate are comparable to those of their precursors, NO<sub>x</sub> and SO<sub>2</sub> (Figure 6). The similar downward trends of NO<sub>x</sub> and particle nitrate indicate that NO<sub>x</sub> emissions may be the limiting precursor to the formation of nitrate. The declining trend suggests that efforts to control PM, either directly or indirectly, have contributed to a lowering of PM concentrations. The decline in fine PM levels may be due, in part, to NO<sub>x</sub> and hydrocarbon controls to reduce ambient ozone, which have helped to reduce the formation of nitrate and organic particles (Dolislager and Motallebi, 1999), and to lowering the sulfur content of motor fuels, which reduces particle sulfate formation.

Figure 6. Three-year-average Concentrations of NO<sub>x</sub>, SO<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>=</sup> in the Los Angeles Air Basin



#### 4. Characterizing Fog Chemistry Across the State

Acidic fog has been associated with harmful air pollution episodes (e.g., London, the Meuse Valley in Belgium, and Donora, Pennsylvania), and reported to adversely affect materials, crops, and forests (Lave and Seskin, 1977; Lipfert and Daum, 1989). From 1982 through 1989, ARB sponsored fog water sampling programs at seven sites in California. Fog water collected in the western portion of the SoCAB were found to be highly acidic, with pH values ranging from 1.7 to 4 (e.g., Jacob et al., 1985). Fog water collected at non-urban, coastal sites was less acidic (i.e., pH ranged from 3 to 7) due, in part, to the low alkalinity of marine atmospheres. In the eastern part of the SoCAB and the southern San Joaquin Valley, fogs were generally not as acidic due to high levels of acid-neutralizing ammonia.

As in rain, the main contributors to fog acidity are nitric and sulfuric acid. Across the state, the nitrate-to-sulfate ratios in fog are typically about 3:1, but local emissions influence measured concentration ratios. For example, the 3:1 ratio typifies areas where motor vehicle emissions of NO<sub>x</sub> dominate (e.g., Los Angeles), but may be close to 1:1 at sites in the southern San Joaquin Valley where sulfur emissions from oil production are significant. Concentrations of ammonium, nitrate, and sulfate ions are commonly 100-times higher in fog than in rain. High concentrations of chemical components in fog correlated well with the occurrence of photochemical smog events, as well as the physical processes of condensation and evaporation.

#### 5. Future Source-Receptor Relationships

Relationships between emissions and acidic pollutant concentrations at receptor areas in California have been characterized using acid deposition simulation models.

##### 5.a. Non-linear, Semi-empirical Long-range Transport Model (STATMOD)

Using a semi-empirical long-range transport model (Karamchandi et al., 1993), it was determined that:

- Dry S deposition tends to be a local phenomenon, while wet S deposition is influenced by long-range transport.
- Dry nitrate deposition has a long-range transport component even for receptors located close to major NO<sub>x</sub> sources. The source-receptor relationships for wet nitrate deposition are similar to those for wet S deposition. The total nitrate deposition is larger than total S deposition at most locations.

- Total S deposition does not always respond linearly to changes in SO<sub>x</sub> emissions. The effect of controlling emissions in a source region was consistent with the source-receptor relationships; larger changes in deposition were observed at receptors that received their largest contribution from the source region being controlled.

#### 5.b. Chemical Mass Balance (CMB) Receptor Model

Using the Chemical Mass Balance (CMB) receptor model, source contributions to PM<sub>2.5</sub> in the Sierra Nevada and the Tehachapi Mountains were estimated (Gertler et al., 1993). The results of the CMB model analysis indicate the following:

- The major sources of particles to Blodgett Forest (El Dorado National Forest) were local sources of geological material and motor vehicle emissions. Direct emissions from motor vehicle and geological sources contribute 30 and 28 percent of daytime particle loadings, respectively, and 17 and 23 percent at night.
- At two other sites in the Sierra Nevada, particle depositions to Yosemite and Sequoia National Parks exhibited a regional San Joaquin Valley source profile and secondary organic carbon, indicating regional transport. At Yosemite, excluding periods of forest vegetation burning, contributions from motor vehicle and geological sources were greatest during the day. At Sequoia, the major day/night difference was in the contribution of the motor vehicle sources, which was greatest during the day.
- In contrast to the Sierra Nevada sites, the major diurnal change at Tehachapi was an increase in the contribution of secondary sulfate and nitrate at night. This is consistent with emissions patterns in nearby regions, coupled with transport and transformation to the site.

#### 5.c. Three-dimensional Gas/Aerosol Air Quality Model

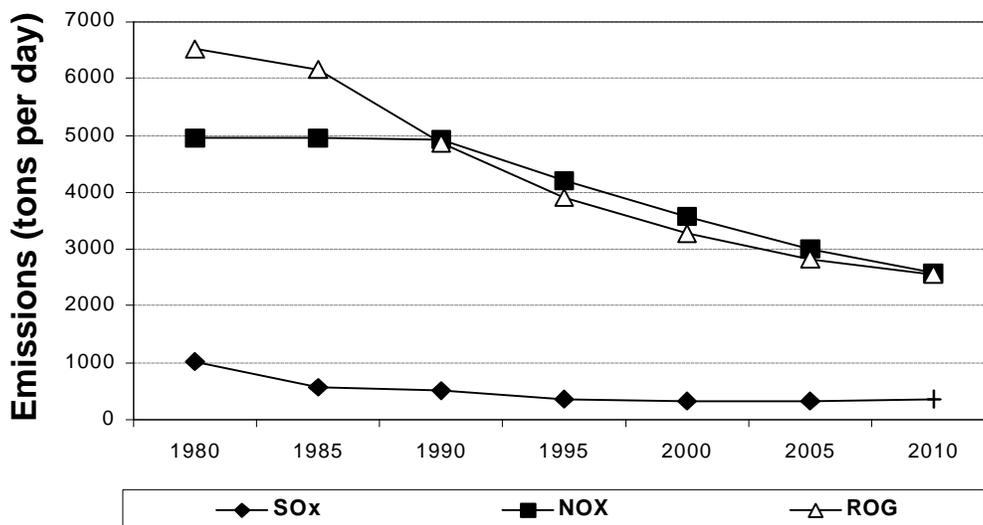
Simple empirical relationships for acid deposition phenomena are dependent upon the state of the atmosphere. Using a three-dimensional gas/aerosol atmospheric model, size-resolved concentrations of all major primary and secondary components of atmospheric particulate matter (including sulfate, nitrate, ammonium, chloride, sodium, elemental carbon, water, and crustal material), were predicted in the SoCAB during the June 24-25 and December 10-11, 1987, episodes of the Southern California Air Quality Study (Lurmann et al., 1997). The results are suspect because the emission inventories for hydrocarbons and ammonia are now known to be in error.

#### 5.d. Overview of Future Source-Receptor Relationships

Results from the three modeling projects (cf. sections 5.a., 5.b., and 5.c.) uncovered some important aspects of acid deposition in California. In the semi-empirical long-range transport model study, it was found that nitrate concentrations in rain and air were accurately estimated, but sulfate levels could be underestimated at selected receptor areas. Better results for sulfate could be obtained by accounting for other sources of sulfate, such as wind blown dust. From the CMB model study, results indicate that source contributions to PM<sub>2.5</sub> in the Sierra Nevada and Tehachapi Mountains may be local, regional, or due to transformation and transport to the site. However, because the model assumptions include conservation of the chemical constituents between source and receptor, it is difficult to identify specific sources and to quantify their contributions to the formation of secondary PM. The three-dimensional gas/aerosol modeling study generated useful predictions of PM levels in the SoCAB, but more accurate emissions inventories are needed to reduce uncertainty, and improvements in model assumptions are needed to distinguish differences in the composition of particles with the same diameter.

Due to the adoption of a range of control measures to reduce NO<sub>x</sub> and SO<sub>x</sub> as part of the ozone and PM control program, air quality improvements are projected to occur across the state through 2010 and beyond (Figure 7). While the aforementioned control measures are part of a comprehensive program to lower ambient concentrations of ozone and PM<sub>10</sub> in future decades, they will also lower concentrations of ambient acidity, and N and S deposition that have contributed to public health and welfare effects.

Figure 7. California NO<sub>x</sub>, ROG, and SO<sub>x</sub> Emissions Trends



## B. Human Health

A substantial body of epidemiological data suggests an association between ambient PM exposure and adverse health effects (Pope, 1996). Interestingly, many of the same health effects associated with ambient PM have also been associated with ambient acidity. The strength of this association increases when analyses are performed using the concentration of sulfate ion vs. the amount of total suspended particles, PM<sub>10</sub> or PM<sub>2.5</sub> (e.g., Dockery et al., 1989).

Many investigations have been conducted on the health effects of sulfuric acid aerosols and acidic sulfates. Some investigators have attributed the adverse effects of acidic aerosols on human health to the hydrogen ion (H<sup>+</sup>) in ambient aerosols (Graham, 1991). In numerous studies, H<sup>+</sup> was primarily contributed by strong acids (e.g., sulfuric acid), but could also have been derived from ammonium bisulfate (Schlesinger et al., 1990). Health effects attributed to H<sup>+</sup> exposure include exacerbation of asthma, development of and/or worsening of bronchitic symptoms, increased rates of hospital admissions for respiratory disease, cough, and reduced lung function (Ostro et al., 1991; Speizer, 1989; Thurston et al., 1994; Studnicka et al., 1995; Neas et al., 1995).

Some epidemiological data suggest that ammonium sulfate, a very weak acid, may also affect human health, while mixed results have been obtained in studies that examined the effects of acidic species in pollutant mixtures containing ozone. These results suggest that sulfate may be serving as a surrogate for H<sup>+</sup> or some other component of fine PM (e.g., particle size or total number of particles).

Unlike the eastern U.S., where ambient acids are largely sulfur-derived, the acidity of ambient air in California is largely due to nitric acid vapor, and to a lesser extent, gaseous hydrochloric acid (Appel et al., 1984; 1991). Under ambient conditions, coastal California fog water can be more acidic than pH 2.0 (Jacob et al., 1985). Peak two-week-average concentrations of H<sup>+</sup> in California fog can reach 376 nmol/m<sup>3</sup>, with annual averages as high as 204 nmol/m<sup>3</sup>. These H<sup>+</sup> concentrations are comparable to levels found to cause adverse effects in numerous epidemiological studies where sulfate analogs or sulfuric acid was the H<sup>+</sup> source.

To date, only a few toxicological studies have been conducted to evaluate the effects of nitric acid vapor on human health. Studies simulating workplace exposures to hydrochloric acid concentrations that are much higher than those found in ambient air provide limited information on human health impacts. Weak organic acids could adversely affect human health in similar ways to ammonium sulfate in the eastern U.S. If the active component of acids is H<sup>+</sup>, as postulated by some investigators (Graham, 1991), the H<sup>+</sup> from nitric acid vapor may have similar effects to that from sulfur-based acids.

Research studies in the human health program of the KADP and AAPP were aimed at determining whether nitric acid, either alone or in combination with other air pollutants (e.g., ozone, particles), posed an acute or chronic health risk to Californians at concentrations characteristic of urban areas. To this end, research projects involving human subjects and laboratory animals were performed: (1) to determine the acute effects of nitric acid vapor alone, and in combination with ozone, on normal and sensitive human populations; (2) to determine the chronic effects of nitric acid vapor alone, and in combination with other pollutants, on public health; (3) to quantify the levels of exposure (i.e., concentration of acidity and duration of exposure) that result in adverse health effects; and (4) to determine whether an atmospheric acidity standard was needed to protect public health.

Animal studies suggest several potentially important effects following multi-day, extended exposures to ambient levels of acidity: (1) lung architecture was altered such that lung elasticity was reduced; (2) macrophage functions that play a key role in lung defense were activated; and (3) when nitric acid was combined with ozone, airway reactivity was decreased. However, these studies were performed with concentrations of acid considerably in excess of ambient (Mautz et al., 1996; Schlesinger et al., 1995).

Evidence for an interaction between nitric acid vapor and ozone also comes from animal studies. A study involving rats showed that an increase in elastase activity (suggesting early fibrotic changes in lung tissues) occurs after short-term exposures to ozone, but the magnitude of the response was decreased in the presence of nitric acid vapor (Phalen et al., 1992). Thus, some responses may show attenuation when ozone is also present, while others may be exaggerated. In rabbits, airway reactivity in normal animals was almost completely absent after extended exposures to a combination of ozone and nitric acid vapor. Similarly, macrophages, a major cell population involved in lung defenses, were more severely affected by combined exposures than by either ozone or nitric acid. Again, the acid concentration was higher than ambient.

Clinical studies indicate that acute exposures to nitric acid (up to 200  $\mu\text{g}/\text{m}^3$  for 2-hour exposures) do not induce adverse respiratory changes in healthy people (Roger et al., 1992). Also, nitric acid in combination with ozone appeared to reduce the effects seen from exposure to ozone alone for a variety of lung functions (e.g., adverse changes in breathing capacity, airway reactivity, and biochemical mediator levels.).

Balmes (1995) compared the responses of allergic asthmatics to 0.2 ppm ozone, and a mixture of 0.2 ppm ozone and 150  $\mu\text{g}/\text{m}^3$  nitric acid. There were no significant differences between the responses of the subjects to the two conditions. Balmes (2000) and Solomon (2000) also compared the responses of healthy subjects exposed to similar conditions. They reported that addition of nitric acid to the exposure did not alter the subjects' pulmonary function or

inflammatory responses, compared to exposure to ozone alone. Thus, there is no indication from these studies that nitric acid exacerbates responses to ozone in either asthmatics or nonasthmatics.

Sheppard et al. (1988) exposed asthmatics to aerosols of sulfuric acid, nitric acid, a 1:1 mixture of sulfuric acid and nitric acid, and physiological saline. All aerosols induced mild bronchoconstriction, although there were no differences between the responses to saline and the three acid conditions in their potency in inducing bronchoconstriction. The authors suggested that hypoosmolarity of the aerosol relative to the osmolarity of the airways was a factor in the degree of response, rather than acid.

The Children's Health Study, a 10-year project that began in 1991, is characterizing exposure-response relationships in 5400 school children in southern California (Peters, 1994). This study evaluated whether long-term exposure to air pollution during childhood leads to changes in lung function, incidence of respiratory disease, or other identifiable adverse health effects during growing years. Various air pollutants, including ambient acidity, were monitored in the 12 communities where the study was conducted. The findings showed associations between  $\text{NO}_x$ , PM10, and nitric acid and decreased rates of lung function growth in the children living in the most polluted cities. However, these are co-pollutants, and it is not known which agent is responsible for the reduced lung function growth.

Overall, sponsored studies suggest that brief exposures (i.e., up to several hours per day) to airborne acidity at above-ambient concentrations do not appear to pose an acute health risk. Concerns regarding health impacts of long-term exposure to California's ambient acidity remain unsettled. The on-going Children's Health Study may provide information relevant to resolving the issue of effects of long-term exposure to nitric acid.

### C. Aquatic Ecosystems

The overall objective was to determine the effects of acidic deposition on water quality and biological populations in high elevation lakes and watersheds of the Sierra Nevada. As surface waters in the Sierra Nevada are among the most dilute (i.e., low dissolved analyte levels) in the world, they are vulnerable to the effects of acidic deposition. The acid neutralizing capacity (ANC) of surface water is a widely used measure of susceptibility to acidification. For example, an  $\text{ANC} \leq 100 \mu\text{eq/L}$  has been used as an indicator for streams or lakes that might be susceptible to acidification (Schindler, 1988). In surveys by the USEPA and University of California at Santa Barbara, 65 and 74 percent of the lakes in the Sierra Nevada have ANC values  $\leq 100 \mu\text{eq/L}$ , respectively (Melack and Stoddard, 1991; Engle and Melack, 1997). Thus, there is a potential for acid-caused damage to lakes and watersheds in the Sierra Nevada. In the following sections, the major findings identified in a summary report by Engle and Melack

(1997), relative to annual solute deposition rates, lake-outflow chemistry, biogeochemical cycles, and biotic effects of episodic acidification are presented.

## 1. Annual Rates of Solute Deposition in the Sierra Nevada

Mean annual wet deposition rates (kg/ha) to high elevation watersheds were 0.03-0.06 for  $H^+$ , 0.3-1.1 for S (from sulfate), 0.3-1.2 for N (from nitrate), and 0.3-1.5 for N (from ammonium). While most of the  $H^+$ , chloride, and base cation (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $K^+$ ) deposition is provided by snowfall in winter, most of the nitrogen, sulfate, and organic acid deposition occurs as rainfall during non-winter months. One or more large rain events in summer or during snowmelt in the spring can cause higher than average solute loading. Summer rains in the Sierra Nevada are acidic, and large rainstorms have lowered the pH and ANC of Emerald Lake, a high elevation watershed in Sequoia National Park that was studied during the KADP and AAPP. Based on work done at Emerald Lake, the concentrations of key N-containing compounds in rainfall are greatly altered after contact with plant foliage. Nitrate concentrations in incident rain nearly doubled after contact with leaves of chinquapin, western white pine, and willow, due to leaching or washoff of dry deposition. In contrast, almost all of the ammonium in incident rain was retained by foliage. The net effect of foliage contact was to increase the concentration of nitrate (a strong acid anion) and to reduce the concentration of ammonium (an alkaline species), thus lowering the ANC of incident precipitation.

## 2. Lake Outflow Chemistry in the Sierra Nevada

Changes in the chemistry of lake outflow result from the interactions between snowmelt water and the soils, rock, and vegetation upstream of the lake, and biological and chemical in-lake processes (Engle and Melack, 1997). In high elevation watersheds, the chemical composition of lake-outflow differs greatly from the chemistry of snowmelt water. The importance of in-lake processes varies with the flushing rate of the lake during snowmelt; when flushing rates are high, the chemical composition of lake outflow differs little from lake inflow (Melack et al., 1998). The most commonly observed pattern was for pH to decrease as discharge increased, with the most acidic pH values occurring near the time of peak runoff. Changes in the pH of lake-outflow during snowmelt were not large, typically about 0.5 pH units. Minimum outflow pH ranged from 5.5 to 6.1, and was fairly consistent among years and among catchments. In comparison, patterns of ANC in lake-outflow were more consistent than patterns in outflow pH. Dilution was the primary factor in ANC depression during snowmelt (Leydecker et al., 1999). Surface water acidification accounted for <10 percent of the ANC decline in shallow, rapidly flushed lakes, and 25-35 percent of the decrease in large volume lakes or those with slower catchment melting rates. In lakes where acidification was important, acidity due to nitrate and sulfate were contributed equally during the first half of snowmelt, while sulfate dominated the latter half. Minimum values of ANC usually occurred at or near

peak runoff. During snowmelt, ANC usually declined by about 50 percent, reaching minimum values of 15-30  $\mu\text{eq/L}$ .

### 3. Biogeochemical Cycles in the Sierra Nevada

Analyses of long-term data sets indicate that biogeochemical cycles are changing in response to selected climatic factors. Drought was responsible for a doubling of sulfate concentrations in Ruby Lake in the eastern Sierra Nevada, and likely contributed to a decline in surface water nitrate levels in Emerald Lake Watershed in Sequoia National Park (Sickman and Melack, 1998). A similar, contemporaneous decline in nitrate was also reported in a nearby, mixed conifer watershed (Williams and Melack, 1997). Phytoplankton growth in Emerald Lake, once thought to be phosphorus limited, has shifted toward N limitation in response to lower inputs of N from catchment runoff (Sickman and Melack, 1998). Because of atmospheric N deposition, Lake Tahoe has shifted from colimitation by N and phosphorus to persistent phosphorus limitation (Jassby et al., 1994). These authors hypothesize that the relative amounts of N and phosphorus available for phytoplankton growth has shifted over the past 10 years due to atmospheric deposition. Long-term monitoring of nitrate concentrations in the Emerald Lake outflow has also shown that N export is sensitive to the duration and longevity of the seasonal snowpack. During wet winters, snowpacks persist well into the summer. Peak nitrate levels in the Emerald Lake outflow were about 50 percent greater than in drier years, and high nitrate levels were observed late into summer. Higher nitrate concentrations may have delayed the N limitation of phytoplankton growth.

### 4. Effects of Episodic Acidification on Aquatic Biota

Currently, surface waters in the Sierra Nevada are not acidic enough to threaten the juvenile or adult stages of Sierra Nevada amphibians (Engle and Melack, 1997). However, chemical factors related to low pH may be responsible for the lack of mountain yellow-legged frog tadpoles in lakes with pH < 6.0. The most important factor governing the distribution of amphibians at high elevation is likely to be the presence/absence of introduced trout species; juvenile stages of amphibians will be excluded by fish predation (Bradford et al., 1994).

Of the five species of trout found at high elevation in the Sierra Nevada, three species spawn in the spring (rainbow, golden, and cutthroat), and two spawn in the fall (brown and brook). Because the most acid-sensitive lifestages of spring- and fall-spawning trout occur at different times of the year, they are differentially at risk from episodic acidification (Jenkins et al., 1994). In spring, the fertilized eggs of spring-spawning trout are at risk from snowmelt water, which is considerably more acidic than pre-melt surface water. In summer, young fish may be damaged by episodic acidification due to runoff from rainstorms.

Episodic acidification of streams due to snowmelt or summer rains may decrease populations of some species of stream invertebrates. Vulnerable species identified in work done at Emerald Lake include the nymphs of mayflies and chironomid fly larvae (Hopkins et al., 1989; Kratz et al., 1994). When pH is lowered to 5.0 or below, for as little as eight hours, drift rates of vulnerable species increase, and much of the increased drift is due to mortality (i.e., drifting insects are killed by low pH). Knowledge that acid pulses in streams can cause temporary increases in drift is useful for developing lists of macroinvertebrate species that may become rare or absent in chronically acidified waters. However, drift induced by episodic acidification may not lead to reduced macroinvertebrate densities in a stream if there are upstream sources of live drift that can reoccupy sites left by acid-killed organisms. The impacts of episodic acidification will only be detectable if repeated acid pulses occur in a headwater stream, which decreases macroinvertebrate densities over large stretches downstream.

Using the 1985 USEPA Western Lakes Survey, it was estimated that none of the 114 lakes sampled in the Sierra Nevada had been episodically acidified ( $ANC < 0$ ) (Leydecker et al., 1999). These workers predicted that approximately six and ten percent of Sierra lakes would become episodically acidified if nitrate and sulfate deposition increases by 50 and 150 percent, respectively. No lakes would be chronically acidified in response to the above increases in nitrate and sulfate deposition.

#### D. Forest Ecosystems

The overall objective of this research program was to evaluate the effects of acidic deposition and ozone on forests, in the context of a long-term, chronic environmental stress (Takemoto, 1999). This objective was chosen in consideration of ozone being the primary air pollution stressor of vegetation in California, and the potential for interactive effects with atmospheric nitrogen. There were three projects that provided the major findings concerning the combined effects of N-derived acidic deposition and ambient ozone on conifer forests in California. In a field chamber study (Helms et al., 1994), exposure to ozone caused moderate reductions in photosynthesis and stomatal conductance in mature branches and seedlings of ponderosa pine. Negative impacts were greater in mature branches than seedlings, suggesting that effects on growth could be greater in older trees vs. seedlings or saplings.

The other two projects (Miller et al., 1996a; 1996b) were conducted at Barton Flats in the San Bernardino Mountains. Barton Flats is about 20 miles east of Camp Paivika, where N-saturation has occurred (Fenn et al., 1996). At Barton Flats, ambient ozone levels (12-hour average daytime concentration  $\approx$  60-65 ppb) and N deposition rates (2-14 kg N/ha/yr) are lower than at Camp Paivika (i.e., 70-80 ppb ozone and 30-40 kg N/ha/yr). Throughout the San Bernardino Mountains, ozone has injured pine tree foliage, and due in part to the large

volume of leaf litter on the forest floor, pine seeds are unable to germinate consistently, and fir and cedar are slowly becoming the predominant tree species in the vegetation zone. Amounts of base cations in soil are high, so the threat of soil acidification/aluminum toxicity is low, especially compared to S-derived acid deposition effects in the eastern U.S. Measured levels of nitrate in soil water were found to be higher than any levels reported in U.S. and European forests. Using the Nutrient Cycling Model (Johnson and Lindberg, 1992) for Barton Flats, it was postulated that at current levels, N deposition was not sufficient to cause N-saturation. However, if levels increased to rates found at Camp Paivika (35 kg N/ha/yr), N-saturation and nitrate contamination of groundwater could occur within the next 40 years.

Following these studies, two important knowledge gaps remain:

- (1) Are projections of N-saturation, based on data collected over a 3-year period, an accurate representation of what may happen over the next 20-50 years?
- (2) If atmospheric N deposition rates decrease due to the NO<sub>x</sub> control measures in the SIP, how quickly will ecological improvements occur, if at all?

Whether N-saturation occurs in forests other than at Camp Paivika can only be determined if forest conditions and air quality are monitored over the next 20-50 years. Reports from Europe indicate that severe nitrate leaching from soil may be reversible within 1-2 years after N deposition rates are lowered to near background levels (5 kg N/ha/yr or less). In consideration of the paradigm for forest N-saturation (Aber et al., 1989), additional research would be of limited benefit, but monitoring forest health and air quality would be useful to determine if changes occur at hypothesized time scales in California, where rainfall amounts are low during the growing season.

#### E. Agricultural Crops

The objectives of this research program were: (1) to assess the acute effects of acidic fog on winter and summer crops, and (2) to investigate acidic deposition effects on agricultural soils.

##### 1. Acute Effects on Crops

The acute effects of acidic fog on crops were of concern in the 1980s following reports of adverse S-derived fog and aerosol effects on human health (Graham, 1991). Two studies were funded to evaluate effects on winter and summer crops (Olszyk et al., 1987), and two species of conifer seedlings (Bytnerowicz et al., 1989). As the most extreme fog exposure, a pH 1.7 fog treatment was applied to simulate the pH 1.69 fog measured in Corona Del Mar by Hoffman and co-workers at the California Institute of Technology (Jacob et al., 1985). The responses of five crops were examined, and four crops exhibited

yield reductions following 11 weeks of exposure to pH 1.7 fog (Olszyk et al., 1987). The damage to leaves caused by pH 1.7 fog decreased the amount of crop leaf area capable of performing photosynthesis. The observed reductions in crop yield were largely explained by decreases in whole plant photosynthesis. Similar findings were reported for white fir and ponderosa pine seedlings exposed to pH 2.0 fog for six weeks (Bytnerowicz et al., 1989).

The results of these two studies, using a predominantly N-derived vs. S-derived acidic fog, were similar to what was found by researchers in the Midwest and East. Unless the acidity of precipitation or fog is more acidic than pH 3.0, there is little damage to crop or seedling-tree leaves, and only minor reductions in growth or yield (Mutters, 1992). The only information gap that needed to be addressed was the effect on soil -- Would annual applications of N and S eventually cause adverse changes in soil quality? In terms of ARB's air quality goals, the findings suggest that current farm practices provide an adequate measure of protection against the harmful effects of acidic deposition, and far greater decrements in growth and yield result from exposure to ambient ozone.

## 2. Effects on Soil Chemistry

Concern over the effects of acidic deposition on agricultural soils emerged as a result of findings that suggested that excess inputs of N and S could lead to trace element nutrient deficiencies (e.g., calcium). In a report by Mutters (1995), the nutrient requirements of selected crops were compared against annual inputs from fertilizer and the atmosphere to determine if imbalances could develop. Of the three elements examined (N, S, and calcium), there was a limited possibility that atmospheric N deposition could contribute to a build-up of nutrients that could adversely affect crop productivity. Given the lack of direct acidic deposition impacts on crop growth or yield, no additional research is needed. In terms of ARB's air quality goals, current farm practices appear to provide adequate protection from the harmful effects of acidic deposition.

## F. Man-made Materials

The objective of this research program was to assess the economic cost of damage caused by atmospheric acidity on man-made materials and structures.

All research for this program was completed in 1993. Studies conducted in both the KADP and AAPP did not identify any significant damage to materials due to atmospheric acidity. While laboratory analyses indicate that NO<sub>2</sub> and nitric acid may damage painted surfaces, aluminum, and nylon fabric (Mansfeld et al., 1988), field studies in southern California found corrosion rates to be similar to rates in sites with clean air (Mansfeld and Henry, 1993). For painted wood surfaces in the SoCAB, estimated annual cost savings from a 10 percent

reduction in ambient NO<sub>2</sub> were well below the cost of NO<sub>x</sub> controls (Horst, 1990). In terms of ARB's welfare protection goals, current levels of ambient acidity pose only a minor threat, in terms of economic cost, to man-made materials in California.

### *III. Recommendations*

#### A. Atmospheric Processes

Acid deposition in California is generally localized within individual air basins, whereas in the eastern U.S. it is regional. The results of air quality modeling studies indicate that most nitric acid, its precursors, and related acidic N compounds deposit soon after they are emitted or formed in the atmosphere (Russell et al., 1985). This implies that long-range transport of acidic compounds is not as significant in California as are local transport phenomena within air basins. California's meteorology and topography also favor local transport over long-range transport in most cases.

While California does not have an ambient air quality standard for acidic air pollutants, emissions of precursors have declined since the 1960s due to changes in industrial practices, improvements in technology, and the adoption of control measures for ozone, PM<sub>10</sub>, SO<sub>2</sub>, sulfate, and NO<sub>2</sub>. Lowering emissions from motor vehicles will continue to be emphasized for numerous reasons and will have the effect of preventing future increases in N deposition. Also, the Board has developed and is currently refining plans for a PM control and research program. These efforts are designed to enable California to meet state and federal PM standards. The PM research efforts will address issues related to the chemical nature, sources, atmospheric transformations, and transport of PM, as well as key aspects of health and welfare impacts. The data will also provide an improved means for estimating impacts on visibility, toxic air contaminants, and acidic aerosol concentrations and composition.

#### B. Human Health

While it is clear that exposure to ambient acidity can be linked to a variety of health effects, most studies have looked only at acidic sulfate particles (Schlesinger and Lippman, 1996). This is of limited value in California because the bulk of ambient acidity in California is due to vapor-phase nitric acid and to a lesser extent, hydrochloric acid (Appel et al., 1984; 1991). Further research on acidic compounds found in California would be required before the need for an ambient air quality standard to protect human health could be considered. Initial efforts should focus on identifying what components of ambient air are responsible for adverse acid-related impacts on human health.

### C. Aquatic Ecosystems

To detect acid deposition-caused changes in the hydrochemistry and biology of high elevation Sierra Nevada watersheds, monitoring activities at selected sites would need to be continued. While future changes in hydrochemistry and biology may result from atmospheric N rather than acidity, excess N could directly affect rates of biogeochemical processes in both the terrestrial and aquatic components of watersheds, and/or indirectly alter the trophic status and species composition of surface waters (Engle and Melack, 1997). Additional research and experimentation on the effects of excess nutrient deposition is needed to understand ecosystem-level effects since efforts to date have revealed inter-annual trends in chemical responses in the Sierra Nevada. Biennial measurements of snow and lake-water chemistry could be performed to track long-term impacts in habitat quality.

### D. Forest Ecosystems

Ambient ozone is the primary air pollution stress that has direct effects on tree health over a multi-year time scale. In comparison, atmospheric N will principally effect soil and groundwater chemistry on a multi-decade scale. The combined, adverse effects of ambient ozone and atmospheric N are evident in the San Bernardino and San Gabriel Mountains in southern California (Miller et al., 1996a), but it remains to be seen whether similar effects will occur in the Sierra Nevada, where adverse effects from ambient ozone alone have been observed (e.g., Sequoia-Kings Canyon National Park).

Among ARB's air quality goals (cf. Health & Safety Code sections 39600-39606) is the protection of human welfare in California. Findings from ARB-sponsored studies provide evidence that in combination, ozone and atmospheric N has adversely impacted some mixed conifer forests in southern California. If exposures to ambient ozone and atmospheric N remain the same, other heavily exposed forests could also become N-saturated (Fenn et al., 1998). In future years, surveys of ozone damage to pines and regional-scale monitoring of ozone and nitrogen gases using passive samplers could be conducted on a triennial-basis to assess changes in forest condition.

In terms of forest structure, the concern is the increased presence of fir and cedar (and a coincident increase in fire susceptibility), and nitrate contamination of water supplies that may be used for human consumption. Critical loads of 10-15 kg N/ha/yr have been proposed to protect forests from N saturation in Europe (Nilsson, 1988), where ozone levels are much lower than in California. A load of similar value may be applicable to California albeit uncertainties with respect to the co-deposition of ozone and lack of concurrent S-derived pollutant deposition. Given that ground water contamination by nitrate may already have occurred, impacts on drinking water supplies are of greatest near-term concern. In recognition of the far-reaching control measures contained

in the State Implementation Plan for ozone (ARB, 1994b), it is unlikely that more can be done to mitigate future ecological deterioration from ozone and atmospheric N.

#### E. Agricultural Crops

As for forest ecosystems, ambient ozone is the air pollutant of greatest concern with respect to crop productivity. Current levels of H<sup>+</sup>, N, and S deposition do not pose a serious threat to agricultural crop production in the state (Olszyk et al., 1987). Unless deposition rates reach levels that are two or more times current rates of deposition, no additional monitoring or research is needed, nor is an ambient air quality standard necessary to protect agricultural vegetation or soil health (Mutters, 1995).

#### F. Man-made Materials

Acidic deposition currently poses only a minor threat to the integrity of man-made materials in the SoCAB (Horst, 1990). Absent significant damage in this region of the state, additional monitoring or research may only be needed to assess potential stone decay to cultural resources (cf. NAPAP, 1993). An ambient air quality standard to protect against damage to man-made materials is not warranted based on current knowledge.

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