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The Atmospheric Acidity Protection Program (AAPP) Assessment Workshop was convened in January 1995 to bring together working groups of the California Air Resources Board, including the Scientific Advisory Committee on Acidic Deposition, the Research Screening Committee, and Air Resources Board staff, with research contractors to review the extent and severity of the acidic deposition problem in California. The AAPP was established by the California State Legislature in 1988 to investigate the causes and effects of acidic deposition in the state. It succeeded the Kapiloff Acid Deposition Act of 1982, and its purpose was to conduct further research in areas of uncertainty identified in the Kapiloff Program. Presently, the AAPP is nearing completion. The presentations of research results by contractors and the discussions of their work are documented herein, and are an important source of scientific information for policy-makers charged with deciding whether an ambient air quality standard for acidic air pollutants should be set in California. Presentations at the Workshop were given in four areas of study: forest ecosystems, atmospheric processes and monitoring, aquatic ecosystems, and human health.

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Atmospheric Acidity Protection Program Assessment Workshop

Final Report

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December 1995

ATMOSPHERIC ACIDITY PROTECTION PROGRAM ASSESSMENT WORKSHOP

Sponsored by:

The California Air Resources Board

January 26 -27, 1995

Chairperson:

William J. Mautz, Ph.D.

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This report was submitted in fulfillment of CARB Contract 93-336, "Atmospheric Acidity Protection Program Assessment Workshop," by the University of California under the sponsorship of the California Air Resources Board. Work was completed as of June 30, 1995.

DISCLAIMER

The statements and conclusions in this report are those of the contractor and workshop participants and not necessarily those of the California Air Resources Board. This report is a transcript of audio recorded proceedings of the workshop. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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I. OBJECTIVE OF THE ATMOSPHERIC ACIDITY PROTECTION PROGRAM ASSESSMENT WORKSHOP.

The objective of this workshop was to present a forum for discussions among the ARB Scientific Advisory Board, ARB Research Screening Committee, ARB staff, and research contractors on the extent and severity of the acidic deposition problem in California. The contractor presentations and discussions will assist policy-makers in deciding whether an ambient air quality standard for acidic air pollutants is needed in California.

The workshop was held at the Country Side Inn and Suites, 325 Bristol St., Costa Mesa, California on January 26 and 27, 1995.

II. AGENDA.

Thursday, January 26, 1995

10:30 **Opening Remarks**

John Holmes

James Morgan

Session 1. Forest Ecosystems

11:15 Brent Takemoto, moderator

Forest Air Quality in California

John Watson, Desert Research Institute

Judith Chow, Desert Research Institute

Atmospheric Deposition in California Forests: Results from Branch Washing and Process-Level Modeling

Andrzej Bytnerowicz, USDA Forest Service

George Taylor, University of Nevada

12:30 LUNCHEON

1:30 **Air Pollution Effects on Tree Health**

Mark Fenn, USDA Forest Service

Patrick Temple, SAPRC, UC Riverside

Air Pollution Impacts on Soil Biogeochemistry: Field Results and Modeling

Mark Poth, USDA Forest Service

Dale Johnson, Desert Research Institute

Session 2. Atmospheric Processes.

2:30 Nehzat Motallebi, moderator

A Summary and Evaluation of CADMP Data

Charles Blanchard, Envair

3:35 BREAK

3:45 **Evaluation of Sampling Methodology for Acidic Species**

Dennis Fitz, CE-CERT, UC Riverside

New Developments Concerning the Size Distributions of Acidic Aerosols

Walter John, Private Consultant

Fog and Cloud Chemistry in California

Michael Hoffmann, California Institute of Technology

Mathematical Modeling and Control of the Dry Deposition Flux of Nitrogen-Containing Air Pollutants

Glen Cass, California Institute of Technology

Development of Urban and Regional Acid Deposition Models for California

John Seinfeld, California Institute of Technology

5:45 Open Discussion

6:30 Closing Comments

Friday, January 27, 1995

8:30 Opening Remarks — John Holmes, James Morgan

Session 3. Aquatic Ecosystems

9:00 Stephen Brown, Moderator

Atmospheric Deposition and Catchment Solute Balances as Assessments of Acidity in the Sierra Nevada

John Melack, UC Santa Barbara

Rock, Water and Soil Interactions at Sierra Nevada High Elevations

Aaron Brown, UC Santa Barbara

Episodic Acidification During Snowmelt in High Elevation Sierra Nevada Lakes

John Stoddard, U.S. EPA

10:35 BREAK

10:45 **Integrated Hydrochemical Modeling Applied to the Emerald Lake Watershed**

Roger Bales, University of Arizona

Evaluation of Acid Deposition Effects on Sierra Nevada Aquatic Invertebrates and Fish

Scott Cooper, U.C. Santa Barbara

Summary of Effects of Acid Deposition on Amphibians in the Sierra Nevada

David Bradford, U.S. EPA

12:30 LUNCH

1:30 **Assessing the Impact of Acid Deposition in Sierra Nevada Aquatic Ecosystems: Tying Together the Hydrochemical, Biogeochemical and Biological Processes**

Diana Engle, U.C. Santa Barbara

Session 4. Human Health

2:05 Dane Westerdahl, moderator

2:30 **Clinical Studies**

John Balmes, U.C. San Francisco

2:40 BREAK

3:00 **Animal Studies**

William Mautz, U.C. Irvine

Richard Schlesinger, New York University

3:30 **Status of Epidemiological Studies**

Dane Westerdahl, CARB

Helene Margolis, CARB

4:15 Open Discussion and Closing Comments

III. WORKSHOP PROCEEDINGS.

A. OPENING REMARKS.

MR. MANJIT AHUJA FOR DR. JOHN HOLMES, CHIEF, RESEARCH DIVISION, AIR RESOURCES BOARD.

I want to welcome you all to this assessment meeting. The purpose of this meeting is to pull together an overview of what we have done over the last 10 years. There is an extensive amount of research conducted under the Kapiloff Act and Share Act over the last 10 years. When we started this research the Air Resources Board was new to ecological research, and we know a lot more today. Thanks should go to the researchers that have helped us in advancing valuable information on the effects of acid deposition. The purpose of this assessment is to come up with the blueprint that will be used by the staff to develop a report to be submitted to the governor and the legislature. Our target is August 1996. Along the way, we received extensive help from the Scientific Advisory Committee. The Scientific Advisory Committee gave us guidance and wisdom, reviewing stacks of proposals and draft final reports at every meeting and helping us go through the research process. At the helm of the Scientific Advisory Committee is Dr. Morgan, who made sure that the state focused on the issues at hand, and I am going to request Dr. Morgan to give you some comments on that process.

DR. JAMES MORGAN, Chairman, Scientific Advisory Committee on Acid Deposition:

The Atmospheric Acidity Protection Program was established by the legislature in 1988. It succeeded the Acid Deposition Act of 1982, known as the Kapiloff Act. The purpose of the Atmospheric Acidity Protection Program is, in fact, to act on the original findings of the Kapiloff Program and to oversee and drive the additional research that would be needed in order to achieve the objectives of the program. It is interesting to read the 1988 act, sometimes known has the Share Bill, because it originated in the legislature with Assemblyman Share carrying it. It found that "the deposition of atmospheric acidity resulting from other than natural sources alone or in combination with other man-made pollutants and naturally occurring phenomena could have potentially significant adverse effects on public health, the environment, and the economy". The Share Bill in 1988 was moving forward from what was learned in the first five years of the program under the Kapiloff Act. The AAPP has been implemented by the Air Resources Board, and (again from the original legislation), "with the active assistance of the Scientific

Advisory Committee on acid deposition". James said that we gave wisdom and guidance; I would say we spent a lot of our time giving grief. In other words, the discussions, as I think they will be today, were frank. Critical questions have to be asked in order that the Air Resources Board benefits as much as possible from the information being provided by you, the researchers. I hope that a lot of the discussion today tries to draw out the significance and the possible policy implications of what we are finding in these different areas, and, with that in mind, let me identify the members of the Scientific Advisory Committee beginning with Dr. Nancy Brown, Dr. John Moore, Dr. Jim Pitts, Dr. Ralph Perhac, Dr. Freeman Allan, and Dr. Paul Miller.

As Manjit has said, the reason for holding the workshop is that the AAPP is nearing the concluding stages of the process which was set in motion in 1988. I quote from the legislation whose purpose is "the development adopted standards, that is the extent supportable by scientific data at levels which are necessary and appropriate to protect public health and sensitive ecosystems from adverse effects resulting from atmospheric acidity". In other words, we are directed to the following question: Are there standards that should be developed on the basis of the scientific information generated in recent 10 years of research work? Every year the Air Resources Board sends a report to the governor and the legislature, and the most recent one of September 1994, I think becomes available for public distribution very soon. In the 1994 report covering the 1993 year, the Board summarized what has been learned and what is still under investigation in six areas: air quality monitoring, atmospheric processes, aquatic ecosystems, forest ecosystems, human health, and manmade materials. We will be hearing on five of those areas in this workshop. We will not addressing the subject of manmade materials in this workshop.

Progress was reviewed in nine specific research objectives, and it is worthwhile noting what they are. If you want to study them more, look for them in the report to the governor in the legislature.

1. Document trends in atmospheric acidity and acidic deposition.
2. Quantify source receptor relationships to relate pollutant emission patterns to acidic deposition patterns.
3. Compute regional deposition flux of acidic gases and particles for the entire state.
4. Examine trends in the chemistry of surface waters and biological populations in watersheds of the Sierra Nevada.
5. Characterize the level to which forests are exposed to acidic deposition and ozone and the extent of air pollution damage to vegetation and soils.
6. Investigate the effects of atmospheric acidity alone and in combination with ozone on human health.

Very early in the work of the Scientific Advisory Committee, we took the position that the acidic deposition problem should not be viewed as a problem in isolation, uncoupled from the larger issue of air pollution and possible interactions with ozone, other oxidants, and other problems that emerge. In

other words, it is not really possible in our view to treat acid deposition as a stand-alone phenomenon, especially in a state as complex as California.

7. Determine the economic cost of damage to manmade materials that results from acidic deposition.

8. Evaluate the need for ambient air quality standard for atmospheric acidity to protect human health, this includes concentration of acidity and possibly specific forms and kinds of acidity in the atmosphere.

9. Lastly, assess the need for an acidic deposition standard to protect sensitive resources in aquatic and terrestrial ecosystems.

Now the ARB aims for an ASSESSMENT - that is the word with a capital A, received from the governor as capital A - an ASSESSMENT of all that has been learned to date on causes and effects of acidic air pollutants and formulating a recommendation on acidity standards.

Do we have a scientific basis for an atmospheric acidity standard? Do we have the scientific basis for an acid deposition standard? This workshop is an initial step in advancing the assessment which the board hopes to complete at least a preliminary level. The Scientific Advisory Committee, and I think I speak for all of us, is delighted to at last meet you, the people who have been doing the research. For years we have seen your names, and we have seen final reports, and now we are going to have the opportunity to discuss science with you as individuals and to get closer to the goal of the assessment. So I look forward to getting contributions and helping to shape the assessment as we move toward next fall and next year.

B. SESSION 1. FOREST ECOSYSTEMS. BRENT TAKEMOTO, MODERATOR.

DR. BRENT TAKEMOTO: Air Resources Board

I am Brent Takemoto, and I am in the research division at the Air Resources Board. The first session today is going to be on the Forest Ecosystems Program. The intent, as Dr. Morgan mentioned earlier, was to look at the combined effects of ozone and nitrogen deposition on both forest vegetation and soils. There were two main projects funded in the Forest Ecosystems Program. Both of these studies looked at the effects of air pollution at Barton Flats in the San Bernardino National Forest. Barton Flats represents a mid point along the west-east gradient of both ozone and nitrogen deposition in that region of California, and various effects on soils and the mix for forests were examined by a team of investigators.

In this morning segment, we will look first at air quality at the Barton Flats site and in other regions of California. Dr. John Watson from the Desert Research Institute will make that presentation. The next presentation will examine levels of ozone and nitrogen dioxide deposition experienced by both forest ecosystems in Barton Flats. That presentation will be made by two investigators, 1) Dr. George Taylor, from the University of Nevada, Reno, and 2) Dr. Andrzej Bytnerowicz of the U.S. Forest

Service in Riverside.

With that introduction, I would like to introduce Dr. John Watson from the Desert Research Institute.

1. Forest Air Quality in California. Dr. John G. Watson and Dr. Judith C. Chow. Desert Research Institute.

DR. JOHN WATSON: Desert Research Institute

I am going to talk today about wet deposition, ozone, and meteorological measurements in the San Bernardino mountains (Fig. 1). I am going to give a brief overview that address these project objectives (Fig. 2). One is to acquire a data base of specified accuracy, precision, and validity for the determination of wet and dry deposition of reactive atmospheric species. Notice the term reactive rather than acidic. Materials that react with each other in the atmosphere and with plant life to cause damage are not necessarily acidic. The second objective is to determine forest exposures to reactive atmospheric species during different times of day and throughout the year. The final objective is to identify relationships between atmospheric concentrations and meteorological conditions. Figures 3 and 4 show measurements from the Statewide Dry Deposition Network throughout the state during winter and summer. The urban sites are Fremont (FR), Sacramento (SR), Bakersfield (BA), Santa Barbara (SB), Long Beach (LB), Downtown Los Angeles (LA), and Azusa. The non-urban sites are Gasgret (GA), Yosemite (YO), and Sequoia (SE). Daytime and nighttime averages are shown. The variables shown correspond precisely to the measurements taken at Barton Flats. The variables shown are sulfur dioxide (SO_2), sulfate (SO_4), nitric acid (HNO_3), particulate nitrate (NO_3p) and ammonium ion (NH_4). Most of the daytime at Yosemite and Sequoia are at the 1 or 2 micrograms per cubic meter range, much lower than urban values. Concentrations of several species, particularly nitric acid are higher during the daytime as opposed to the night. During winter, concentrations of reactive species are not significant at Yosemite and Sequoia. During the summer (Fig. 4), however, concentrations are higher, especially for nitric acid.

Although reactive species are quantifiable at these forested sites, they are not found at extremely high levels that might allow effects on forests to be detected. The concentrations suggest a north-to-south gradient. These results indicated that a worse case situation should be studied. Barton Flats in the San Bernardino Mountains northwest of Los Angeles was a candidate (Fig. 5). This site, located nearly 7000 ft above sea level, is a potential recipient for some of the pollutants that are generated in the South Coast Air Basin.

The measurements (Fig. 6) were similar to those in the California Acid Deposition Monitoring

Program (CADMP) which are still being taken today. Measurements were taken on a six day schedule with morning, and afternoon samples and including deposition and ambient air samples. Wet deposition samples were taken on a weekly basis, and hourly-average ozone measurements were taken continuously. The measurements were compatible with other measurements taken throughout the state and with comparable methodologies.

The variable measured are summarized in Figure 7, and they are incorporated in a data base that has been extensively validated and includes regular meteorological measurements and hourly ozone data measurements. When we talk about dry deposition (Fig. 8) we are really talking about ambient concentration data that are converted to deposition based on certain assumptions about the movement of air and forest's capacity to remove these species from the air.

Figure 9 shows a ozone and meteorological values for January of 1992. As expected, there is little photo-chemical activity; ozone levels are not high and peak at 60 parts per billion and 40 parts per billion. This is what we expect to see as background levels. The dotted line represents solar radiation, and it peaks near 1200 PST except when clouds and storms are present. Wintertime is a period of very low temperatures, high relative humidity and frequent precipitation. Much of the deposition is due to precipitation during winter.

Figure 10 shows ozone and meteorological data for April 1992, and we see more of a diurnal cycle in the ozone. Ozone peaks at about 1500 PST, later than the ozone peak in the South Coast air basin (1200 to 1300 PST). Notice also as time progresses, there is a little hump on the edge at about 2100 to 2200 PST. We will see a reason for that later on. This occurs quite frequently in hourly ozone concentrations at Barton Flats and reaches 200 parts per billion at mid-month. There are significant violations of the Ozone National Ambient Air Quality Standard (120 ppb) at this forested site. Notice that the ozone peak follows the maximum solar intensity by about three hours, and that very often we see a little bump on the edge of the peak occurring later in the evening. This bump appears a little earlier about 2000 to 2100 PST in the summertime when compared to spring, and it appears more frequently. Figure 12 shows results for October 1992, and there are similar to those of figure 10. Ozone follows the expected trend. We observed more intense ozone in the summertime, and we see a lag in timing of the ozone peak with respect to the time of peak ozone in the South Coast air basin. We also see the little secondary peak that pops up on the edge of the primary peak.

Figures 13 and 14 show examples of the ionic concentrations, and these are always less than or equal to the mass concentration, as they should be. In Figure 14, the ammonium ion concentration is calculated by assuming that all sulfate and nitrate are present as ammonium sulfate, and ammonium nitrate equals measured ammonium. Notice that when acidic ammonium bisulfate is assumed, excess ammonium ion is observed. All acidic sulfate has been neutralized by the time it arrives at Barton Flats.

With respect to the wet deposition (Fig. 15), the summer and fall are fairly dry. Precipitation events are few, and the amount of precipitation is low; most precipitation events are less than 1 inch. The pH values are not less than 4.3, and is often in the 5 and 6 range which is typical of water in equilibrium with dissolved carbon dioxide. We did record significant amounts of precipitation in the wintertime, predominantly as snow, as expected (Fig. 16), pH was lower than 5 in only a few cases, and wet deposition was not greatly acidic. When a low pH event occurred, the precipitate water volume was small.

Figures 17 through 20 show ionic composition of the wet deposition for different measurement periods. Ammonium nitrate and sulfate were present at significant levels. All ionic concentrations appear to rise and fall together between events. These ions are completely balanced in most of the samples with positive charges equivalent to negative charges. This is consistent with the neutral pH values observed.

Figure 18 and 20 show two events, on 3/3/92 and 5/11/92, that have very high concentrations relative to other events. Notice in Figure 16, however, that the amount of precipitation is very low. This indicates that most wet deposition probably occurs at the beginning of an event, and that subsequent precipitation tends to dilute these concentrations.

Figures 21 through 24 show daytime and nighttime concentrations exceeded 10 $\mu g/m^3$ on several occasions during October. Daytime and nighttime concentrations were often similar, except during October. Nonvolatile nitrate in Figures 21 through 24 does not account for changes during sampling owing to the changing equilibrium of ammonium nitrate particles. Actual particle nitrate concentrations are at least double what we are reporting in Figures 21 through 24. These values are comparable to nitrate concentrations measured by the South Coast Air Quality Management District. We saw a little chloride every now and then, but it was very low.

During winter (Fig. 22), all fine particle concentrations are low compared to other seasons. During the first part of the project when pH was measured, we never measured levels below pH 4 in the sample solutions. Figure 14 shows why pH is so low. Figure 14 compares ammonium concentrations calculated by assuming all fine particle nitrate was present as ammonium nitrate, and sulfate assuming sulfate was present as ammonium bisulfate or ammonium sulfate with measured ammonium. The squares in Figure 14 indicate ammonium assuming ammonium sulfate, and the X's represent the ammonium assuming ammonium bisulfate. We get a nearly perfect relationship between the measured and predicted ammonium for the ammonium sulfate assumption. This indicates that the fine particles are not very acidic.

Figures 26 and through 39 show total nitrate expressed as nitrate for four different seasons. Non-volatile nitrate is that which is measured on a normal PM10 sample. It is relatively stable and remains on the filter between sampling and chemical analysis. Volatilized nitrate was present in the atmosphere,

but owing to changes in temperature and relative humidity during and after sampling, it evaporates from the filter. Volatilized nitrate was captured in this study. The sum of volatilized and non-volatilized nitrate represents the total particle nitrate to which trees are exposed. Nitric acid (HNO_3) represents nitrate in the gas phase, though this can connect rapidly to particulate ammonium nitrate when sufficient ammonia is present and when temperatures decrease. Notice that the volatilized nitrate is typically two or three times higher than non-volatilize nitrate (Figs. 26-30). Total nitrate, the sum of all three components, is sometimes as high as 15 micrograms per cubic meter and it varies by time of day. Figure 30, which shows samples taken during the early morning, during the afternoon, and at night, demonstrates that nitrate concentrations are highest during afternoon. We suspect that the nitric acid values may be a lower limit owing to losses in the sampler prior to filter collection. This is because nitric acid sticks to everything. Our samplers are teflon-coated thoroughly washed, but still we believe that there may be some losses. The highest concentrations of the nitrate occurred in the fall period (Fig. 26), and this corresponds exactly to what we see within the South Coast Air Basin. Typically, the highest ammonium nitrate values at the Riverside and the Rubidoux sites exceed 100 micrograms per cubic meter during October. Figures 40-42 show the correspondence between concentrations in the basin and those found at Barton Flats.

Let's look at how concentrations at Barton Flats relate to those measured in the South Coast Air Basin. Figures 36-39 show wind roses for the 0700-1900, and 1900-1700 hours at the Barton Flats site. Barton Flats is in a valley that curves from the west to the south. During the daytime, we see very clear evidence of up slope flows from the west. Pollutants moves up from the Los Angeles basin into the mountains with these winds. At night there are very clear down slope flows from the south. Only during the winter are deviations from this pattern observed, probably owing to less solar heating of snow-covered slopes.

Figures 43 through 51 show typical flow patterns in the South Coast Air Basin during summer. From 0000 through 0500 hours, winds are calm in the basin with a strong down slope flow at Barton Flats. At 0600 (Fig. 45), the sun rises and heats mountain slopes and land surfaces, and the sea breeze commences. Notice there still is a down slope flow, but it is weakening. By 0700 (Fig. 46) we see a complete, full reversal at Barton Flats to an up slope flow. It is still pretty calm in the basin at 0700, but by noon (Fig. 47), easterly to northwesterly flow in the basin is well-established. The afternoon samples at Barton Flats commence, and Figures 40-42 show that this is when particle concentrations are highest. Everything moves up into the mountains at the same time as there is up slope flow. At 1600 (Fig. 48) flows are well developed, and there are high levels of ozone measured at Barton Flats. The highest ozone at Riverside is usually found between 1300 and 1400 hours, and the highest ozone at Barton Flats occurs a few hours later.

By 1700 hours (Fig. 49), the winds taper off. There is still a vigorous flow in the basin, but cooling of the slopes in shadow at Barton Flats decreases the up slope flow reversal. Even though there is good circulation and upward momentum there is a in the basin, the wind direction changes at Barton Flats by 1900 hours (Fig. 51), and the flow has completely reversed to its nighttime, down slope mode.

Remember that little ozone peak that followed the primary peak in figures 11 and 12? The pollutants move up the mountains in the afternoon, then we had the flow reversal, and the ozone came back down to produce a little peak in concentration after sunset. By the time we get to nighttime (Fig. 52), the flow is calm in the basin, but there is a vigorous down slope flow which has brought the ozone back down to Barton Flats. The pattern repeats itself during the summer and fall day after day with few exceptions.

Our conclusions at this point in the study are outlined in figures 53-54. First of all, ozone is the most frequently found reactive compound, and hourly peaks exceed 200 parts per billion. This exceeds the National Ambient Air Quality Standard of 120 ppb.

Wet deposition is not acidic, and pH normally exceeds 5.5. The lowest value is not below 4, and low values occurred in less than 1 inch of precipitation. Suspended particles are not acidic. Sulfate and nitrate concentrations are neutralized by ammonium. Sulfate is not a major component in suspended particles at Barton Flats, and concentrations rarely exceed 3 micrograms per cubic meter. I recently attended an EPA meeting in the eastern U.S. where it was claimed that "Sulfates are our biggest problem in this country. We really have to reduce sulfates". In the west, however sulfate is the major reactive component on only a few occasions. Particle nitrate is high at Barton Flats during summer and fall with daytime concentrations often exceeding 10 micrograms per cubic meter. Nitric acid is the most significant acidic species and achieves afternoon concentrations exceeding 6 micrograms per cubic meter. Actual levels may be higher than this owing to potential sampling losses, and we should consider this a lower limit for the nitric acid. The wind data at Barton Flats indicates that air moves up and down the valley during all seasons except in winter. Up valley flows correspond to transport from the South Coast Air Basin. The largest exposure in which trees experience all the reactive species from nitric acid to ozone, takes place between about noon and sunset during the summer. During other times of day and during winter, exposure is much less. There is no way to reduce this exposure without decreasing the reactive species concentrations that are generated in the South Coast Air Basin and transported to Barton Flats by afternoon up slope flows.

Q (AUDIENCE) I want to point out one thing. Since you have nitric acid only in the summer, this is really consequential to the state's epidemiologic study where they are making assumptions about children's habits, and they are assuming that children are spending 80-85% of their time indoors. They are not spending the time indoors in the summer, and the people that are doing the exposure

analysis should really take that into consideration when they look at the effects of acids.

A (DR. WATSON) I agree with that, and it is not just a matter of the season; the time of day is also important. During the nighttime or the early morning, when children are indoors, is not the time of highest nitric acid.

Q (AUDIENCE) One of the concerns of the committee has been the reliability of measurements involving the nitrate species. Several times in your presentation you made remarks to suggest that routine measurements are one thing and research measurements are another thing. If you look down the road for such testing standards, the ability to measure things meaningfully is going to be very crucial. What is your sense of that with respect to current studies?

A (DR. WATSON) I think this is a big issue not only in terms of forest studies but also for health effects studies. For example, EPA is considering use of a continuous device to monitor hourly mass concentrations. It is a well-engineered monitor, but it needs to heat the sample to 50 degrees C to operate properly. Particulate nitrate disappears at these temperatures. Ammonium nitrate concentrations are very sensitive to temperature. Nitric acid sticks to nearly everything, and the samples we used had Teflon coated surfaces to minimize HNO_3 deposition. Nevertheless, we believe were losing some HNO_3 prior to sampling, Dennis Fitz from UC Riverside will discuss this problem. However, we feel very confident about the particle values we measured. With a standard PM10 compliance monitor, one is not measuring up to 80% of the particulate nitrate during the summer. One alternative is to measure total nitrate, gaseous and particulate, and use this concentration as an upper limit on what the particle nitrate might be. When one inhales nitric acid, is there enough ammonia in the body to neutralize it and convert the gas to particles?

Q (DR. PITTS) What is your feeling about the contribution of organic acids (eg. formic and acetic acid) to the forest ecosystem, to the population exposed and to the general smog mass across the basin?

A (DR. WATSON) Organic acids are surly present in the forest, through we did not measure them. Most of them are in the gas as opposed to particle phase, and they do not shift between gas and particle phases as much as ammonium nitrate does. Organic acid concentrations have been commonly measured in forested areas, and I did not come prepared to discus organic levels. I remember that the formic and acetic acid concentrations measured at Yosemite and Sequoia during summer 1990 were higher than expected. As to health effects of organic acids, I don't believe the problem has been well studied.

Q (AUDIENCE) In regard to the risk assessment studies, that would be an area that is really important to follow through.

A (DR. WATSON) If there is concern about organic acids having adverse effects are forest

and health, their concentrations and exposure should certainly be quantified.

Q (AUDIENCE) What was the EPA's response to measuring mass at 50 degrees C?

A (DR. WATSON) The measurement method is designated as an equivalent method for determining compliance with the PM10 standards. It is a way to meet the standard, that is to volatilize particle mass so it won't be measured, but it is not necessarily the way to protect public health. If you come to me and say "Hey, I want to put in a monitoring network that is EPA approved and meets the standard", I can tell you exactly how to do that. I know every trick, and evaporating the particles is one of them.

DRY AND WET DEPOSITION, OZONE, AND METEOROLOGICAL MEASUREMENTS IN THE SAN BERNARDINO MOUNTAINS

Dr. John G. Watson
Dr. Judith C. Chow
Mr. Clifton A. Frazier

Desert Research Institute
Energy and Environmental Engineering Center
University and Community College System of Nevada
Reno, NV

Figure 1

PROJECT OBJECTIVES

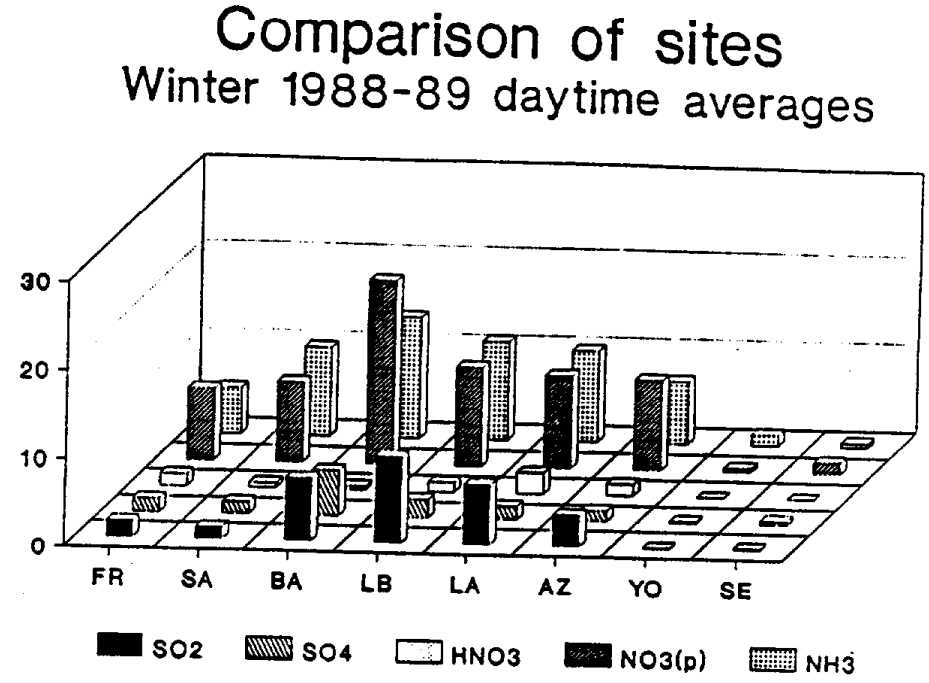
Acquire a data base of specified accuracy, precision, and validity for the determination of wet and dry deposition of reactive atmospheric species in forests.

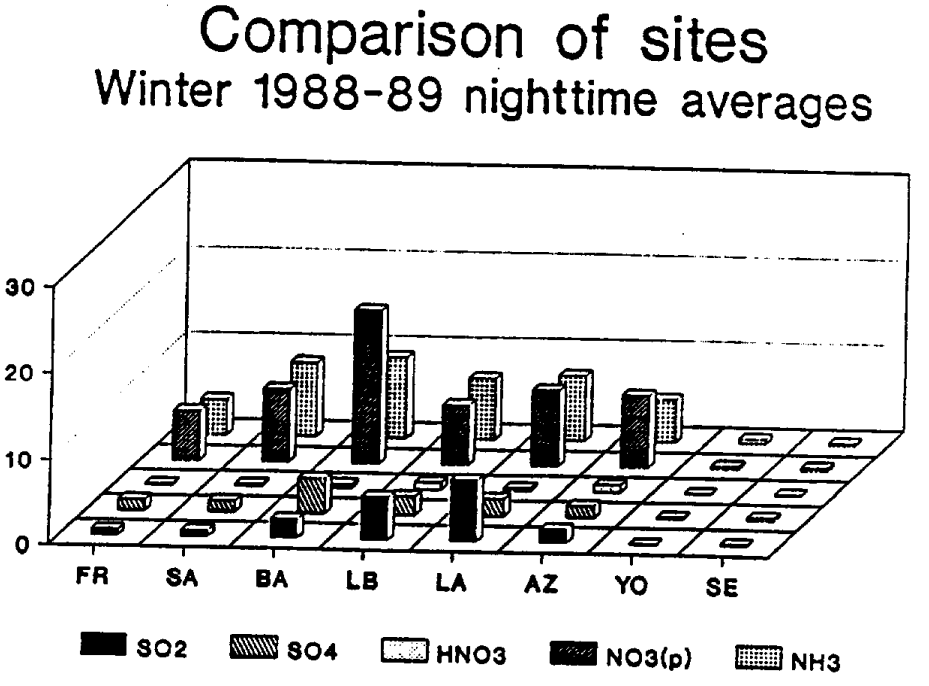
Determine forest exposures to reactive atmospheric species over multi-year, seasonal and daily time periods.

Identify relationships between atmospheric concentrations and meteorological conditions that affect transport and deposition.

Figure 2

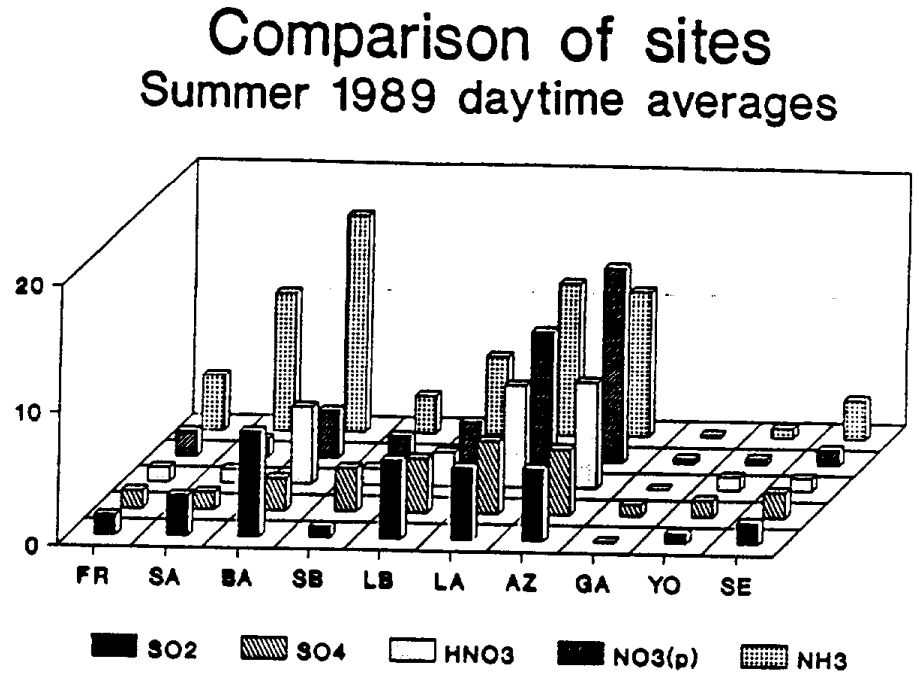
Figure 3

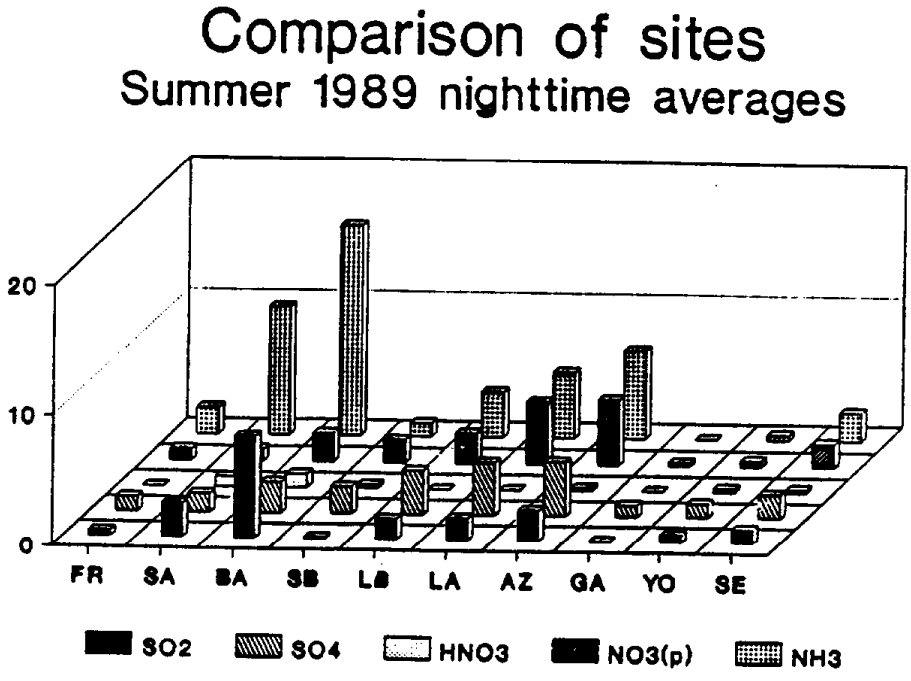




Comparison of December, January, and February Average Concentrations at Different Sampling Locations. (Sufficient data were not available from Santa Barbara and Gasquet for this period.)

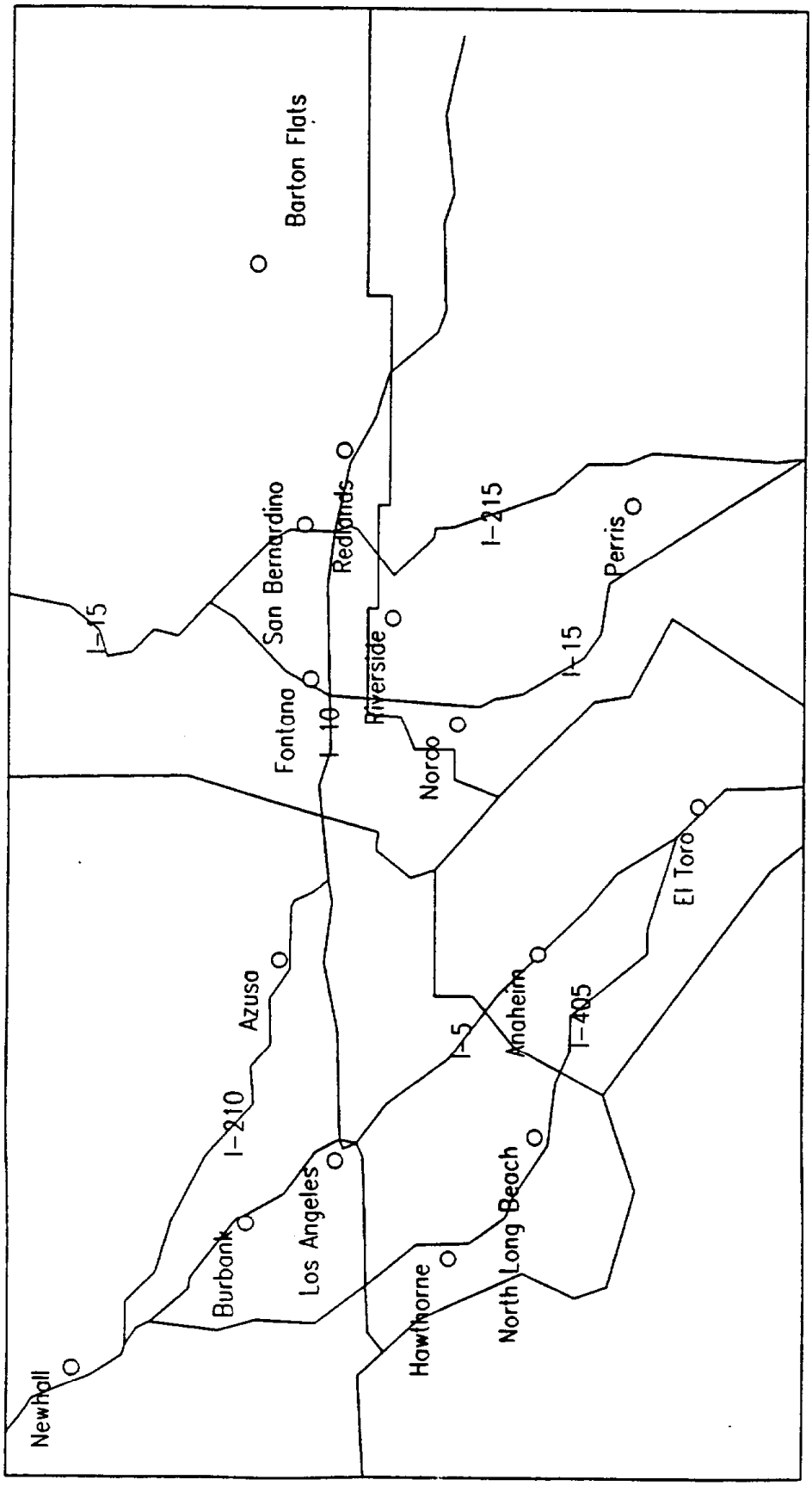
Figure 4





Comparison of June, July, and August Average Concentrations at Different Sampling Locations.

Figure 5


Barton Flats
San Bernardino
Redlands
I-215
Perris
I-15
Riverside
Fontana
I-10
Norco
El Toro
Azusa
I-210
Anaheim
I-5
I-405
Burbank
Los Angeles
Hawthorne
North Long Beach
Newhall

FOREST MEASUREMENTS

Task	Schedule
Monitoring Period	10/30/91 to 9/30/93 and 6/1/94 to 8/31/94
Ozone and Meteorological Measurement	Hourly, 24 Hours/Day
Dry Deposition Sampling Durations	Daytime (0600 to 1800 PST) and Nighttime (1800 to Next Day 0600 PST) Sampling, Once Every Sixth Day between 11/02/91 and 9/28/93, and between 6/1/94 and 8/30/94
	Morning (0600 to 1200 PST), Afternoon (1200 to 1800 PST) and Nighttime (1800 to Next Day 0600 PST) Sampling, Daily between 7/18/93 and 7/31/93
Wet Deposition Sampling Frequency	Once/Week (Precipitation > 0.015 inches)

Figure 6

DATA BASES FOR FOREST MEASUREMENTS BETWEEN 10/31/91 and 9/30/93, and 6/1/94 and 8/31/94

Category	Measured Parameters	Data Points
Meteorology	Wind Speed, Wind Direction, Sigma Theta, Temperature, Solar Radiation, and Time of Wetness	794 Days 19,056 Hours (10/30/91 to 9/30/93 and 6/1/94 to 8/31/94)
Ozone	O_3	794 Days 19,056 Hours (10/30/91 to 9/30/93 and 6/1/94 to 8/31/94)
Dry Deposition	$PM_{2.5}$ Mass, Cl^-, NO_3^-, $SO_4^=$, NH_4^+ Gaseous SO_2, NO_2, NH_3, and HNO_3	146 Day and Night Pairs (11/02/91 to 9/28/93 and 6/1/94 to 8/31/94) 14 Sets of Morning, Afternoon, and Night Samples (7/18/93 to 7/31/93)
Wet Deposition	pH and Conductivity Cl^-, NO_3^-, $SO_4^=$, NH_4^+, Na^+, Mg^{++}, K^+, and Ca^{++}	51 Periods (11/5/91 to 9/28/93 and 6/1/94 to 8/31/94)

Figure 7

FOREST MEASUREMENTS

I. Dry Deposition

Measurements	Method
$PM_{2.5}$ Mass	Gravimetric Analysis
$PM_{2.5}$ Cl^-, NO_3^-, and $SO_4^=$	Ion Chromatography
$PM_{2.5}$ NH_4^+	Automated Colorimetry
Sulfur Dioxide (SO_2)	Ion Chromatography
Nitrogen Dioxide (NO_2)	Automated Colorimetry
Ammonia (NH_3)	Gravimetric Analysis
Denuder Difference Nitric Acid (HNO_3)	Ion Chromatography

Figure 8a

FOREST MEASUREMENTS

II. Wet Deposition

Measurements	Method
pH	pH Meter
Conductivity	Conductivity Meter
Cl^-, NO_3^-, and $SO_4^=$	Ion Chromatography
Ammonium (NH_4^+)	Automated Colorimetry
Na^+, Mg^{++}, K^+, and Ca^{++}	Atomic Absorption Spectrophotometry

Figure 8b

FOREST MEASUREMENTS

III. Continuous Gas

Measurements	Method
Ozone (O_3)	Ultraviolet Absorption Monitor

IV. Meteorology

Measurements	Method
Wind Speed	Anemometer

Figure 8c

FOREST MEASUREMENTS

IV. Meteorology (continued)

Measurements	Method
Wind Direction	Wind Vane
Sigma Theta	Wind Vane
Temperature	Thermister
Relative Humidity	PCRC-11 Sensor
Solar Radiation	Pyranometer
Times of Wetness	Electric Cell

Figure 8d

PHASE II MONITORING (6/1/94 TO 8/31/94)

Date	Action
4/18/94 to 4/20/94	Provide a Three Day Training Course on Continuous Data Processing and Validation
4/25/94	Clean and Calibrate Sampler
6/1/94	Initiate 2 Times/Day (0600 to 1800, 1800 to Next Day 0600 PST) Every Sixth Day Aerosol/Gas Dry Deposition Monitoring

Figure 8e

LABORATORY OPERATIONS

- Substrate Preparation and Acceptance Testing
- Sample Preparation, Shipping, and Receiving
- Gravimetric Analysis
- Filter Sectioning and Extraction
- Anion and Cation Chemical Analysis

Figure 8f

Figure 9

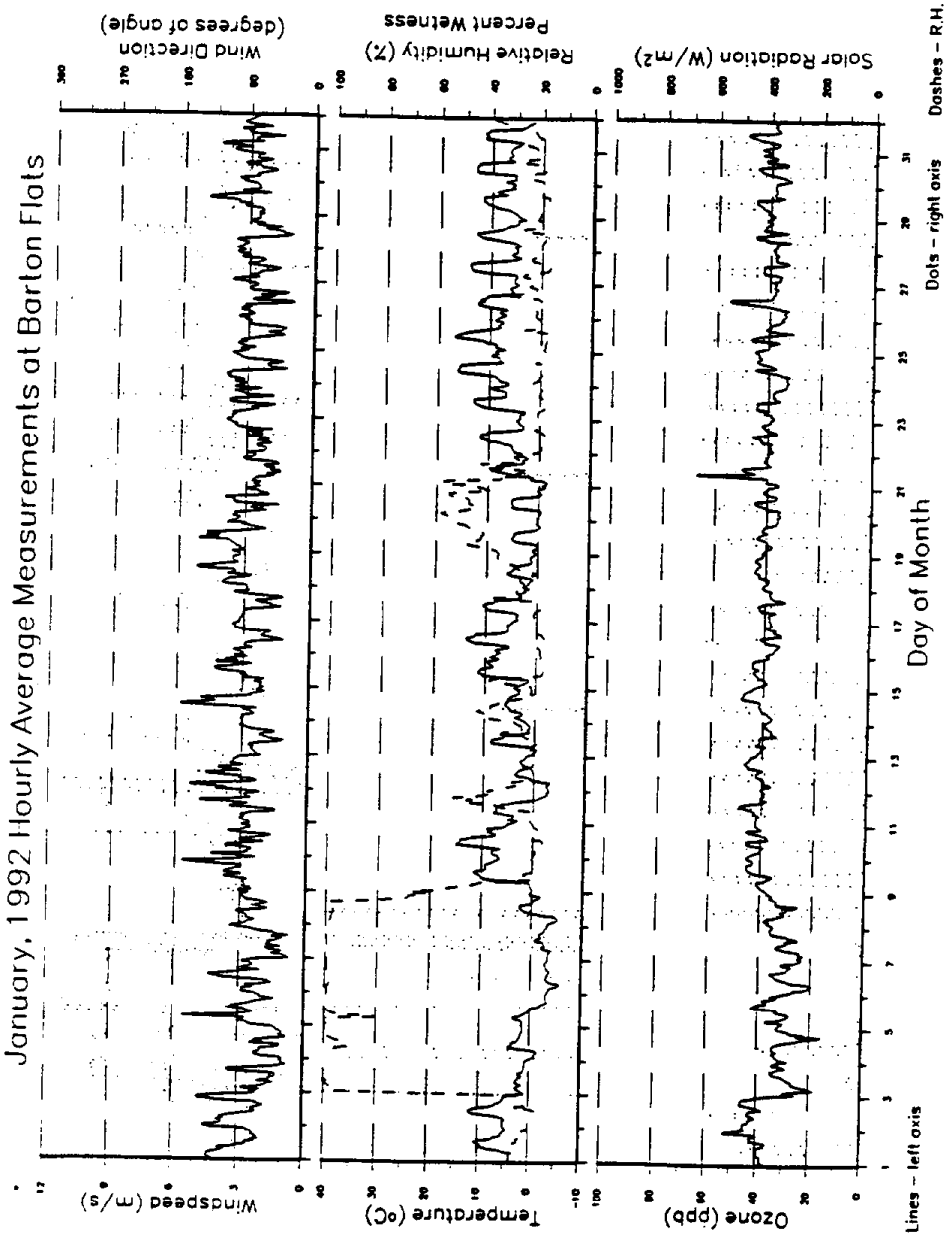

January, 1992 Hourly Average Measurements at Barton Flats
Windspeed (m/s)
Wind Direction (degrees of angle)
Temperature (oC)
Relative Humidity (%) Percent Wetness
Ozone (ppb)
Solar Radiation (W/m2)
Day of Month
Lines – left axis
Dots – right axis
Dashes – R.H.

Figure 10

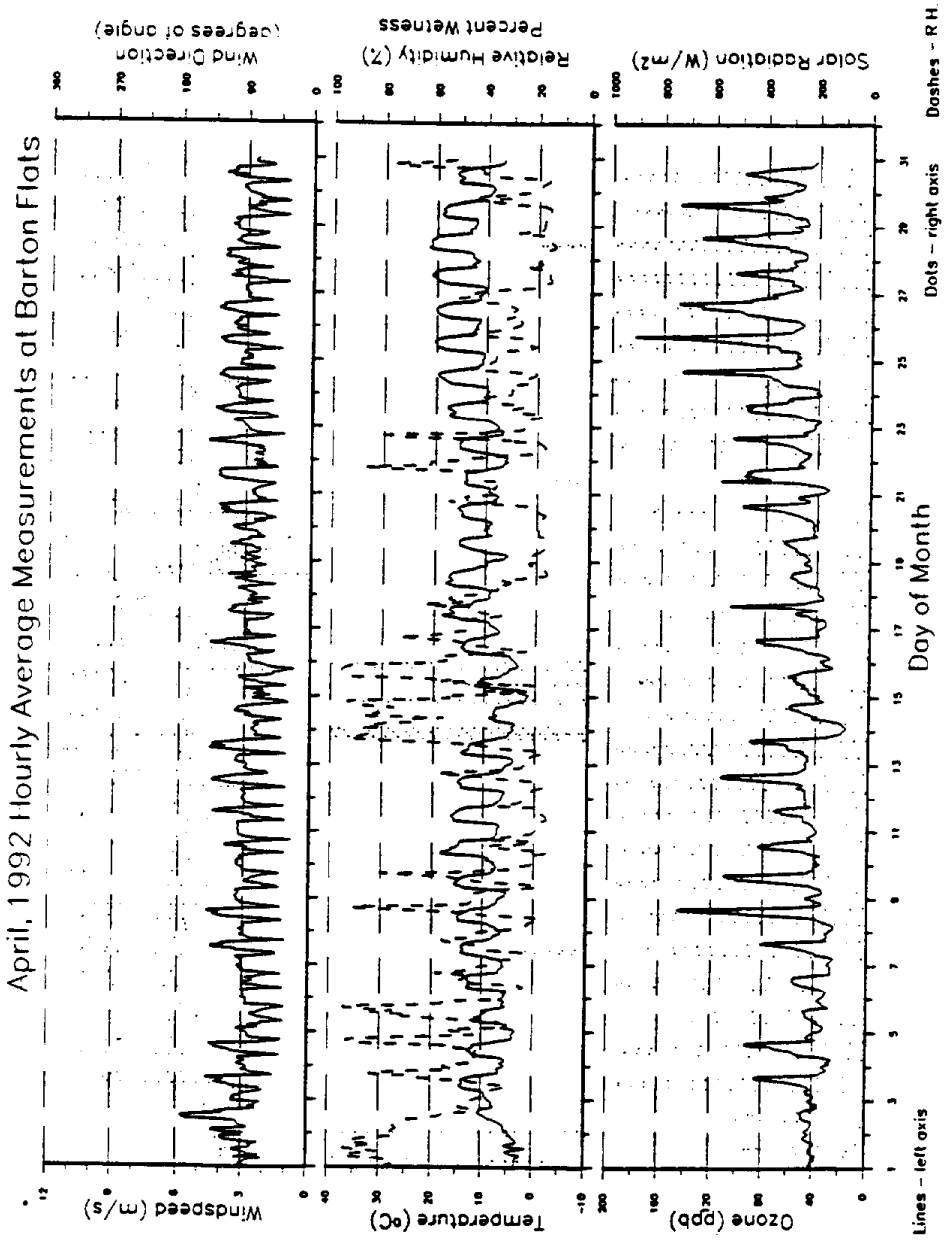

April, 1992 Hourly Average Measurements at Barton Flats
Windspeed (m/s)
Wind Direction (degrees of angle)
Temperature (°C)
Relative Humidity (%) Percent Wetness
Ozone (ppb)
Solar Radiation (W/m2)
Day of Month
Lines – left axis
Dots – right axis
Dashes - R.H.

Figure 11

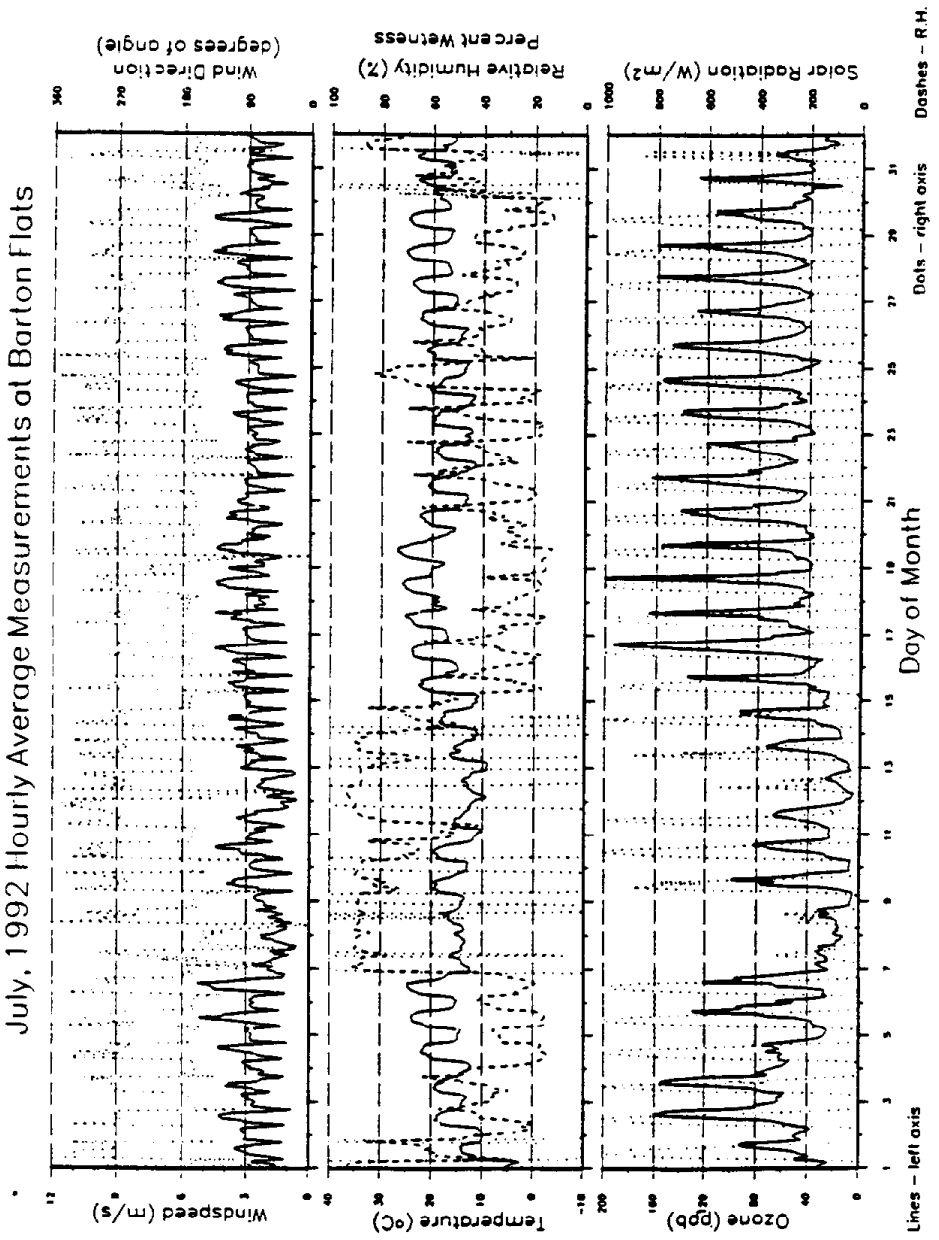

July, 1992 Hourly Average Measurements at Barton Flats
Windspeed (m/s)
Wind Direction (degrees of angle)
Temperature (°C)
Relative Humidity (%) Percent Wetness
Ozone (ppb)
Solar Radiation (W/m2)
Day of Month
Lines – left axis
Dots – right axis
Dashes – R.H.

Figure 12

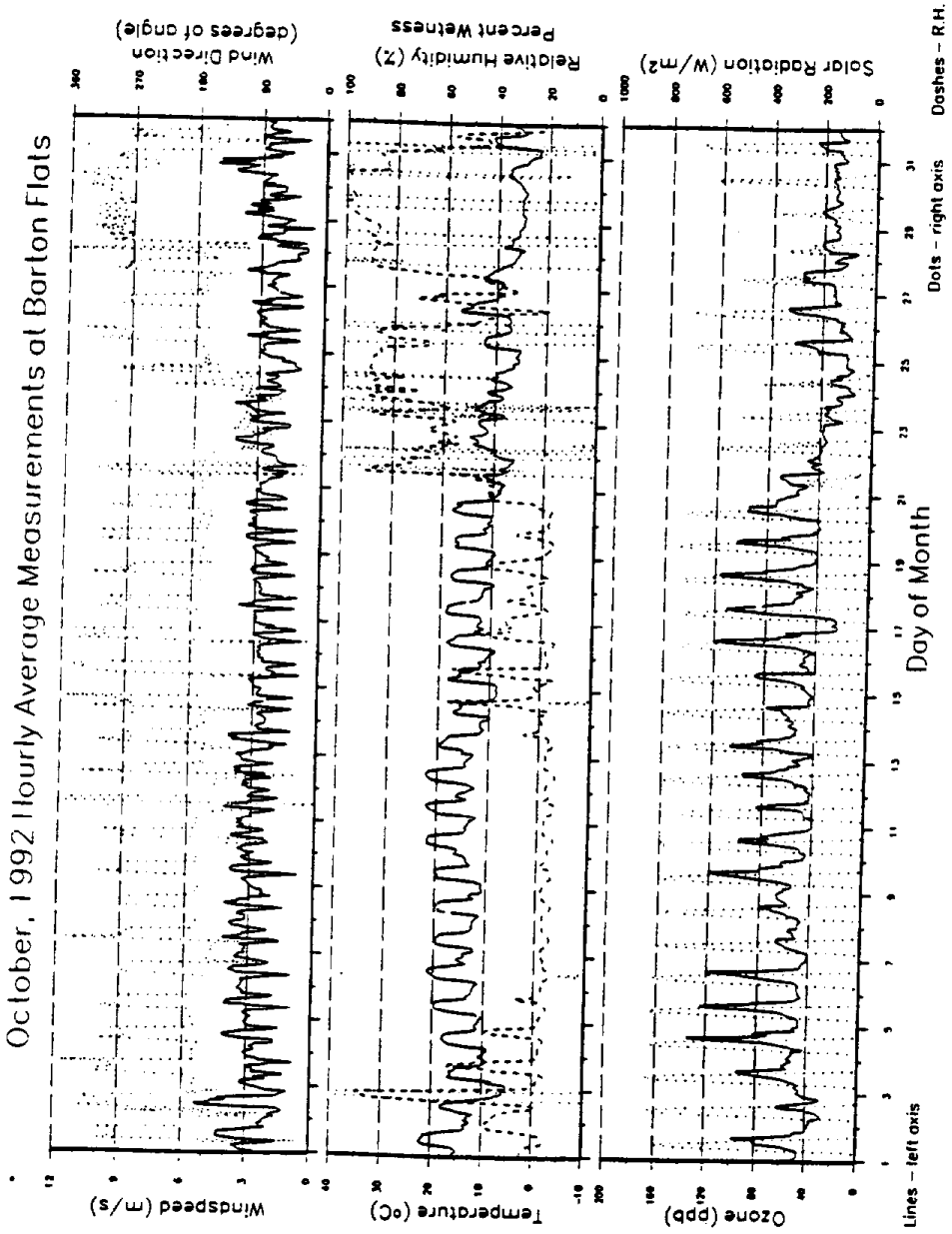

October, 1992 Hourly Average Measurements at Barton Flats
Windspeed (m/s)
Wind Direction (degrees of angle)
Temperature (oC)
Relative Humidity (%) Percent Wetness
Ozone (ppb)
Solar Radiation (W/m2)
Day of Month
Lines – left axis
Dots – right axis
Dashes – R.H.

Figure 13

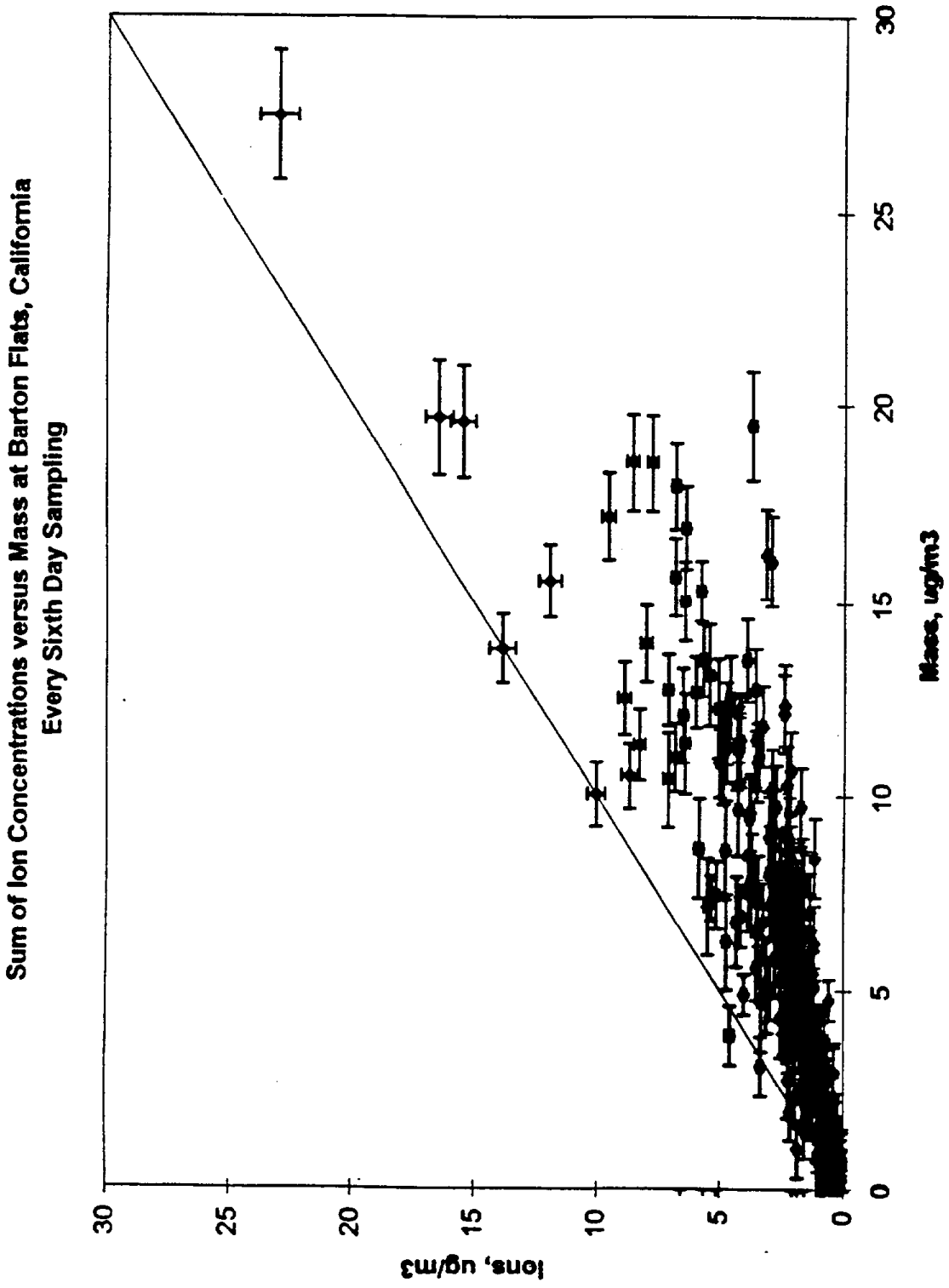

Sum of Ion Concentrations versus Mass at Barton Flats, California
Every Sixth Day Sampling
Ions, ug/m3
Mass, ug/m3
0
5
10
15
20
25
30

Figure 14

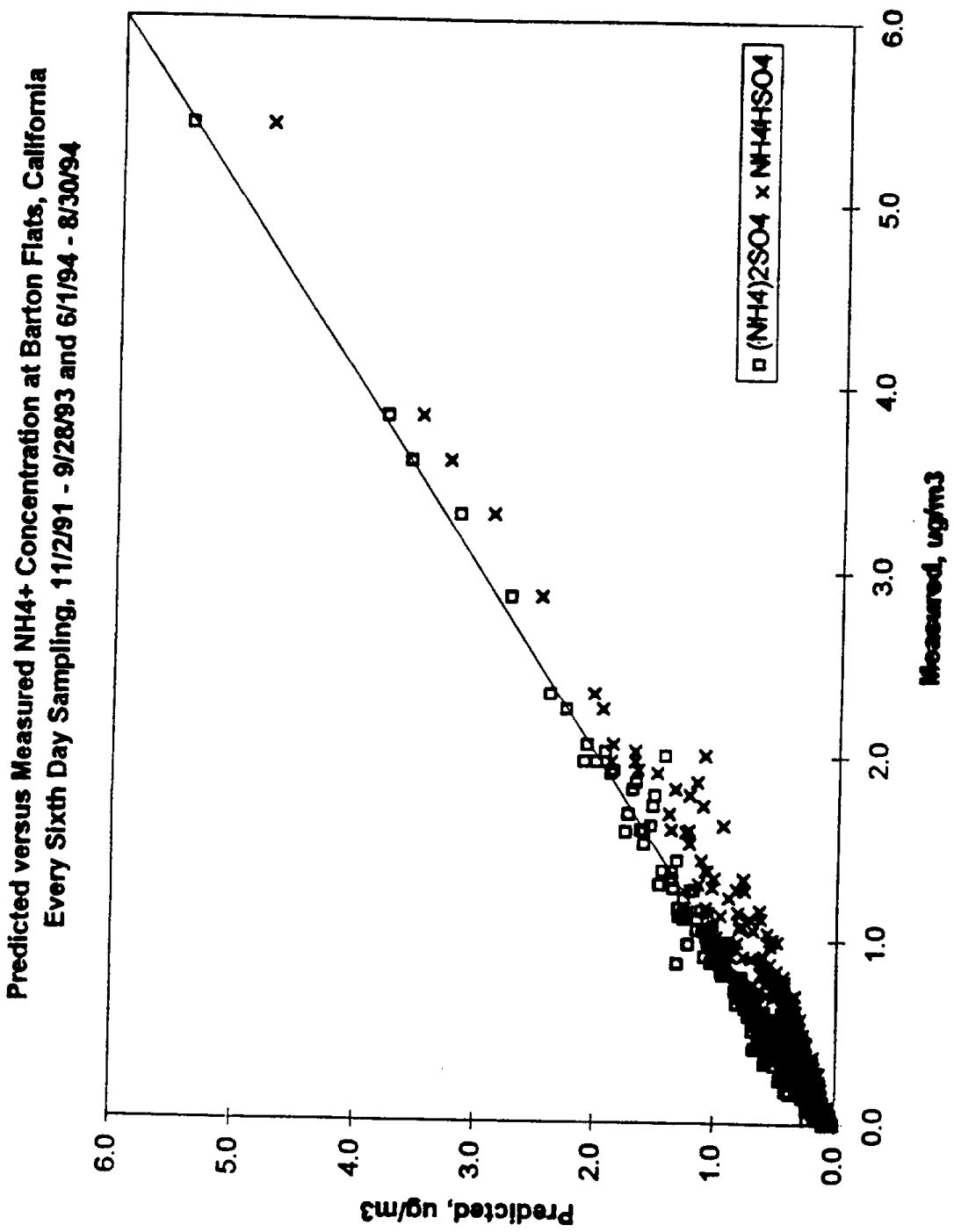

Predicted versus Measured NH4+ Concentration at Barton Flats, California
Every Sixth Day Sampling, 11/2/91 - 9/28/93 and 6/1/94 - 8/30/94
(NH4)2SO4 x NH4HSO4
Predicted, ug/m3
Measured, ug/m3
0.0
1.0
2.0
3.0
4.0
5.0
6.0

Figure 15

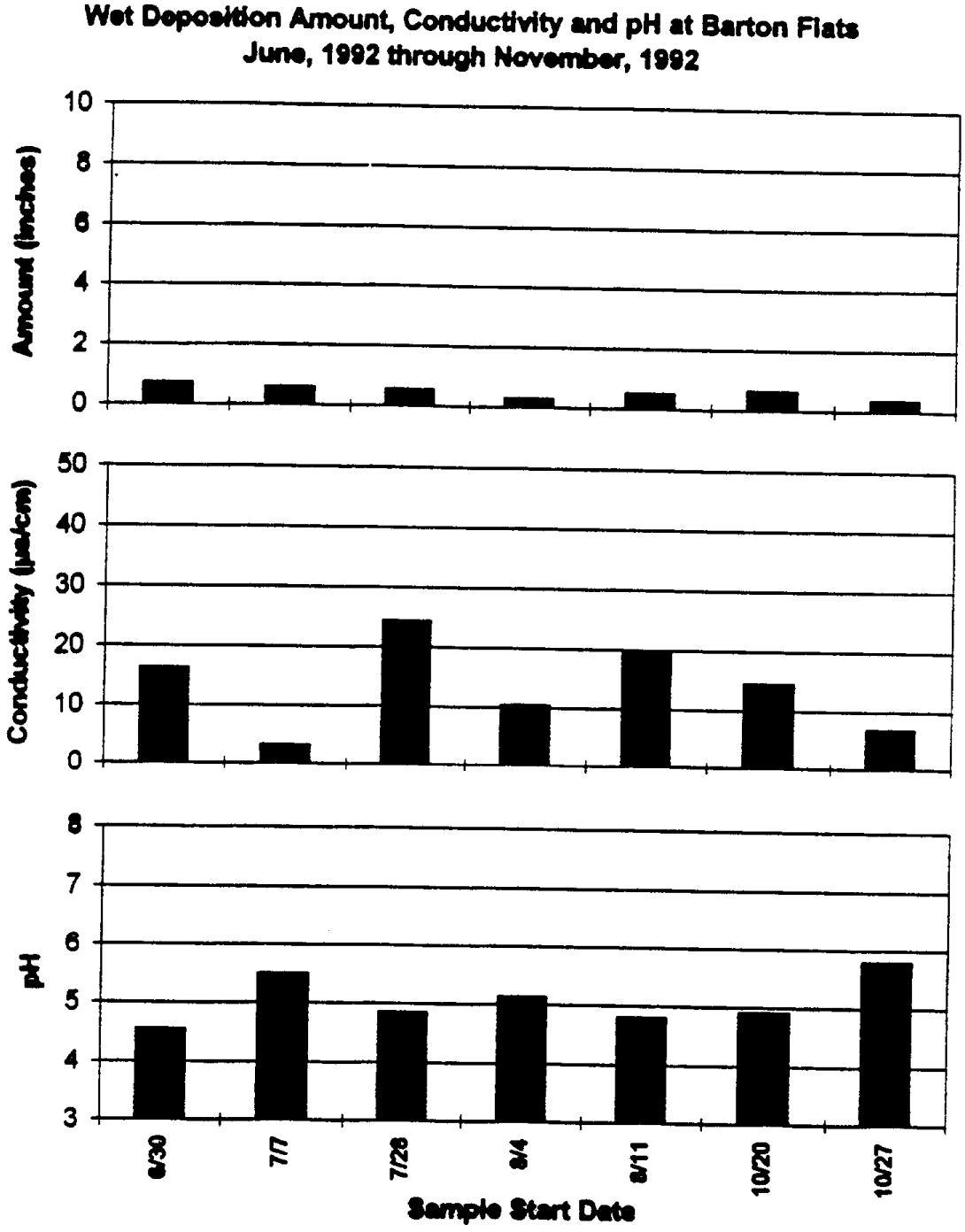

Wet Deposition Amount, Conductivity and pH at Barton Flats
June, 1992 through November, 1992
Amount (inches)
10
8
6
4
2
0
Conductivity (µs/cm)
50
40
30
20
10
0
pH
8
7
6
5
4
3
6/30
7/7
7/28
8/4
8/11
10/20
10/27
Sample Start Date

Figure 16

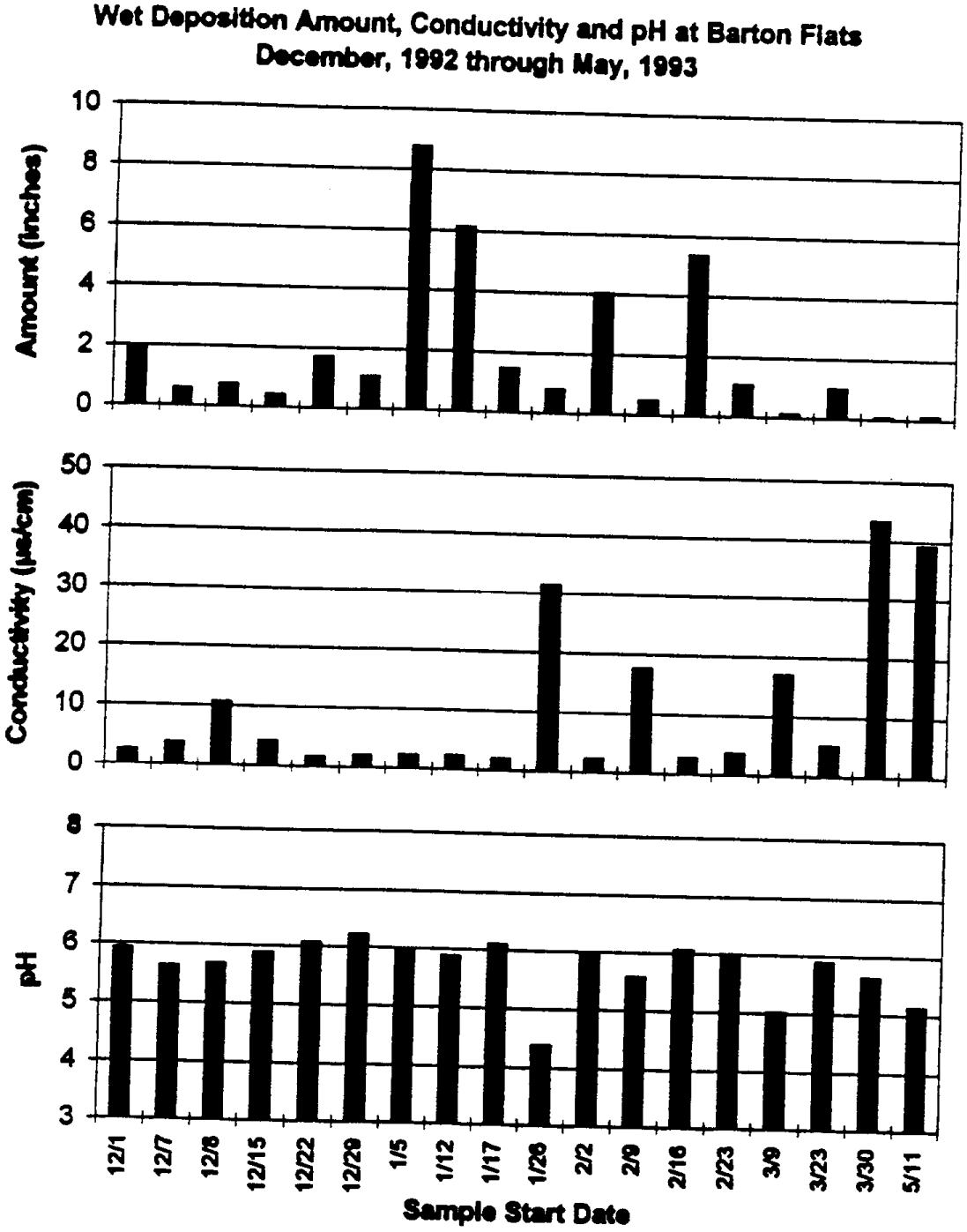

Wet Deposition Amount, Conductivity and pH at Barton Flats
December, 1992 through May, 1993
Amount (inches)
10
8
6
4
2
0
Conductivity (µs/cm)
50
40
30
20
10
0
pH
8
7
6
5
4
3
12/1
12/7
12/8
12/15
12/22
12/29
1/5
1/12
1/17
1/26
2/2
2/9
2/16
2/23
3/9
3/23
3/30
5/11
Sample Start Date

Figure 17

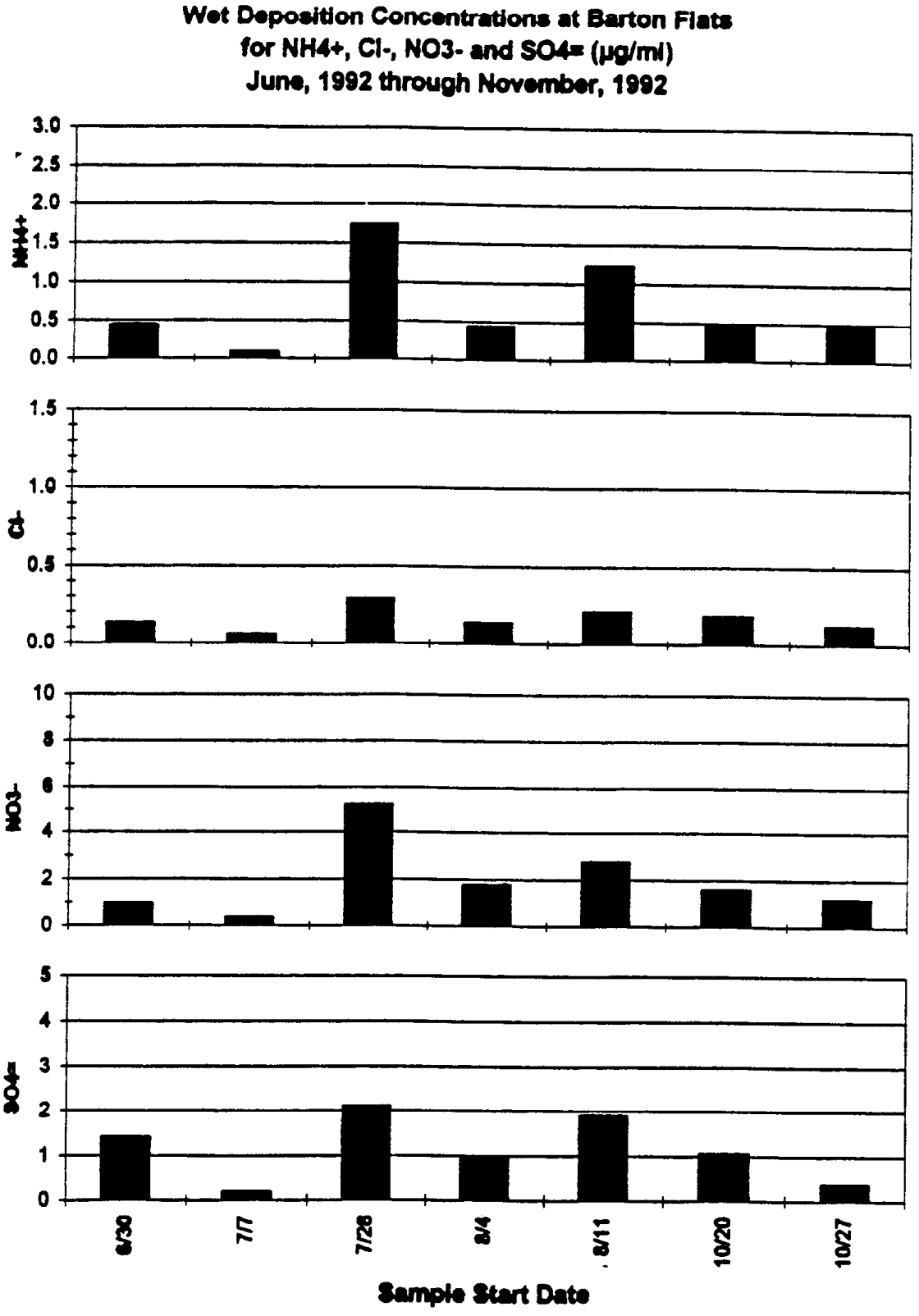

Wet Deposition Concentrations at Barton Flats
for NH4+, Cl-, NO3- and SO4= (µg/ml)
June, 1992 through November, 1992
NH4+
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cl-
1.5
1.0
0.5
0.0
NO3-
10
8
6
4
2
0
SO4=
5
4
3
2
1
0
6/30
7/7
7/28
8/4
8/11
10/20
10/27
Sample Start Date

Figure 18

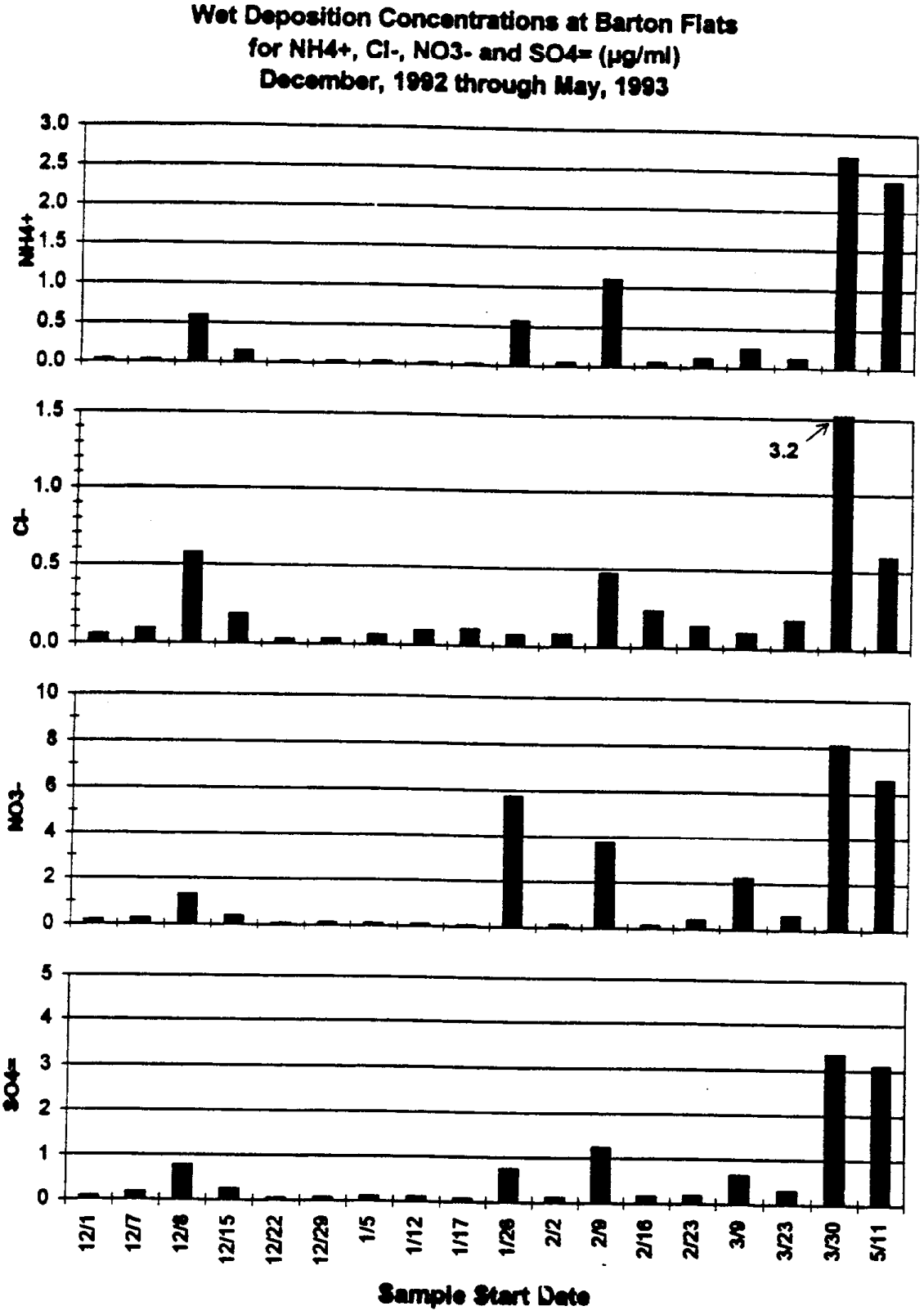

Wet Deposition Concentrations at Barton Flats
for NH4+, Cl-, NO3- and SO4= (µg/ml)
December, 1992 through May, 1993
NH4+
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cl-
1.5
1.0
0.5
0.0
3.2
NO3-
10
8
6
4
2
0
SO4=
5
4
3
2
1
0
12/1
12/7
12/8
12/15
12/22
12/29
1/5
1/12
1/17
1/26
2/2
2/9
2/16
2/23
3/9
3/23
3/30
5/11
Sample Start Date

Figure 19

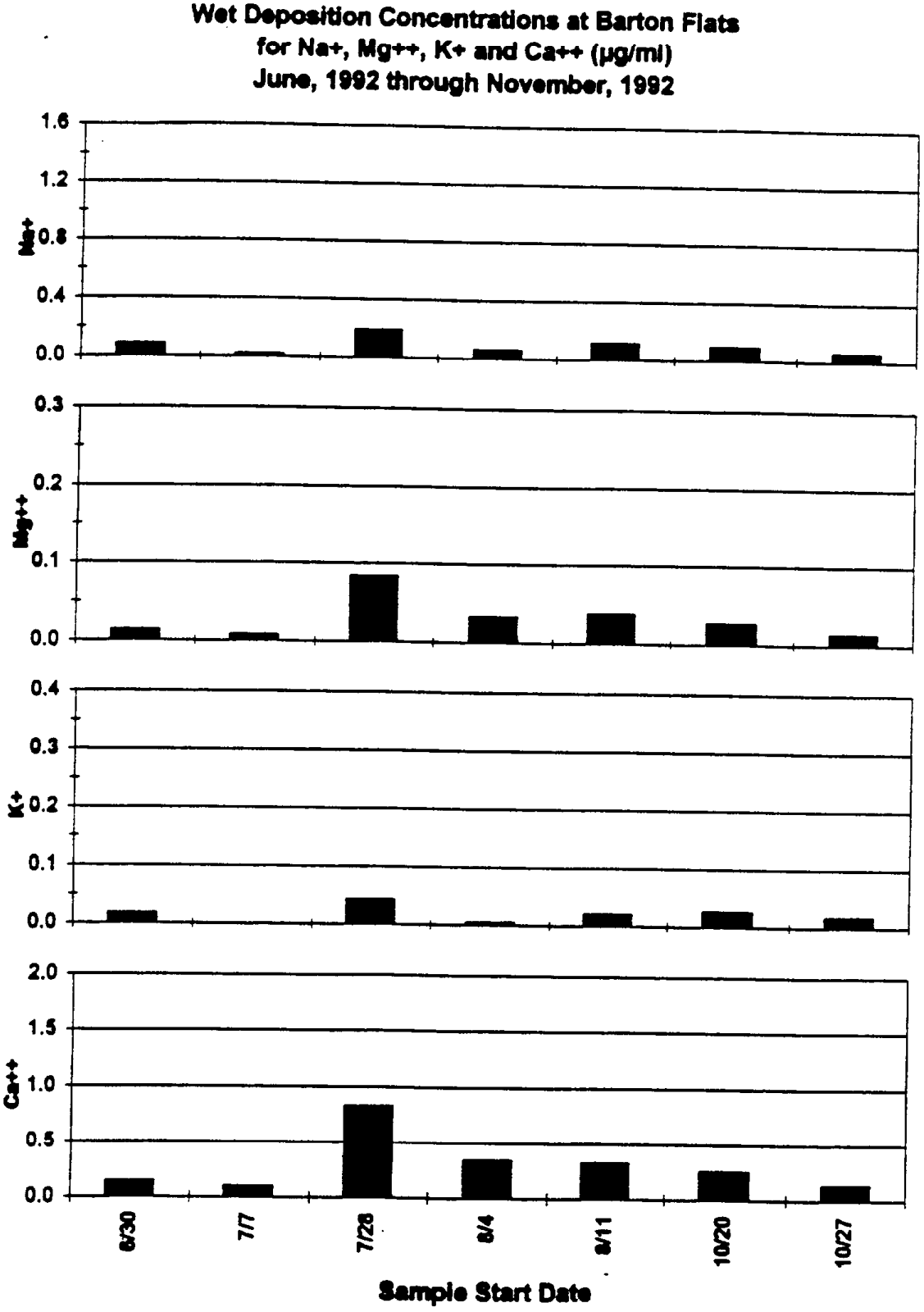

Wet Deposition Concentrations at Barton Flats
for Na+, Mg++, K+ and Ca++ (µg/ml)
June, 1992 through November, 1992
1.6
1.2
0.8
0.4
0.0
Na+
0.3
0.2
0.1
0.0
Mg++
0.4
0.3
0.2
0.1
0.0
K+
2.0
1.5
1.0
0.5
0.0
Ca++
6/30
7/7
7/28
8/4
8/11
10/20
10/27
Sample Start Date

Figure 20

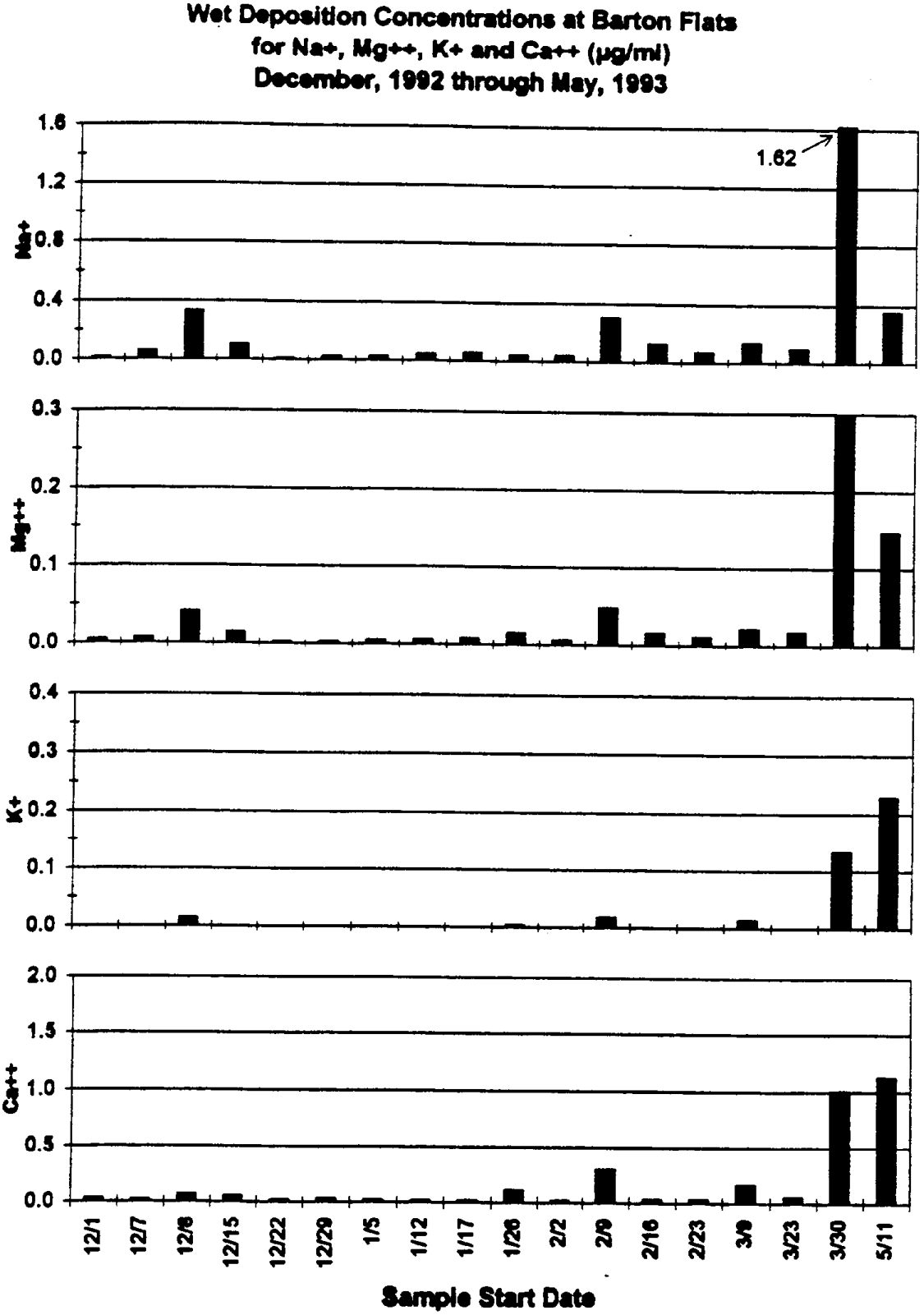

Wet Deposition Concentrations at Barton Flats
for Na+, Mg++, K+ and Ca++ (µg/ml)
December, 1992 through May, 1993
1.62
Na+
Mg++
K+
Ca++
12/1
12/7
12/8
12/15
12/22
12/29
1/5
1/12
1/17
1/26
2/2
2/9
2/16
2/23
3/9
3/23
3/30
5/11
Sample Start Date

Figure 21

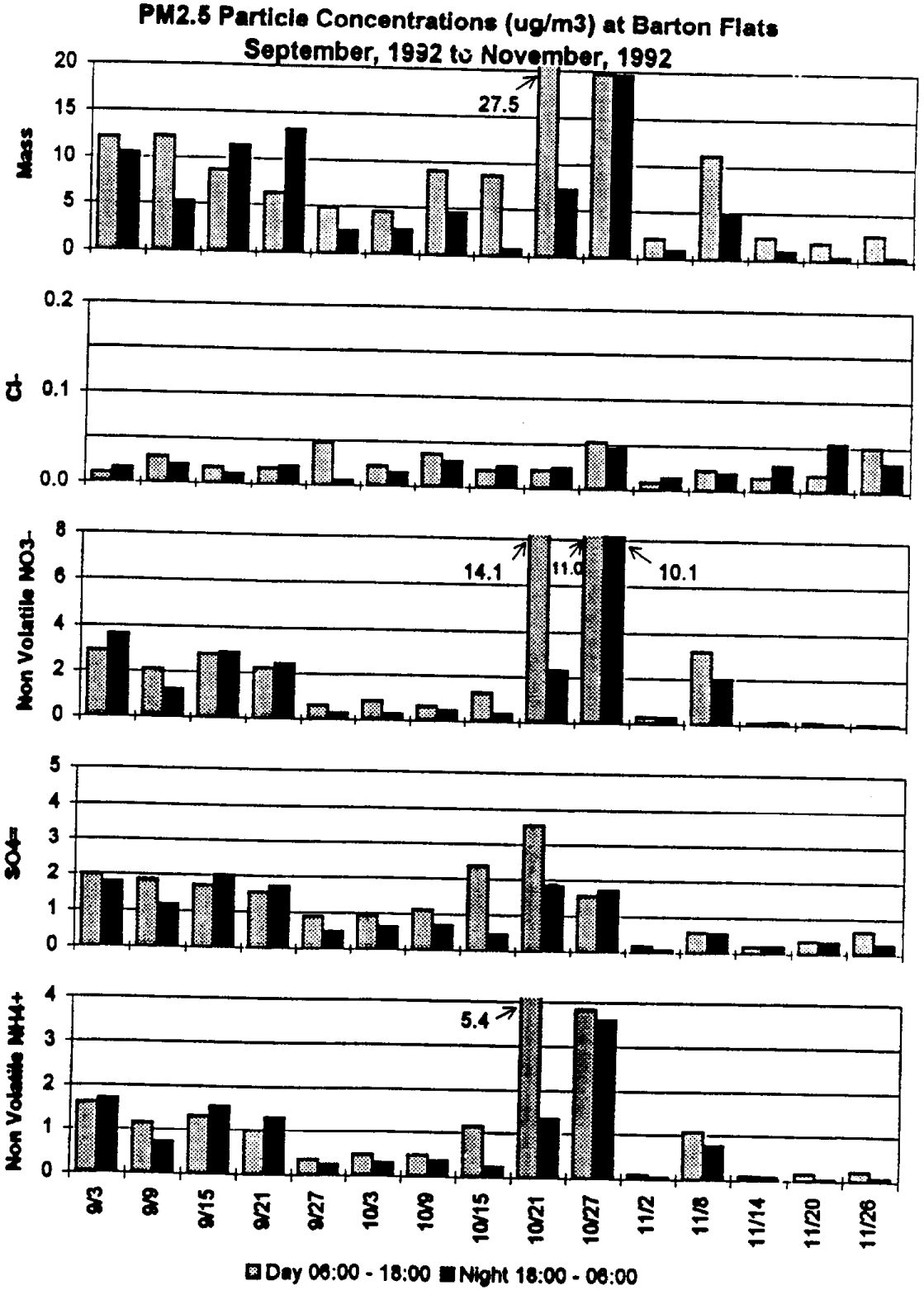

PM2.5 Particle Concentrations (ug/m3) at Barton Flats
September, 1992 to November, 1992
Mass
27.5
Cl-
Non Volatile NO3-
14.1
11.0
10.1
SO4=
Non Volatile NH4+
5.4
9/3
9/9
9/15
9/21
9/27
10/3
10/9
10/15
10/21
10/27
11/2
11/8
11/14
11/20
11/26
Day 06:00 - 18:00
Night 18:00 - 06:00

Figure 22

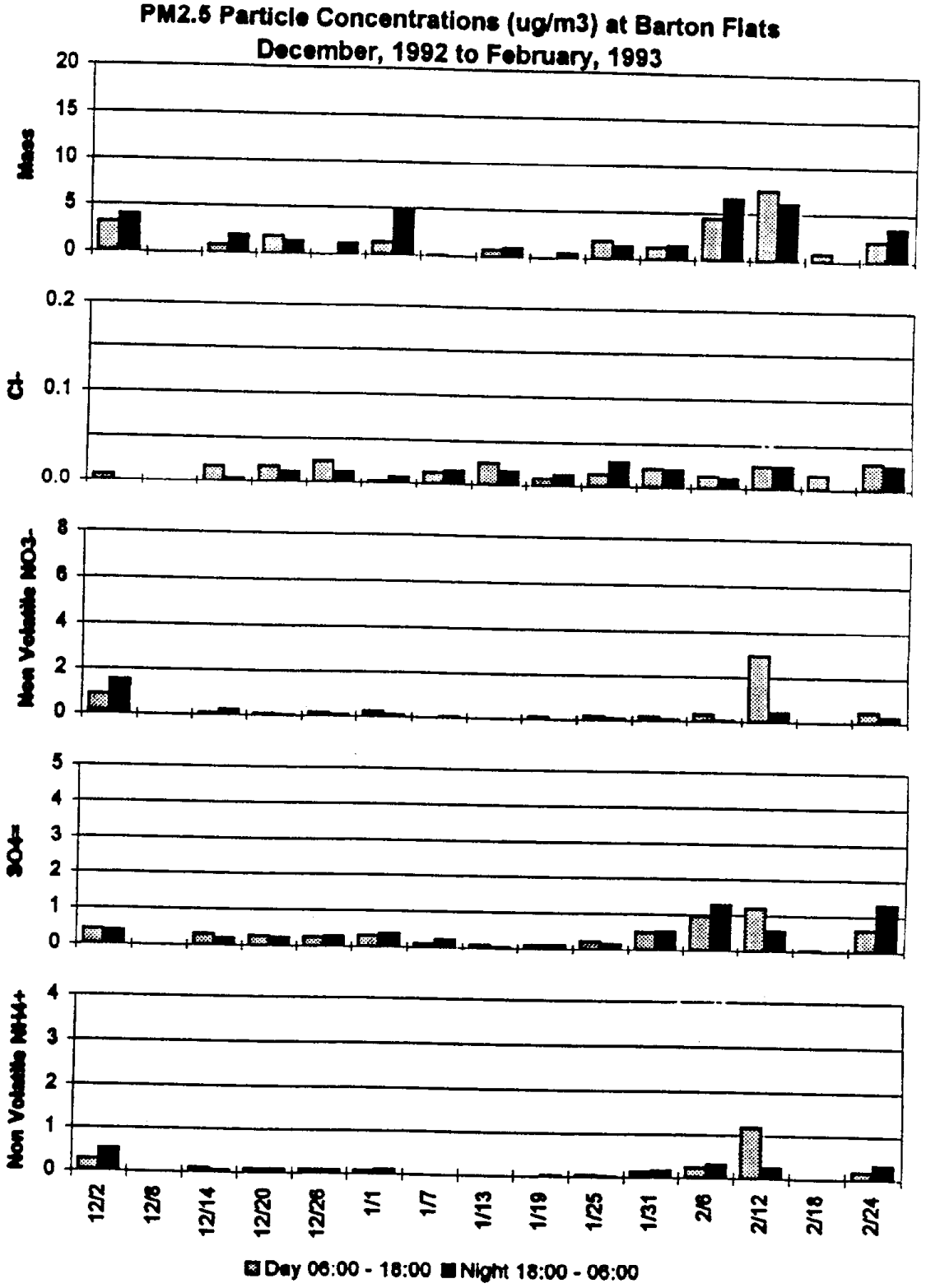

PM2.5 Particle Concentrations (ug/m3) at Barton Flats
December, 1992 to February, 1993
Mass
Cl-
Non Volatile NO3-
SO4=
Non Volatile NH4+
12/2
12/8
12/14
12/20
12/26
1/1
1/7
1/13
1/19
1/25
1/31
2/6
2/12
2/18
2/24
Day 06:00 - 18:00
Night 18:00 - 06:00

Figure 23

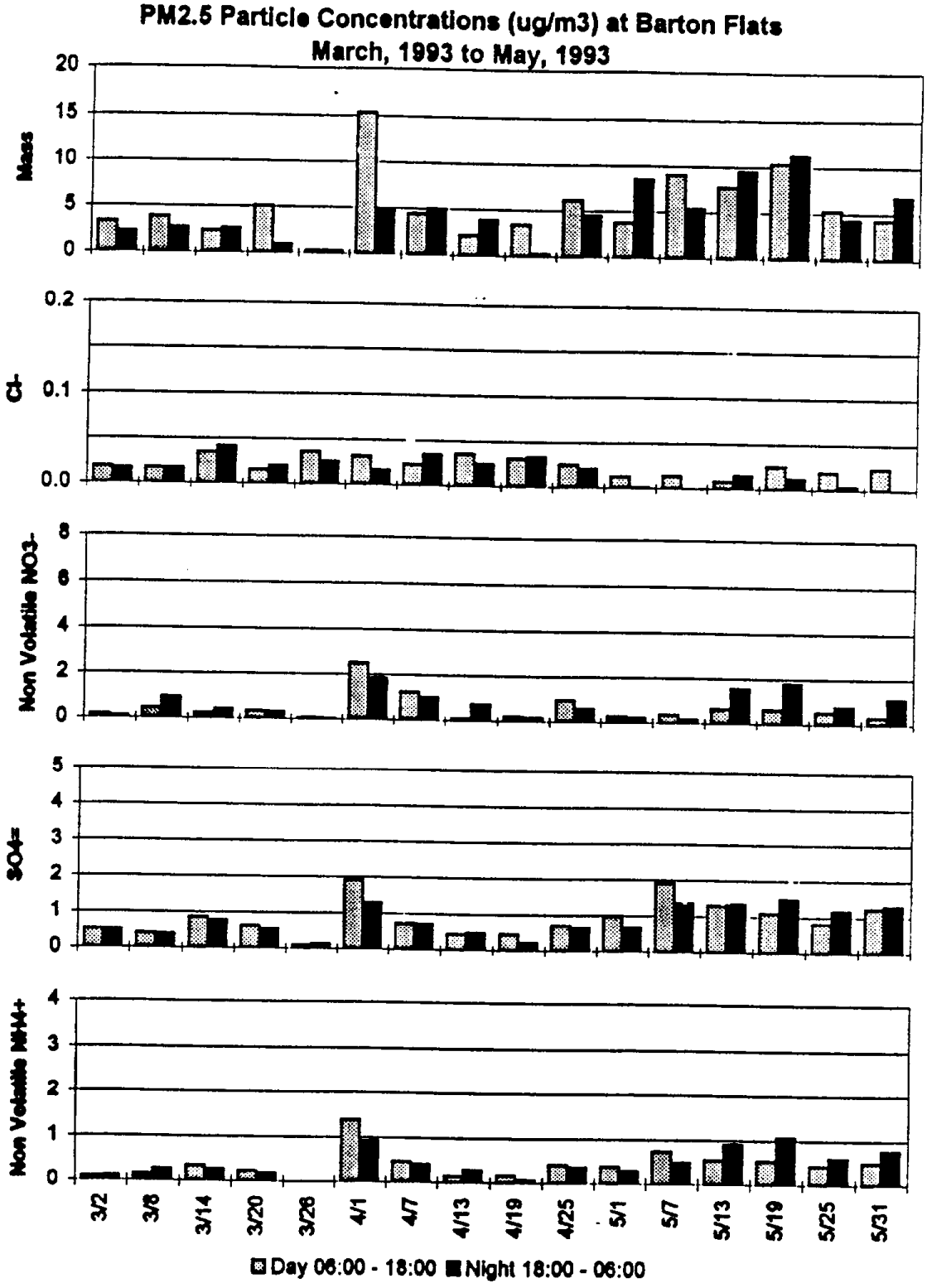

PM2.5 Particle Concentrations (ug/m3) at Barton Flats
March, 1993 to May, 1993
Mass
Cl-
Non Volatile NO3-
SO4=
Non Volatile NH4+
3/2
3/8
3/14
3/20
3/26
4/1
4/7
4/13
4/19
4/25
5/1
5/7
5/13
5/19
5/25
5/31
Day 06:00 - 18:00
Night 18:00 - 06:00

Figure 24

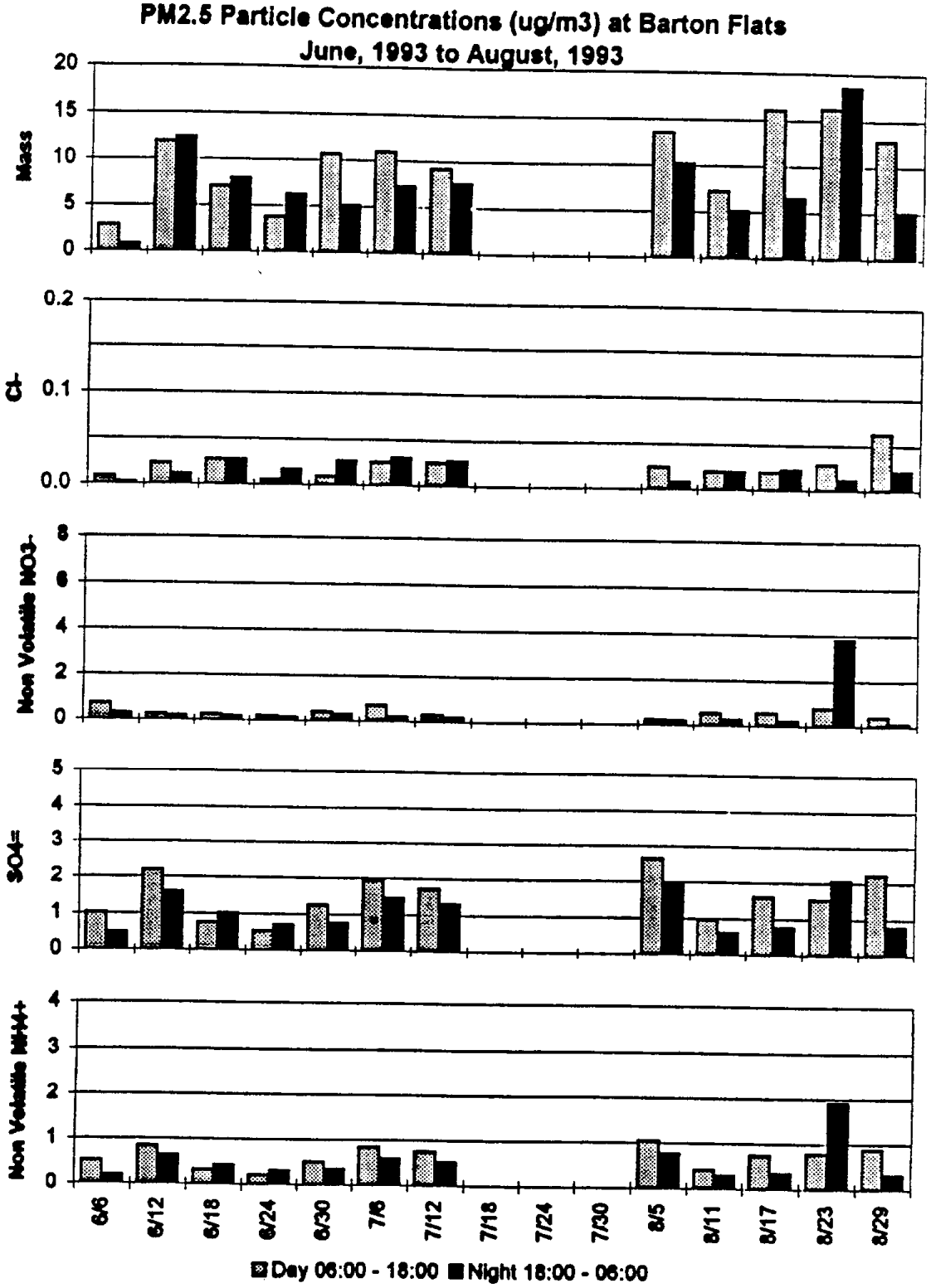

PM2.5 Particle Concentrations (ug/m3) at Barton Flats
June, 1993 to August, 1993
Mass
Cl-
Non Volatile NO3-
SO4=
Non Volatile NH4+
6/6
6/12
6/18
6/24
6/30
7/6
7/12
7/18
7/24
7/30
8/5
8/11
8/17
8/23
8/29
Day 06:00 - 18:00
Night 18:00 - 06:00

Figure 25

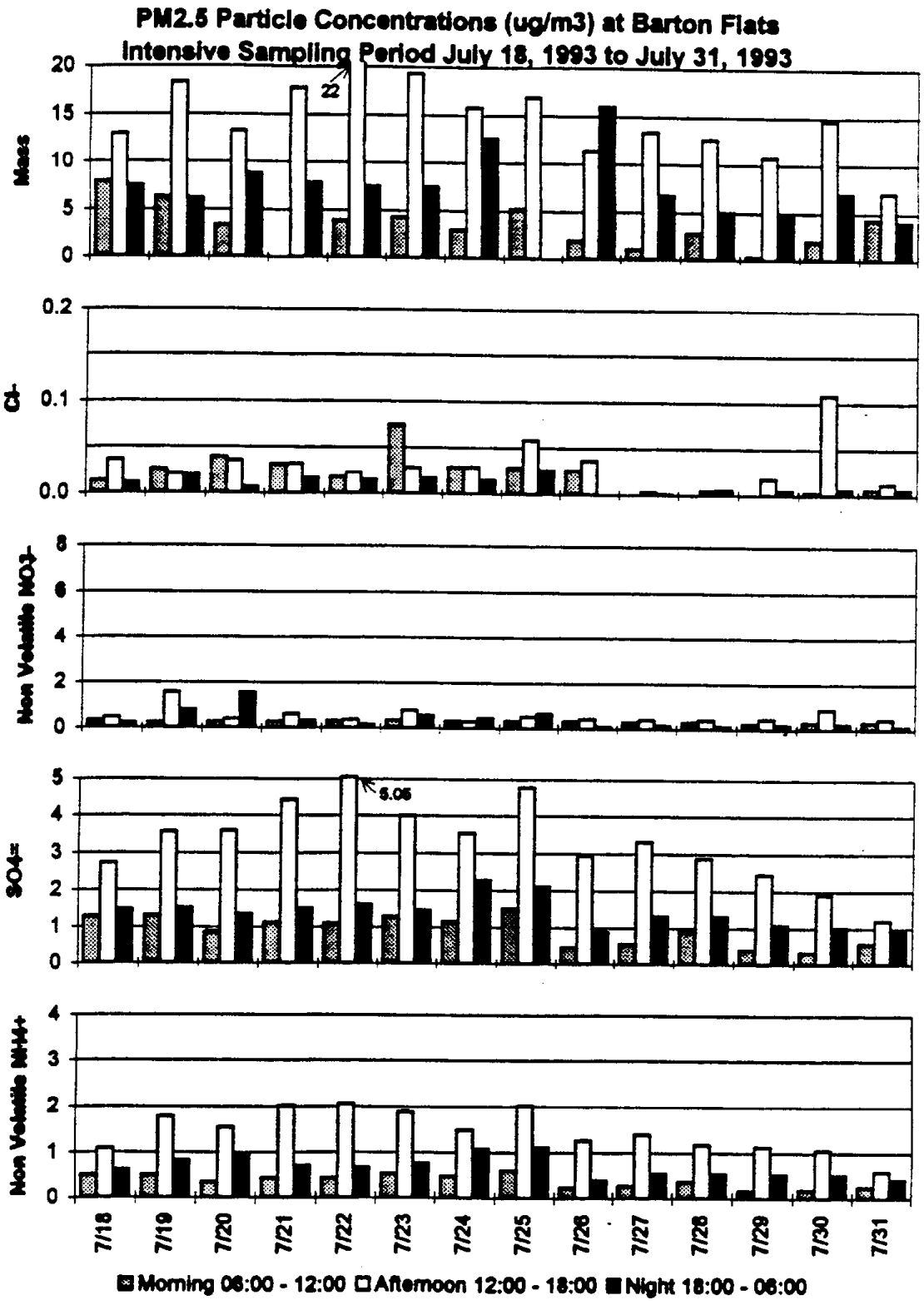

PM2.5 Particle Concentrations (ug/m3) at Barton Flats
Intensive Sampling Period July 18, 1993 to July 31, 1993
Mass
22
Cl-
Non Volatile NO3-
SO4=
5.06
Non Volatile NH4+
7/18
7/19
7/20
7/21
7/22
7/23
7/24
7/25
7/26
7/27
7/28
7/29
7/30
7/31
Morning 06:00 - 12:00
Afternoon 12:00 - 18:00
Night 18:00 - 06:00

Figure 26

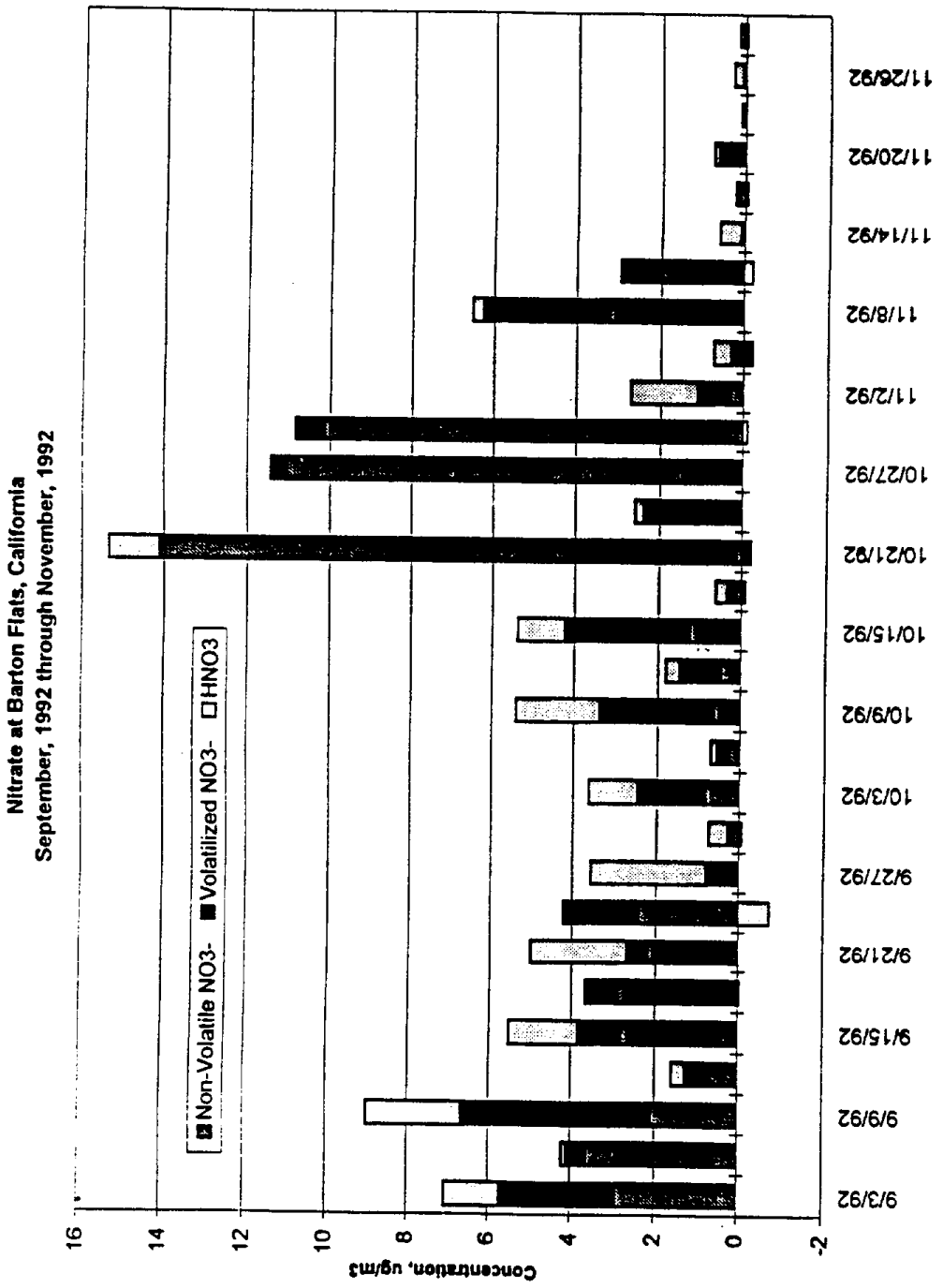

Nitrate at Barton Flats, California
September, 1992 through November, 1992
Non-Volatile NO3-
Volatilized NO3-
HNO3
Concentration, ug/m3
16
14
12
10
8
6
4
2
0
-2
9/3/92
9/9/92
9/15/92
9/21/92
9/27/92
10/3/92
10/9/92
10/15/92
10/21/92
10/27/92
11/2/92
11/8/92
11/14/92
11/20/92
11/26/92

Figure 27

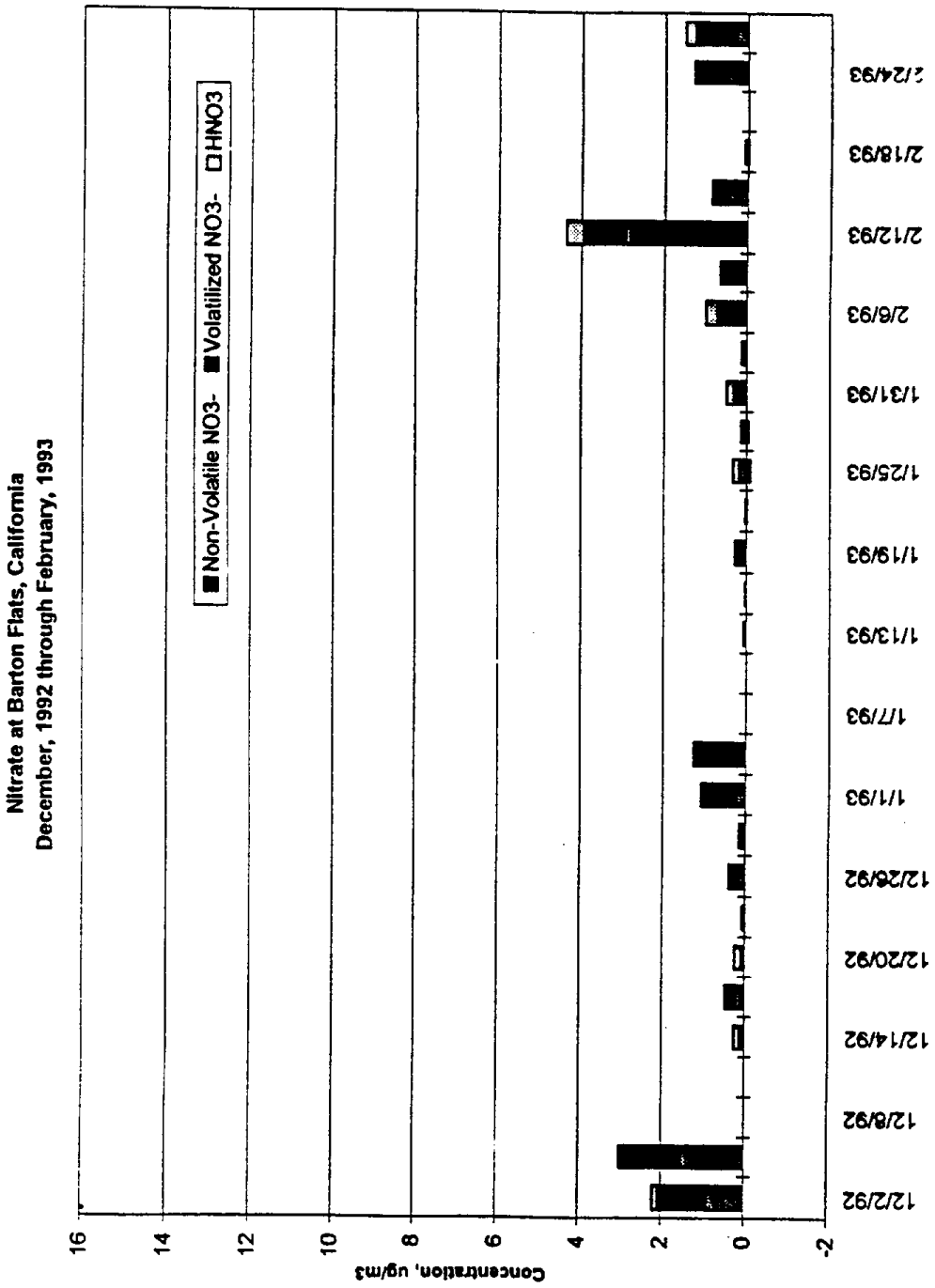

Nitrate at Barton Flats, California
December, 1992 through February, 1993
Non-Volatile NO3-
Volatilized NO3-
HNO3
Concentration, ug/m3
16
14
12
10
8
6
4
2
0
-2
12/2/92
12/8/92
12/14/92
12/20/92
12/26/92
1/1/93
1/7/93
1/13/93
1/19/93
1/25/93
1/31/93
2/6/93
2/12/93
2/18/93
2/24/93

Figure 28

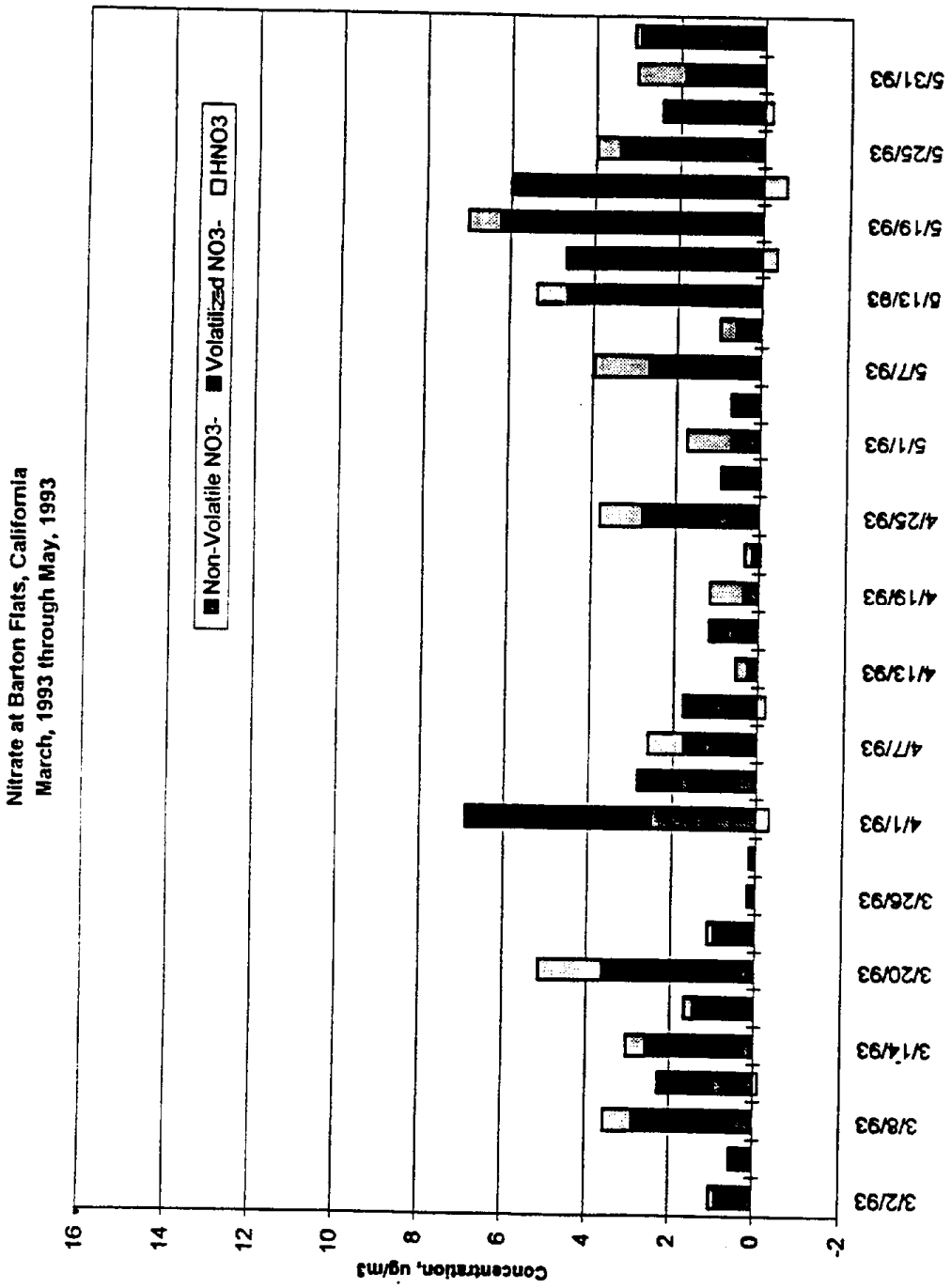

Nitrate at Barton Flats, California
March, 1993 through May, 1993
Non-Volatile NO3-
Volatilized NO3-
HNO3
Concentration, ug/m3
16
14
12
10
8
6
4
2
0
-2
3/2/93
3/8/93
3/14/93
3/20/93
3/26/93
4/1/93
4/7/93
4/13/93
4/19/93
4/25/93
5/1/93
5/7/93
5/13/93
5/19/93
5/25/93
5/31/93

Figure 29

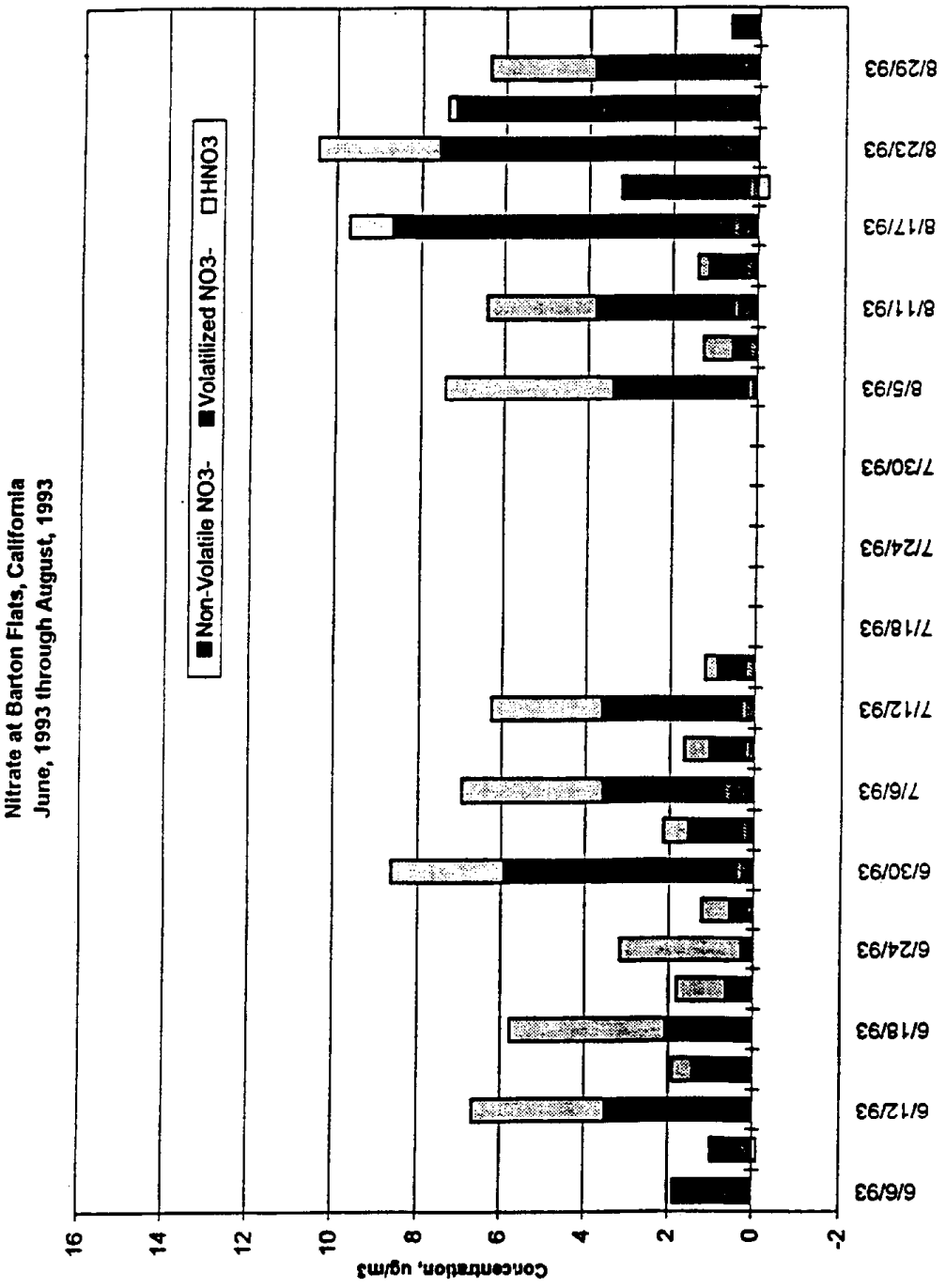

Nitrate at Barton Flats, California
June, 1993 through August, 1993
Non-Volatile NO3-
Volatilized NO3-
HNO3
Concentration, ug/m3
16
14
12
10
8
6
4
2
0
-2
6/6/93
6/12/93
6/18/93
6/24/93
6/30/93
7/6/93
7/12/93
7/18/93
7/24/93
7/30/93
8/5/93
8/11/93
8/17/93
8/23/93
8/29/93

Figure 30

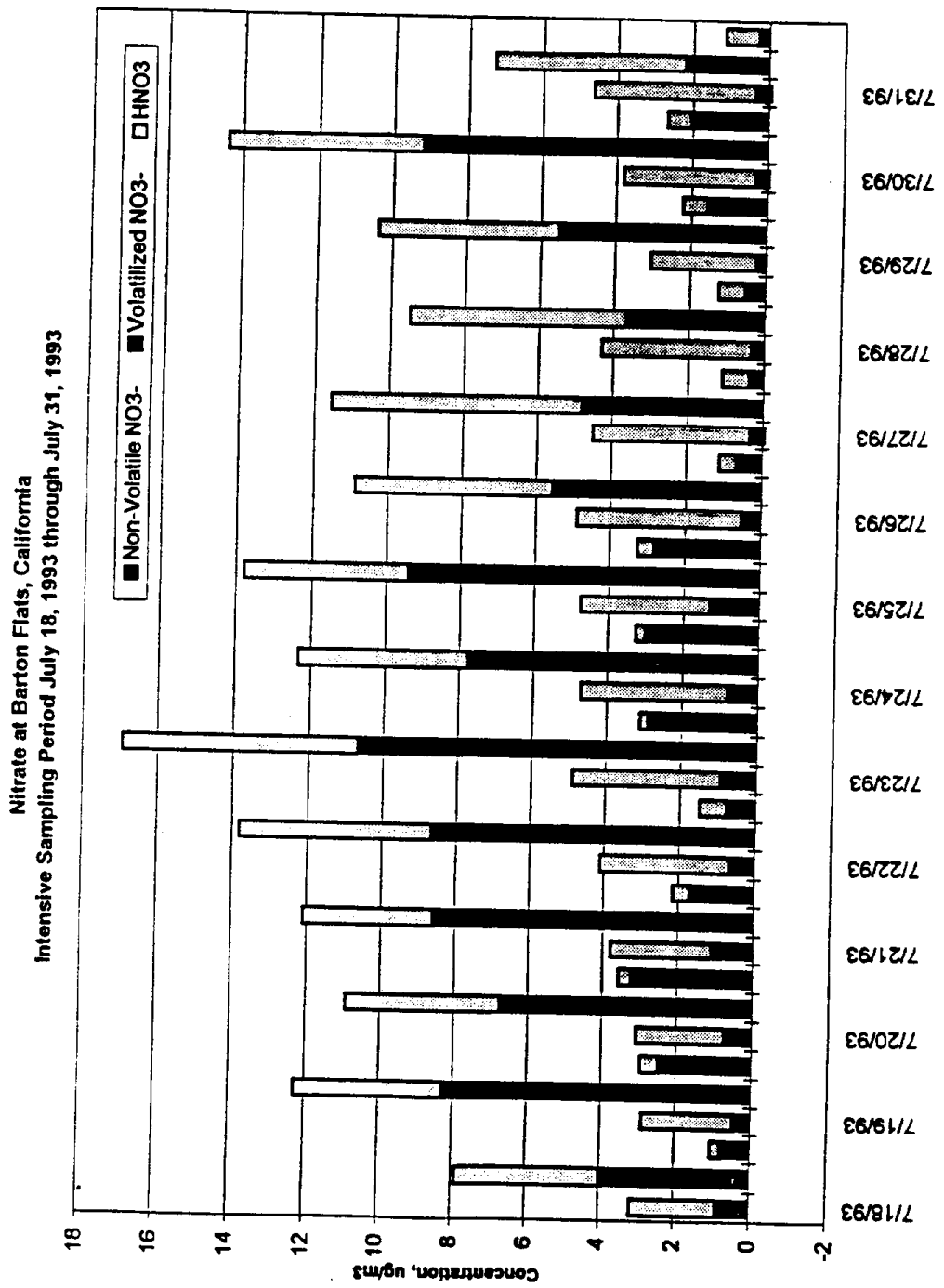

Nitrate at Barton Flats, California
Intensive Sampling Period July 18, 1993 through July 31, 1993
Non-Volatile NO3-
Volatilized NO3-
HNO3
Concentration, ug/m3
18
16
14
12
10
8
6
4
2
0
-2
7/18/93
7/19/93
7/20/93
7/21/93
7/22/93
7/23/93
7/24/93
7/25/93
7/26/93
7/27/93
7/28/93
7/29/93
7/30/93
7/31/93

Figure 31

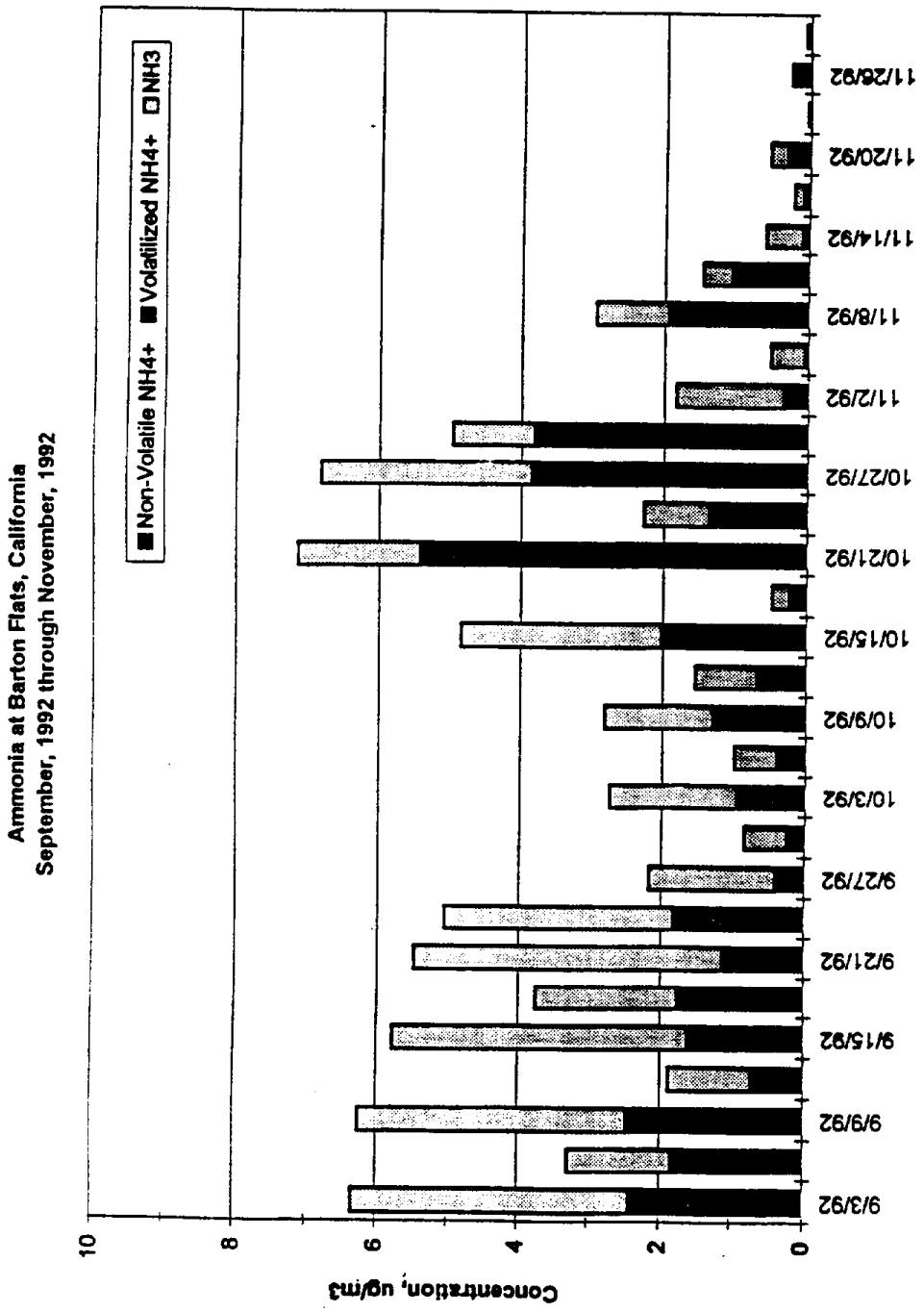

Ammonia at Barton Flats, California
September, 1992 through November, 1992
Non-Volatile NH4+
Volatilized NH4+
NH3
Concentration, ug/m3
0
2
4
6
8
10
9/3/92
9/9/92
9/15/92
9/21/92
9/27/92
10/3/92
10/9/92
10/15/92
10/21/92
10/27/92
11/2/92
11/8/92
11/14/92
11/20/92
11/26/92

Figure 32

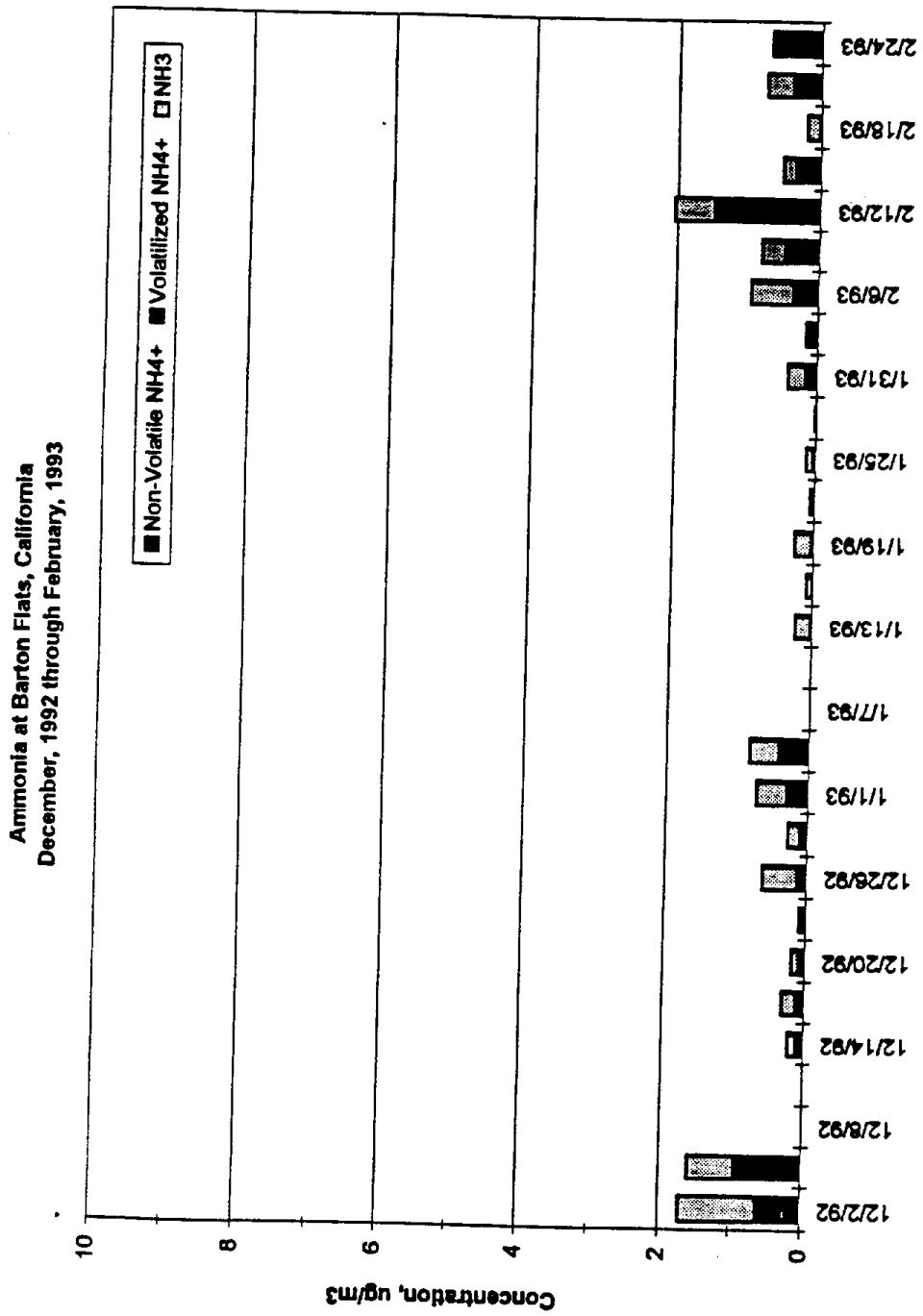

Ammonia at Barton Flats, California
December, 1992 through February, 1993
Non-Volatile NH4+
Volatilized NH4+
NH3
Concentration, ug/m3
0
2
4
6
8
10
12/2/92
12/8/92
12/14/92
12/20/92
12/26/92
1/1/93
1/7/93
1/13/93
1/19/93
1/25/93
1/31/93
2/6/93
2/12/93
2/18/93
2/24/93

Figure 33

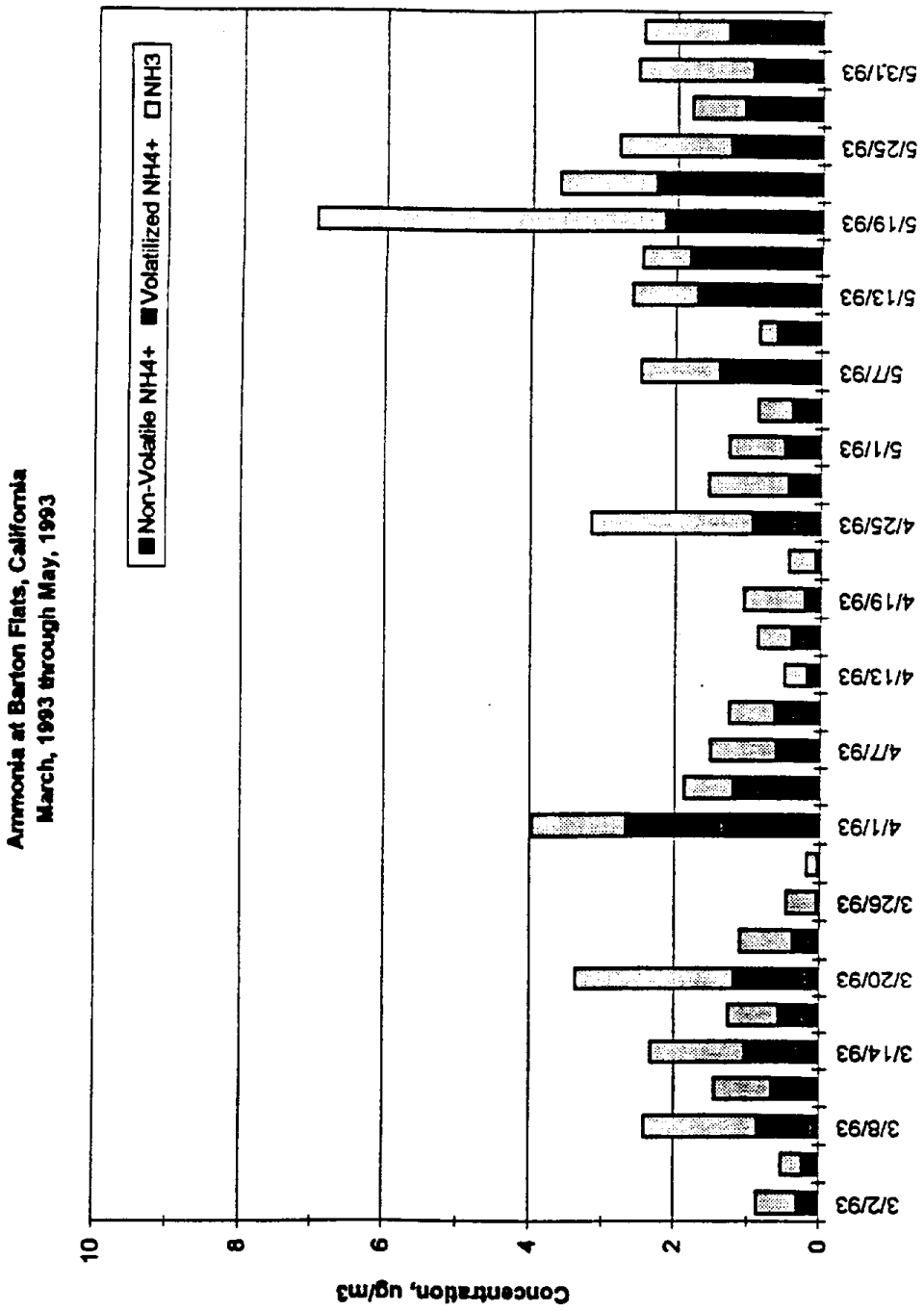

Ammonia at Barton Flats, California
March, 1993 through May, 1993
Non-Volatile NH4+
Volatilized NH4+
NH3
Concentration, ug/m3
0
2
4
6
8
10
3/2/93
3/8/93
3/14/93
3/20/93
3/26/93
4/1/93
4/7/93
4/13/93
4/19/93
4/25/93
5/1/93
5/7/93
5/13/93
5/19/93
5/25/93
5/31/93

Figure 34

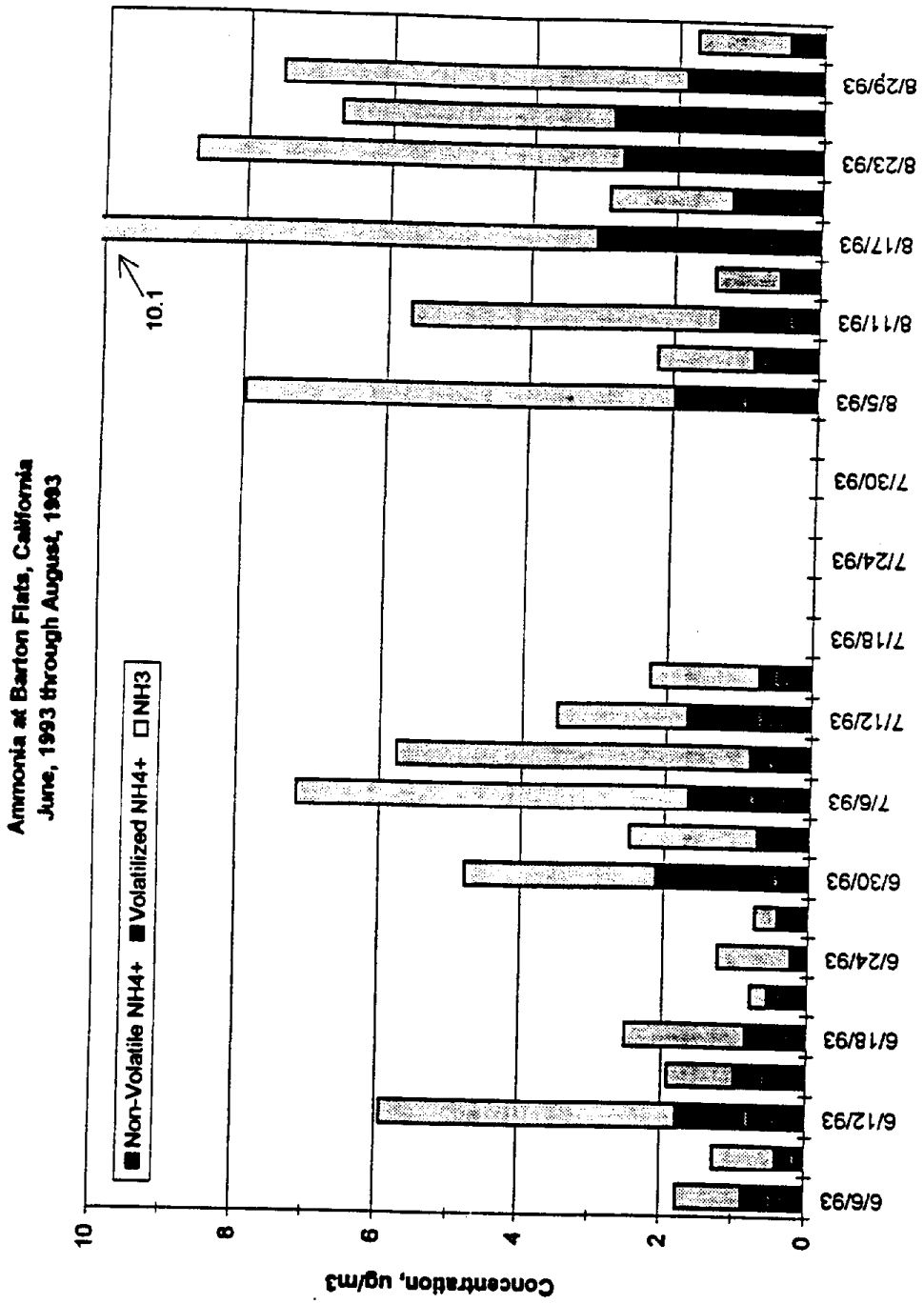

Ammonia at Barton Flats, California
June, 1993 through August, 1993
Non-Volatile NH4+
Volatilized NH4+
NH3
10.1
Concentration, ug/m3
0
2
4
6
8
10
6/6/93
6/12/93
6/18/93
6/24/93
6/30/93
7/6/93
7/12/93
7/18/93
7/24/93
7/30/93
8/5/93
8/11/93
8/17/93
8/23/93
8/29/93

Figure 35

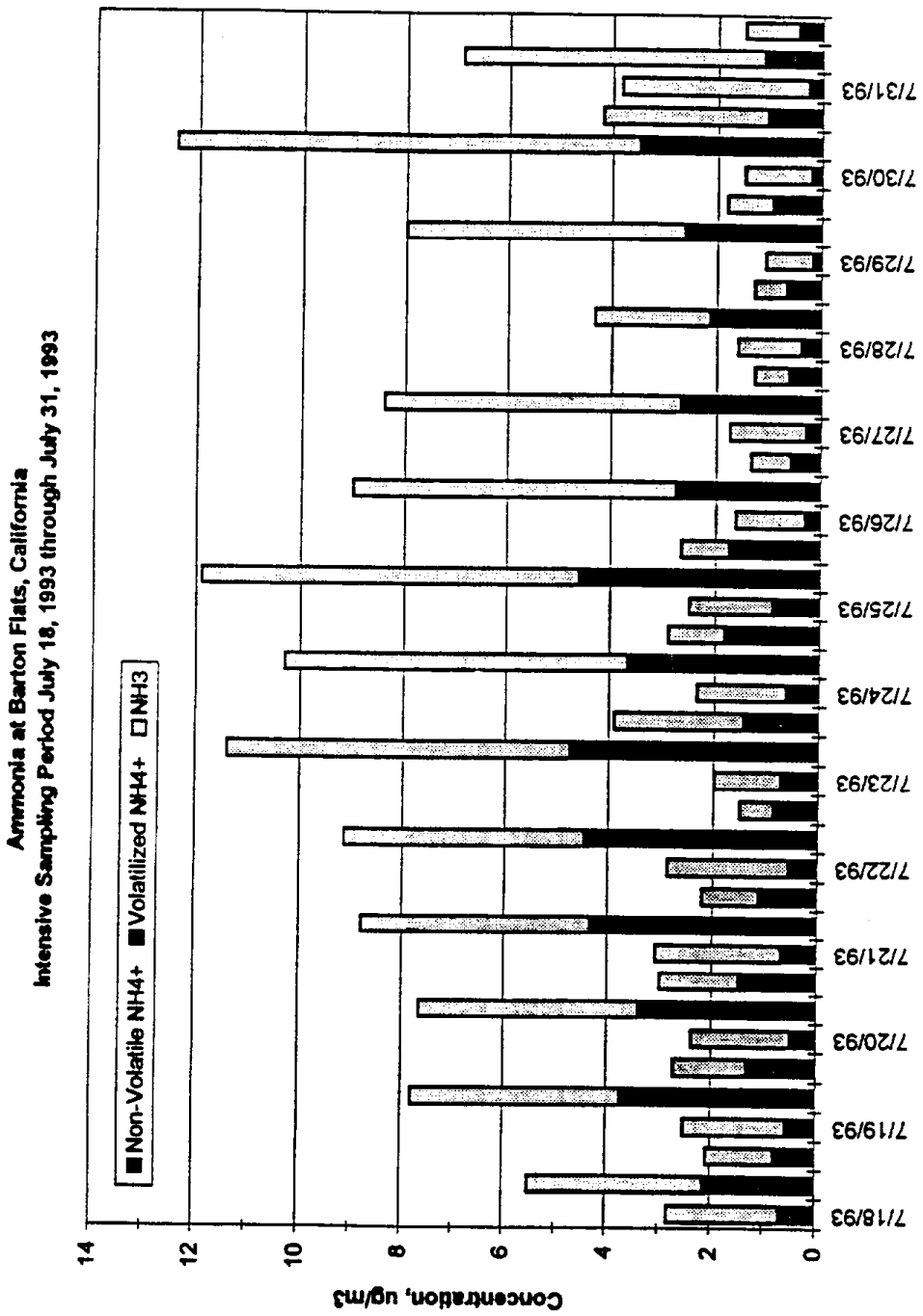

Ammonia at Barton Flats, California
Intensive Sampling Period July 18, 1993 through July 31, 1993
Non-Volatile NH4+
Volatilized NH4+
NH3
Concentration, ug/m3
0
2
4
6
8
10
12
14
7/18/93
7/19/93
7/20/93
7/21/93
7/22/93
7/23/93
7/24/93
7/25/93
7/26/93
7/27/93
7/28/93
7/29/93
7/30/93
7/31/93

Figure 36

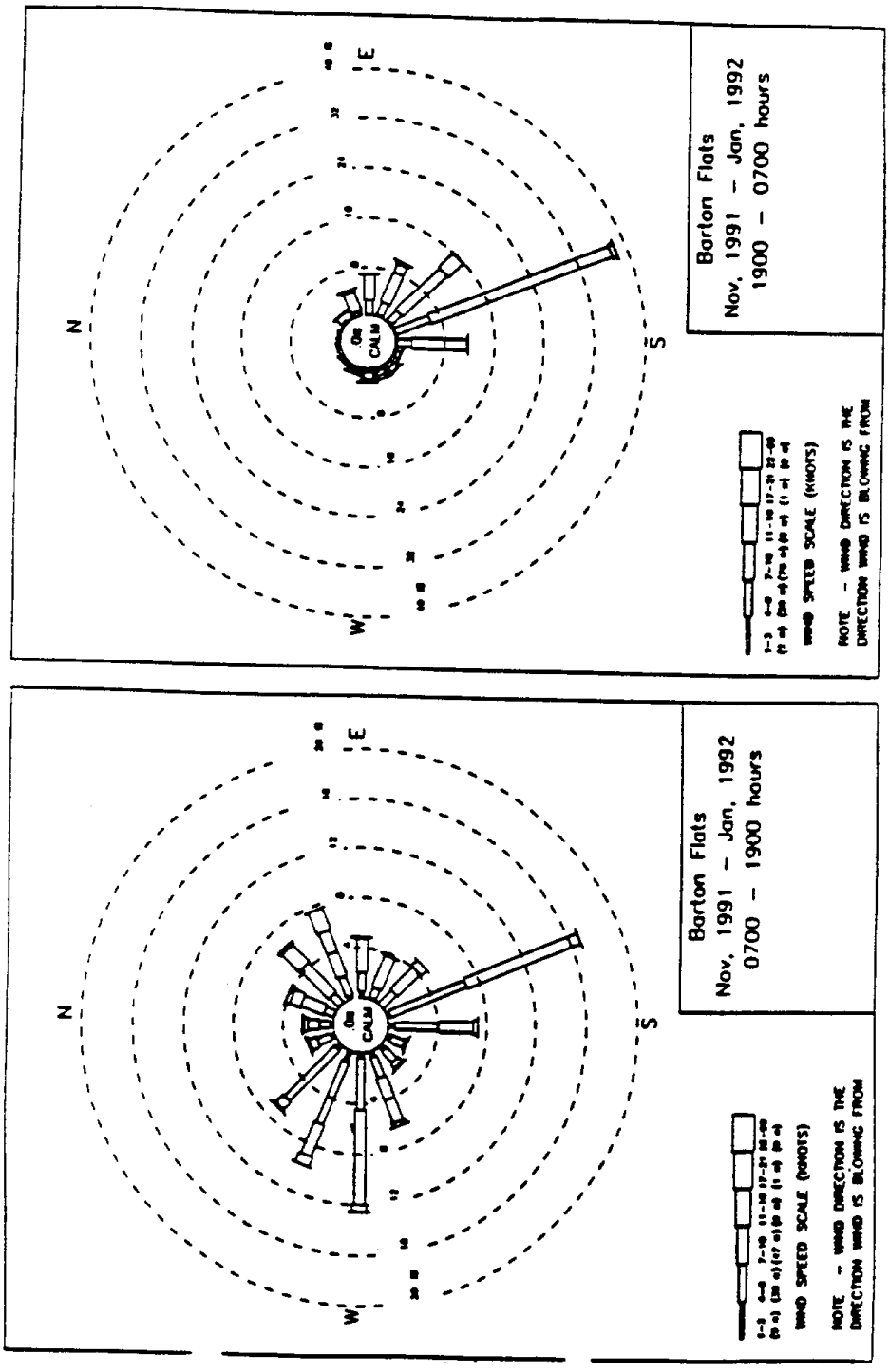

Barton Flats
Nov, 1991 – Jan, 1992
1900 – 0700 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM
Barton Flats
Nov, 1991 – Jan, 1992
0700 – 1900 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM

Figure 37

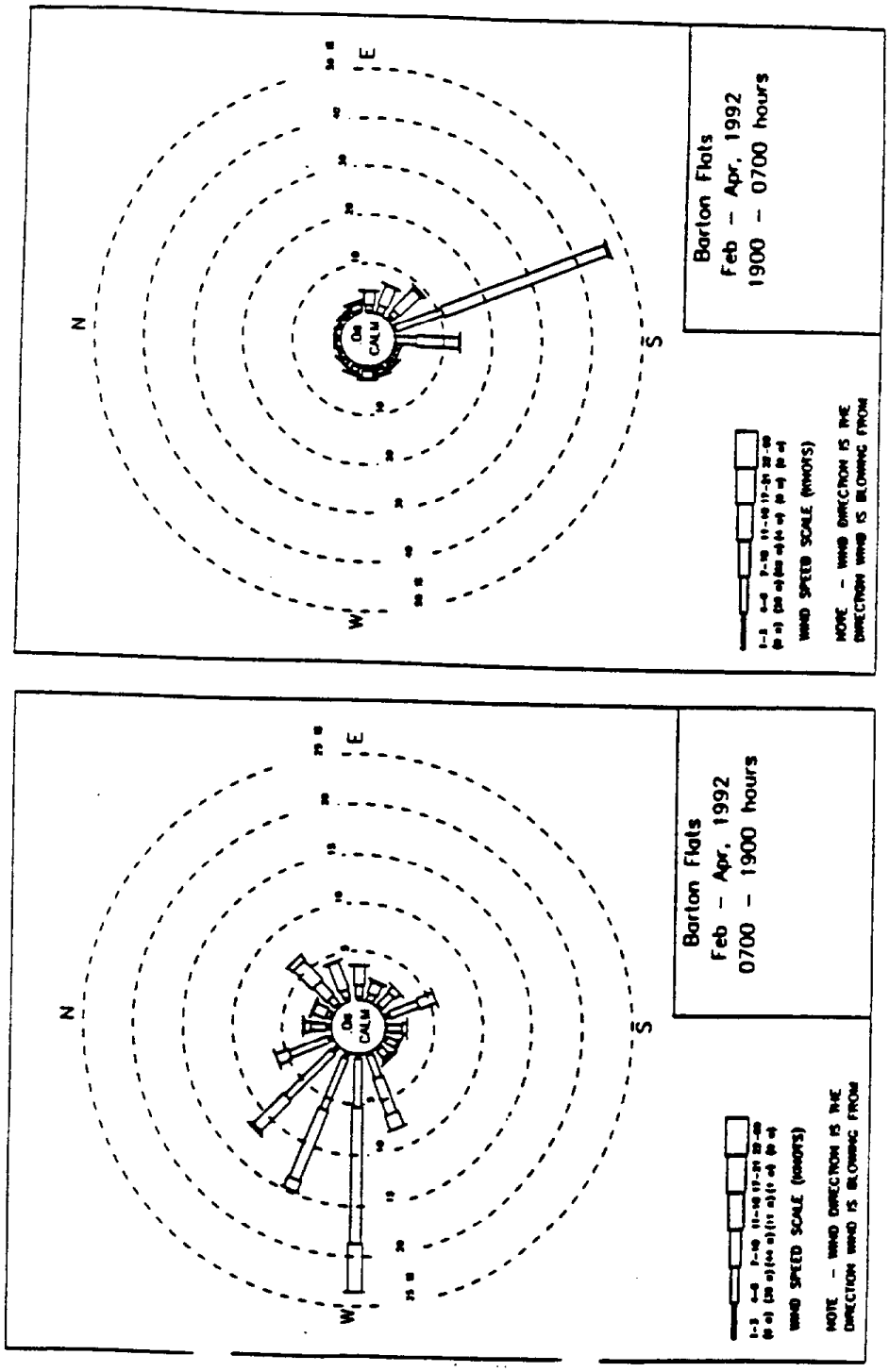

Barton Flats
Feb – Apr, 1992
1900 – 0700 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM
Barton Flats
Feb – Apr, 1992
0700 – 1900 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM

Figure 38

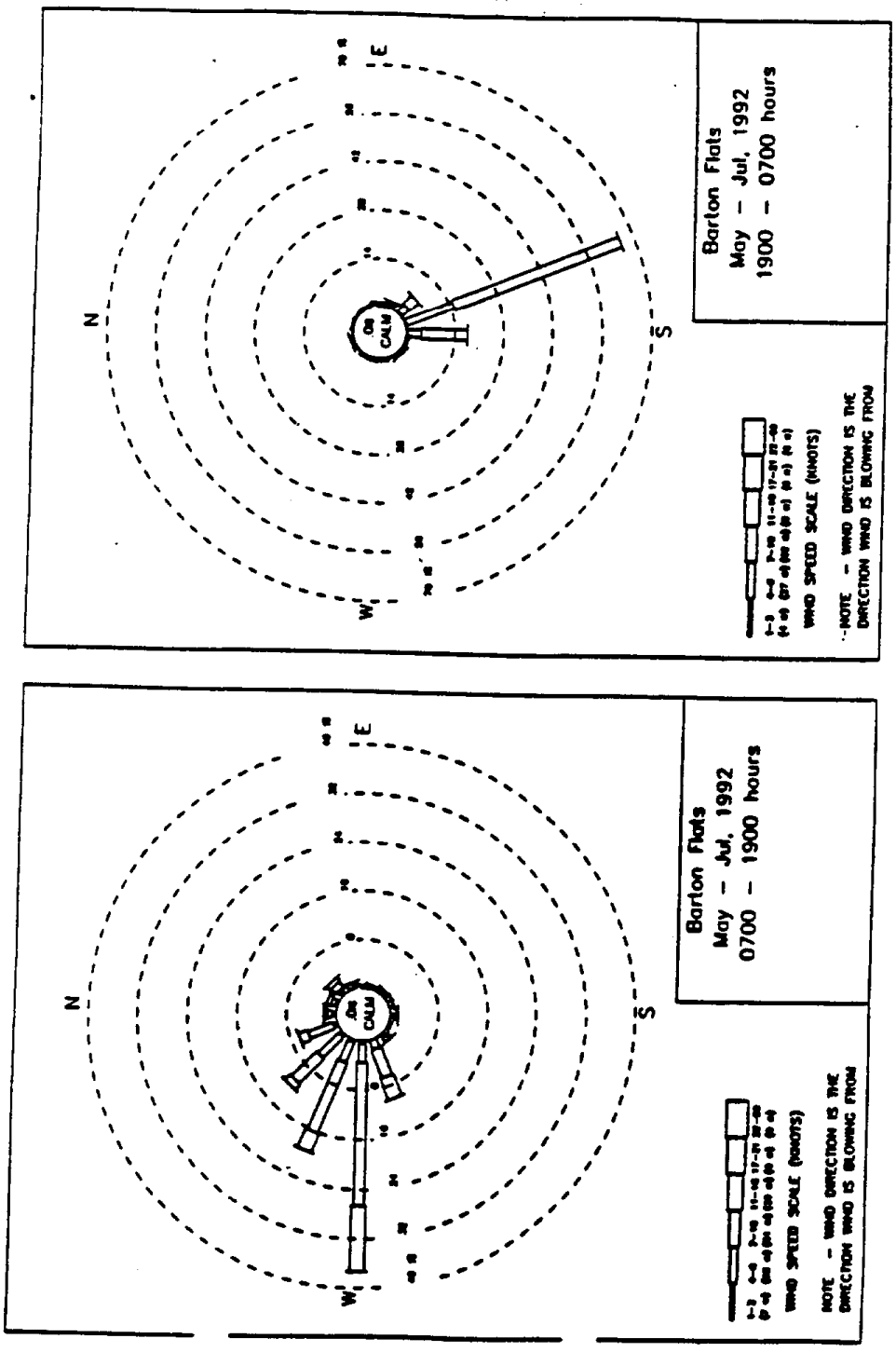

Barton Flats
May – Jul, 1992
1900 – 0700 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM
Barton Flats
May – Jul, 1992
0700 – 1900 hours
N
E
S
W
CALM
WIND SPEED SCALE (KNOTS)
NOTE – WIND DIRECTION IS THE DIRECTION WIND IS BLOWING FROM

Figure 39

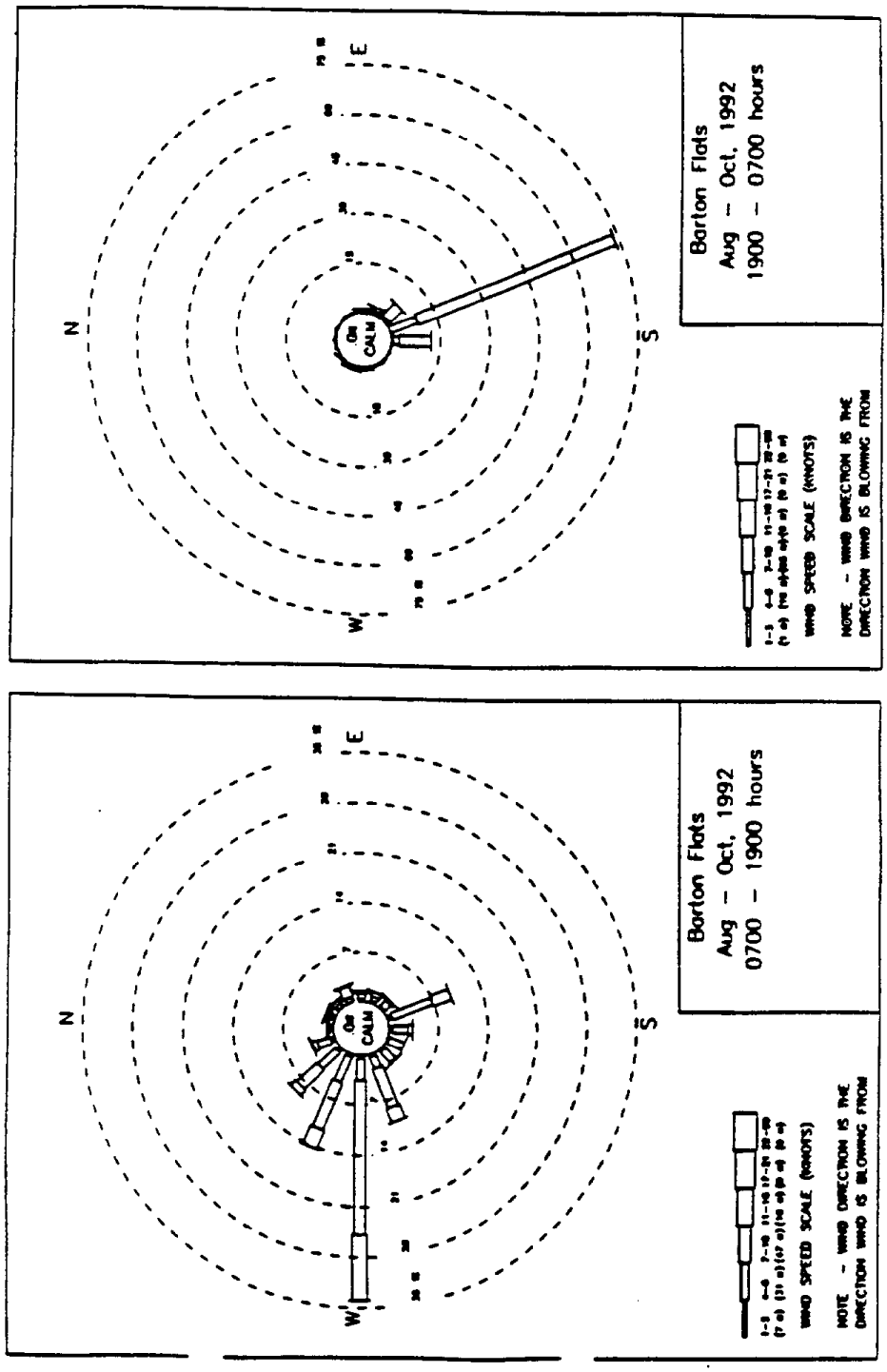

Barton Flats
Aug - Oct, 1992
1900 - 0700 hours
Barton Flats
Aug - Oct, 1992
0700 - 1900 hours
N
E
S
W
CALM

Figure 40

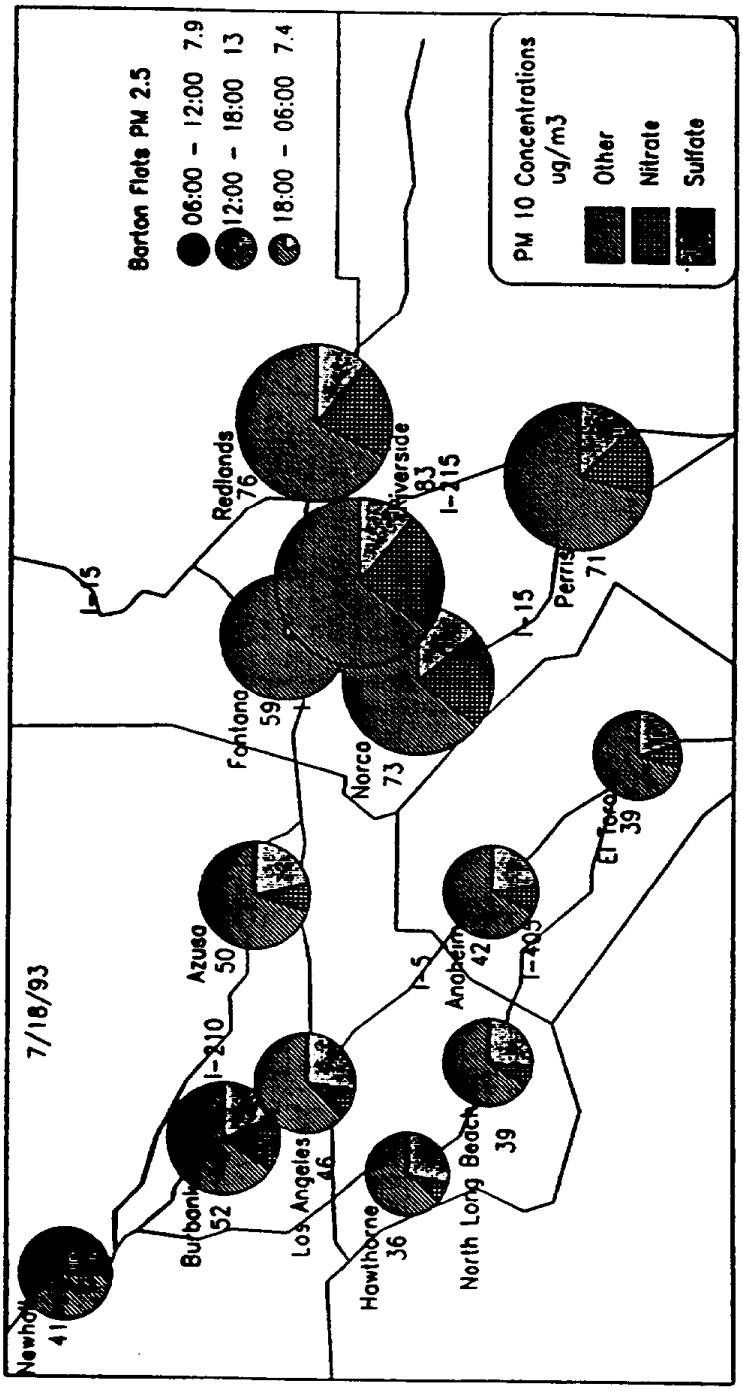

Barton Flats PM 2.5
06:00 - 12:00 7.9
12:00 - 18:00 13
18:00 - 06:00 7.4
PM 10 Concentrations ug/m3
Other
Nitrate
Sulfate
7/18/93
Redlands 76
Riverside 83
Fontana 59
Norco 73
Perris 71
Azusa 50
Anaheim 42
El Toro 39
Burbank 52
Los Angeles 46
Hawthorne 36
North Long Beach 39
I-15
I-215
I-210
I-5
I-405

Figure 41

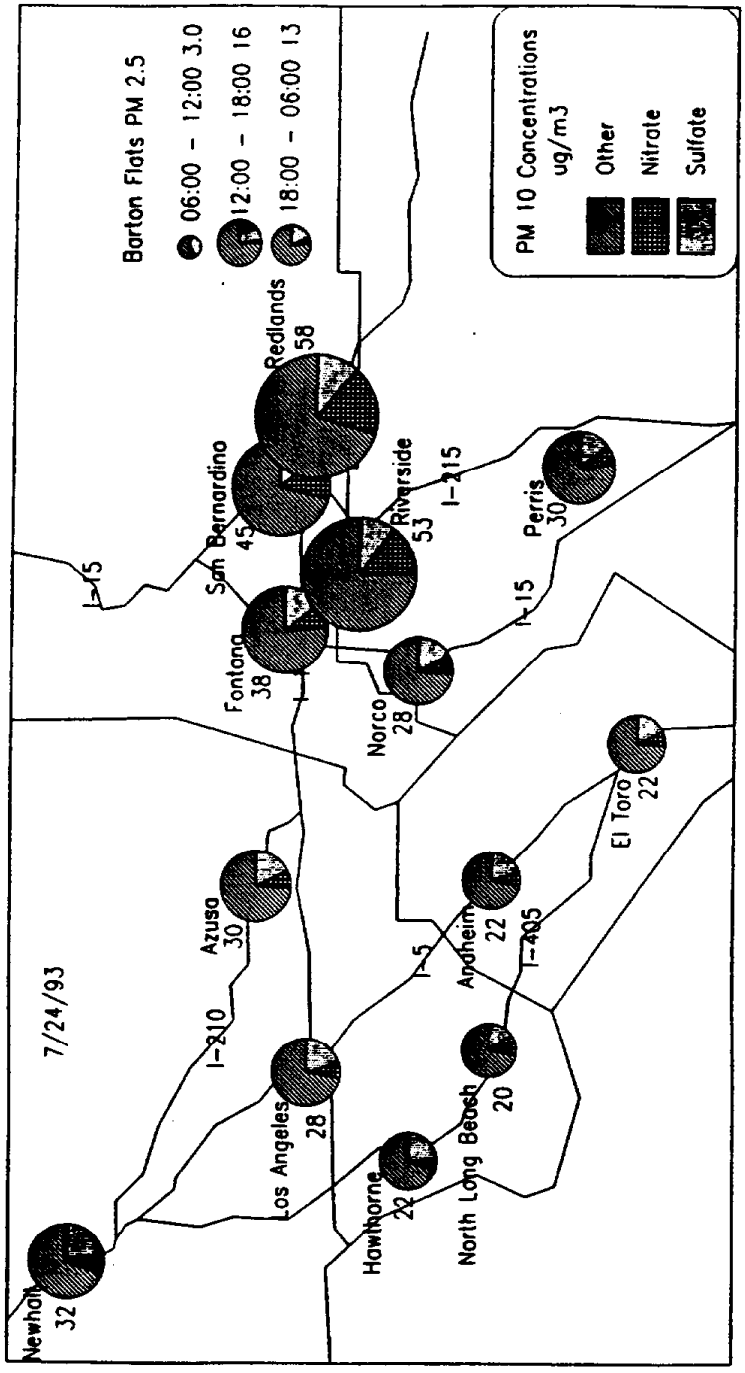

Barton Flats PM 2.5
06:00 - 12:00 3.0
12:00 - 18:00 16
18:00 - 06:00 13
PM 10 Concentrations ug/m3
Other
Nitrate
Sulfate
7/24/93
Redlands 58
San Bernardino 45
Riverside 53
Perris 30
Fontana 38
Norco 28
El Toro 22
Azusa 30
Anaheim 22
Los Angeles 28
North Long Beach 20
Hawthorne 22
Newhall 32
I-15
I-215
I-210
I-5
I-405

Figure 42

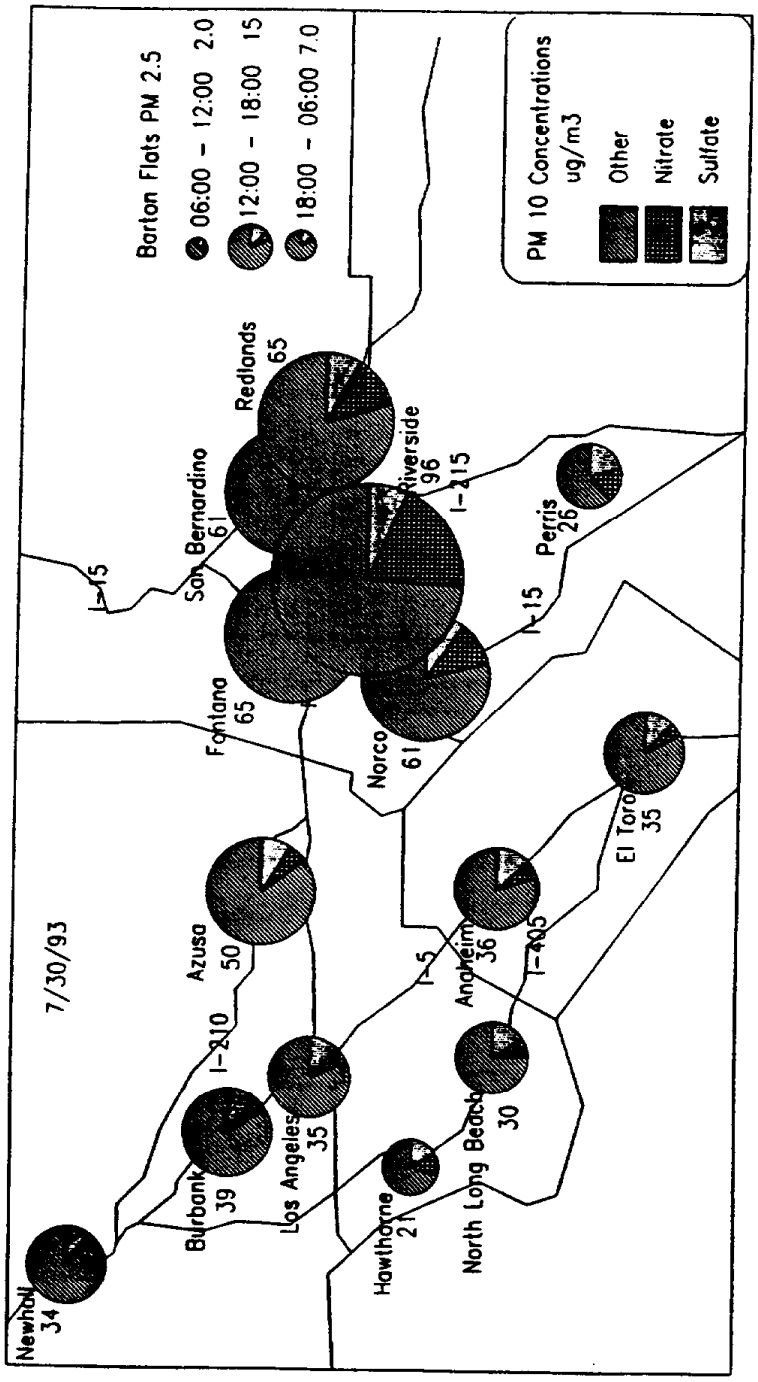

Barton Flats PM 2.5
06:00 - 12:00 2.0
12:00 - 18:00 15
18:00 - 06:00 7.0
PM 10 Concentrations ug/m3
Other
Nitrate
Sulfate
7/30/93
Redlands 65
San Bernardino 61
Riverside 96
Perris 26
Fontana 65
Norco 61
Azusa 50
Anaheim 36
El Toro 35
Burbank 39
Los Angeles 35
Hawthorne 21
North Long Beach 30
Newhall 34
I-15
I-215
I-210
I-5
I-405

Figure 43

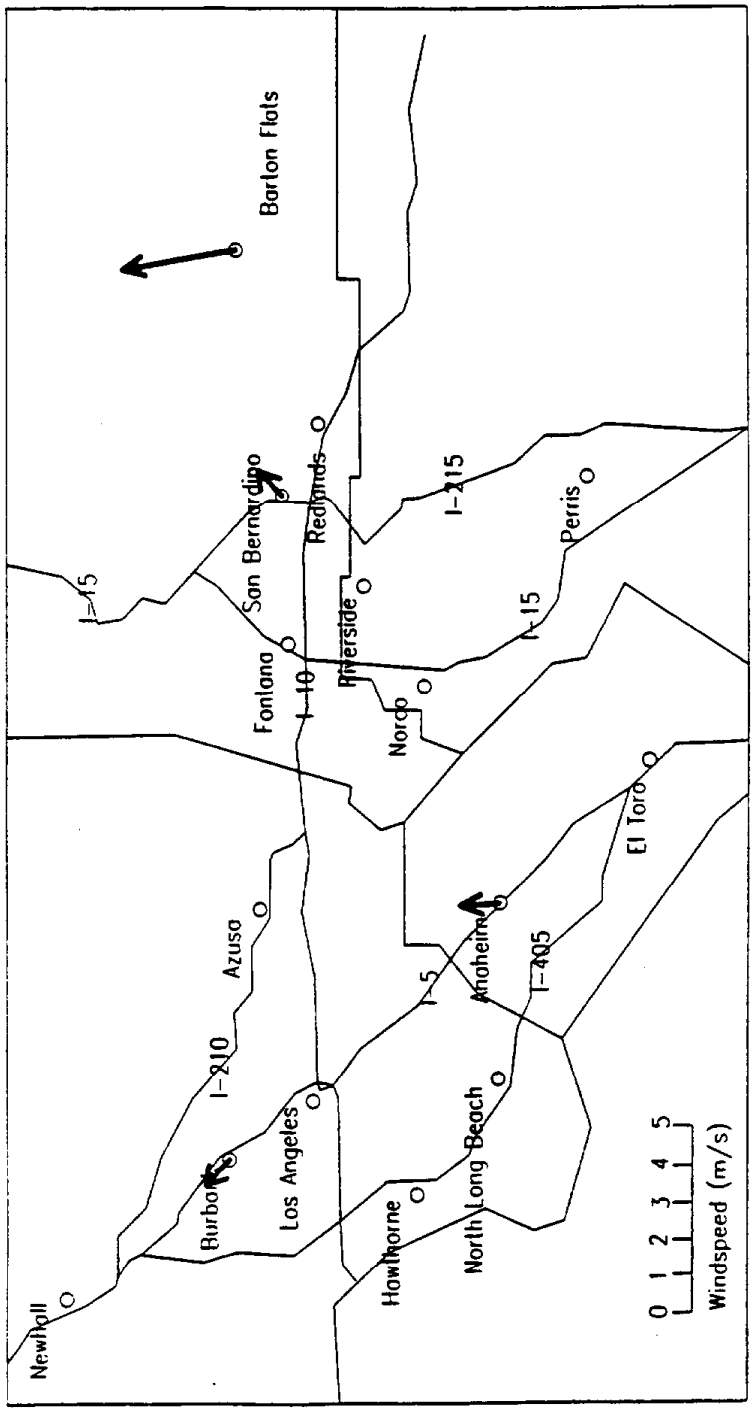

Barton Flats
San Bernardino
Redlands
I-215
Perris
I-15
Riverside
Fontana
I-10
Norco
I-15
El Toro
Azusa
I-210
Anaheim
I-5
I-405
Los Angeles
Burbank
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 00:00

Figure 44

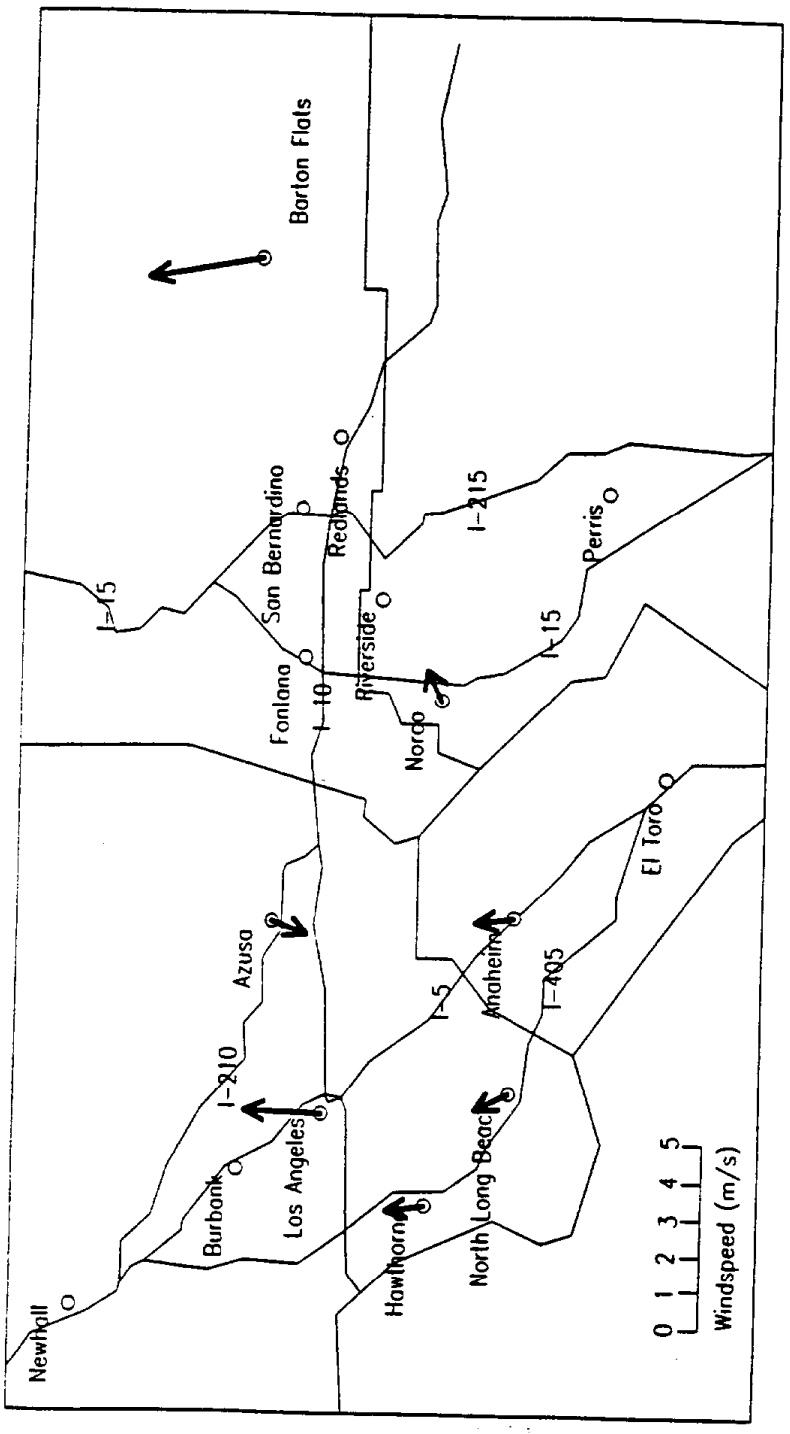

Barton Flats
I-15
San Bernardino
Redlands
I-215
Perris
Riverside
I-15
Fontana
I-10
Norco
El Toro
Azusa
I-210
I-5
Anaheim
I-405
Burbank
Los Angeles
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 05:00

Figure 45

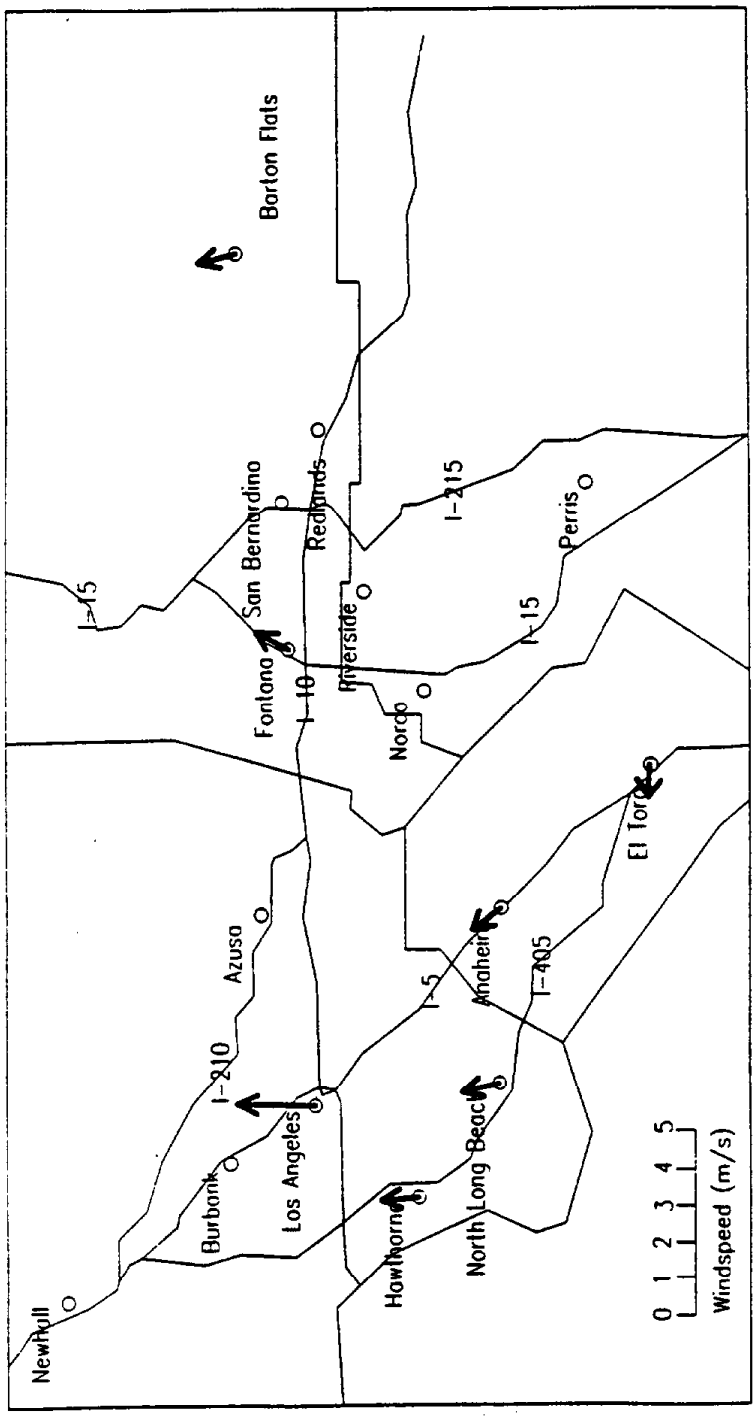

Barton Flats
San Bernardino
Redlands
I-215
Perris
I-15
Riverside
Fontana
I-10
Norco
I-15
El Toro
Azusa
Anaheim
I-5
I-405
I-210
Los Angeles
Burbank
Long Beach
Hawthorne
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 06:00

Figure 46

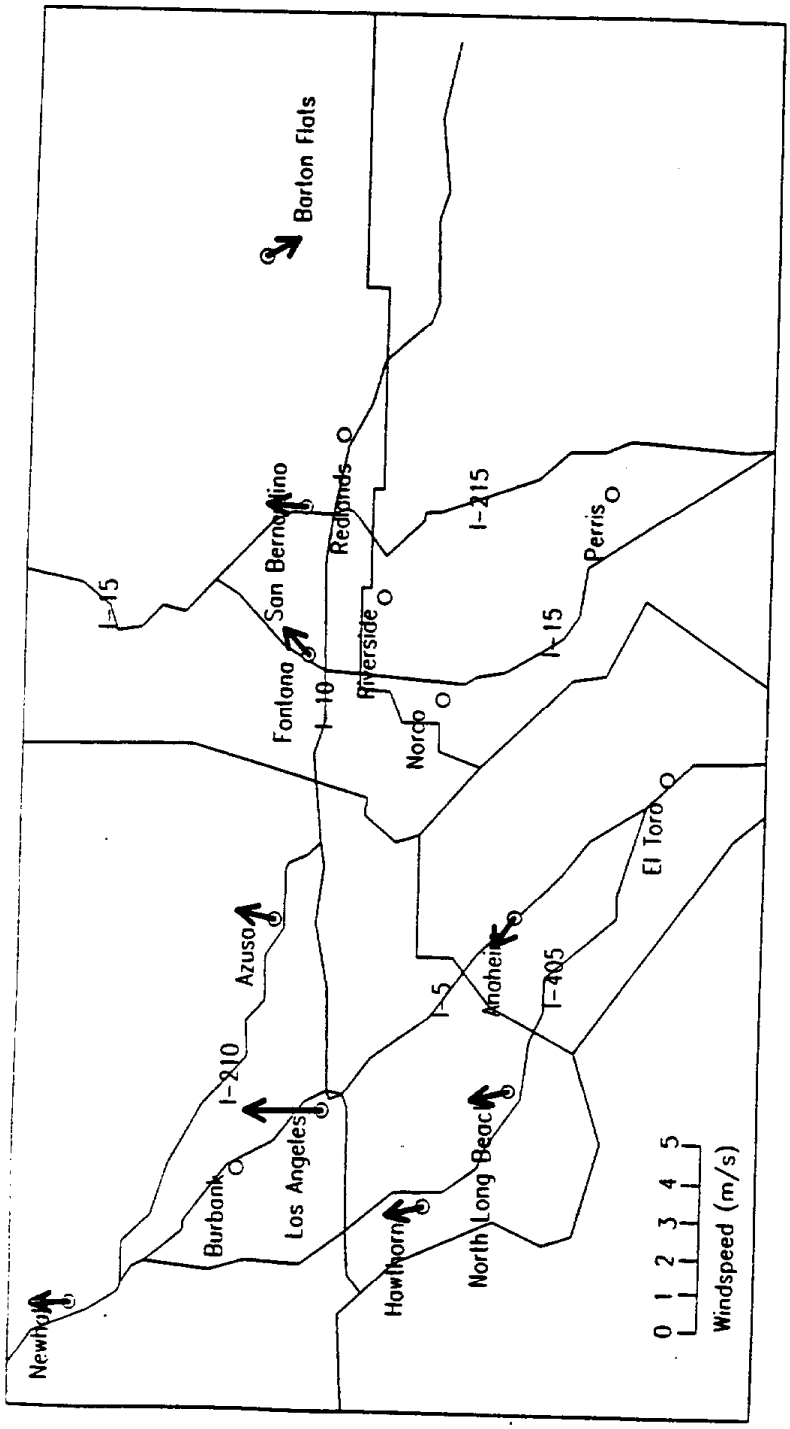

Barton Flats
San Bernardino
Redlands
I-215
Perris
I-15
Riverside
Fontana
I-10
Norco
El Toro
Azusa
I-210
Burbank
Los Angeles
I-5
Anaheim
I-405
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 07:00

Figure 47

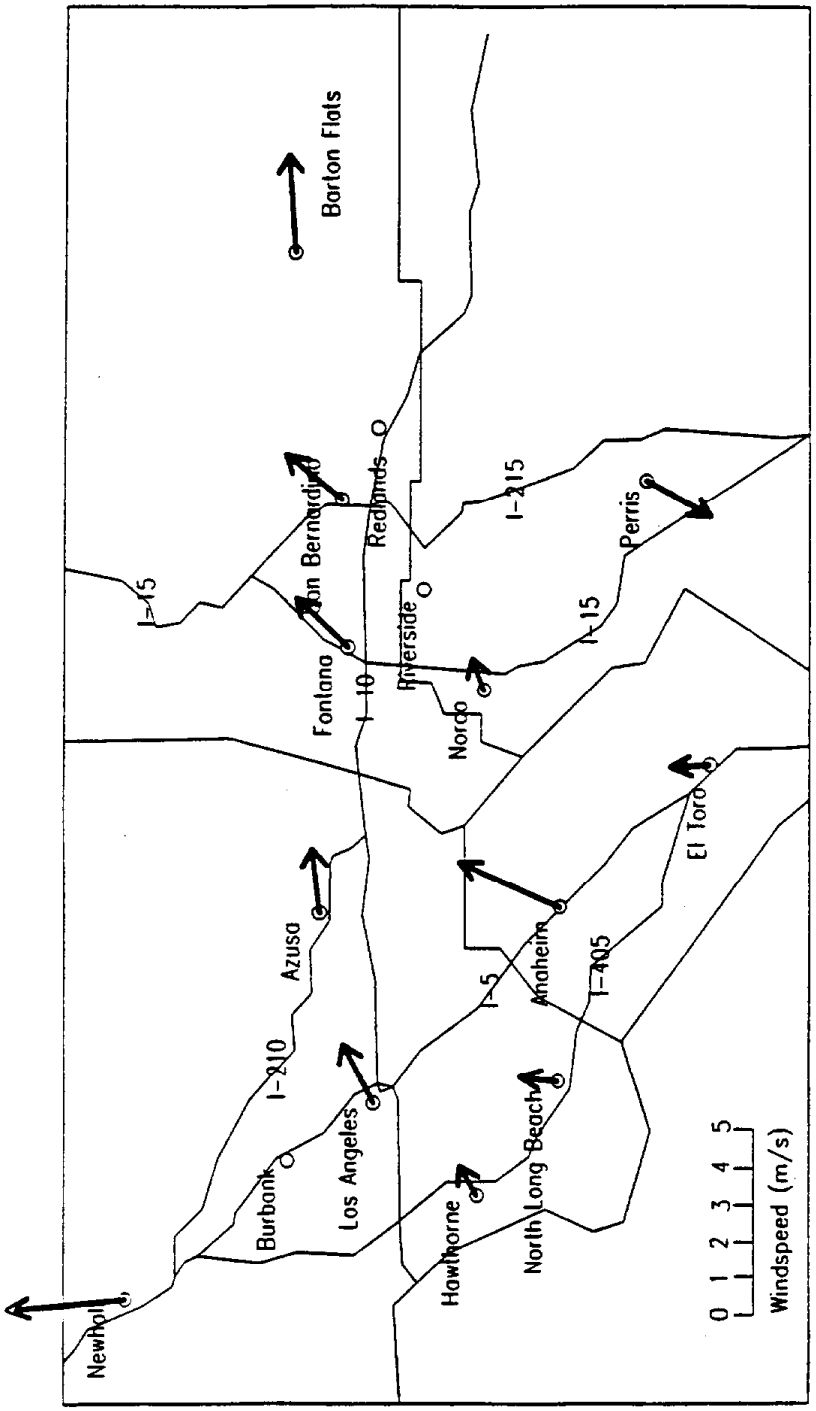

Barton Flats
I-15
San Bernardino
Redlands
I-215
Perris
Riverside
I-10
I-15
Fontana
Norco
El Toro
Azusa
I-210
I-5
Anaheim
I-405
Burbank
Los Angeles
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 12:00

Figure 48

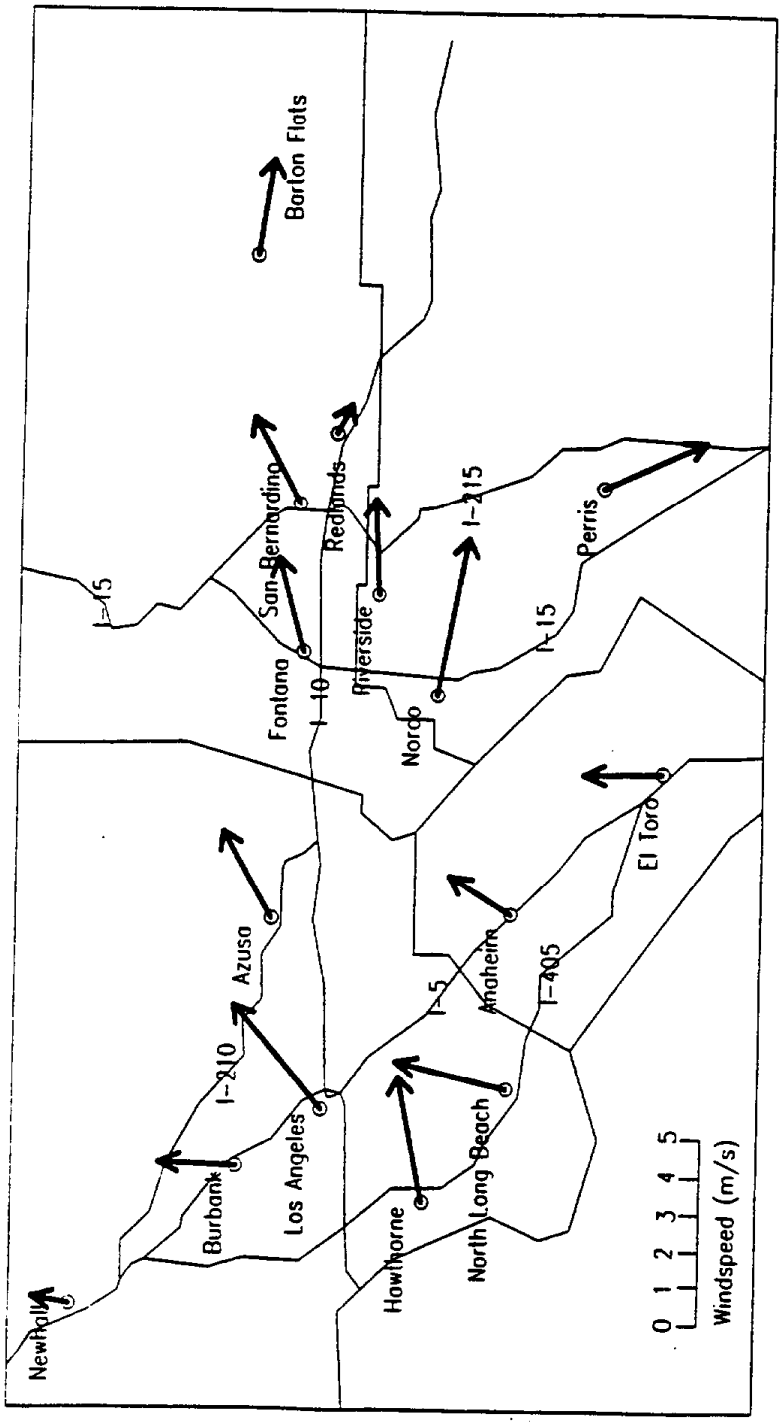

Barton Flats
San Bernardino
Redlands
Fontana
Riverside
Norco
Perris
I-15
I-10
I-215
I-15
Azusa
I-210
Burbank
Los Angeles
Hawthorne
North Long Beach
I-5
Anaheim
I-405
El Toro
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 16:00

Figure 49

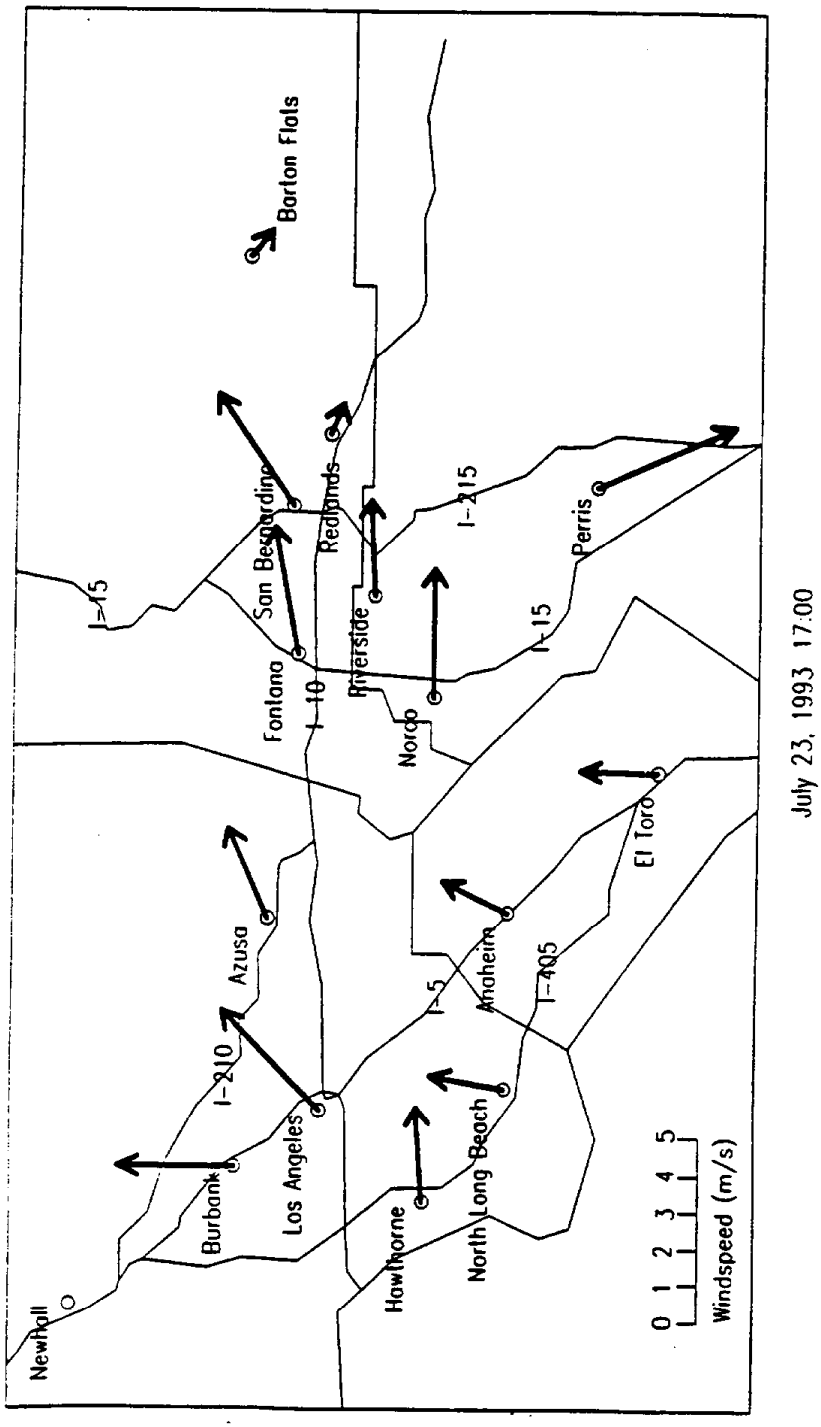

Barton Flats
San Bernardino
Redlands
Riverside
Fontana
Norco
Perris
I-15
I-10
I-215
I-210
Azusa
Los Angeles
Burbank
Newhall
I-5
Anaheim
I-405
El Toro
Hawthorne
North Long Beach
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 17:00

Figure 50

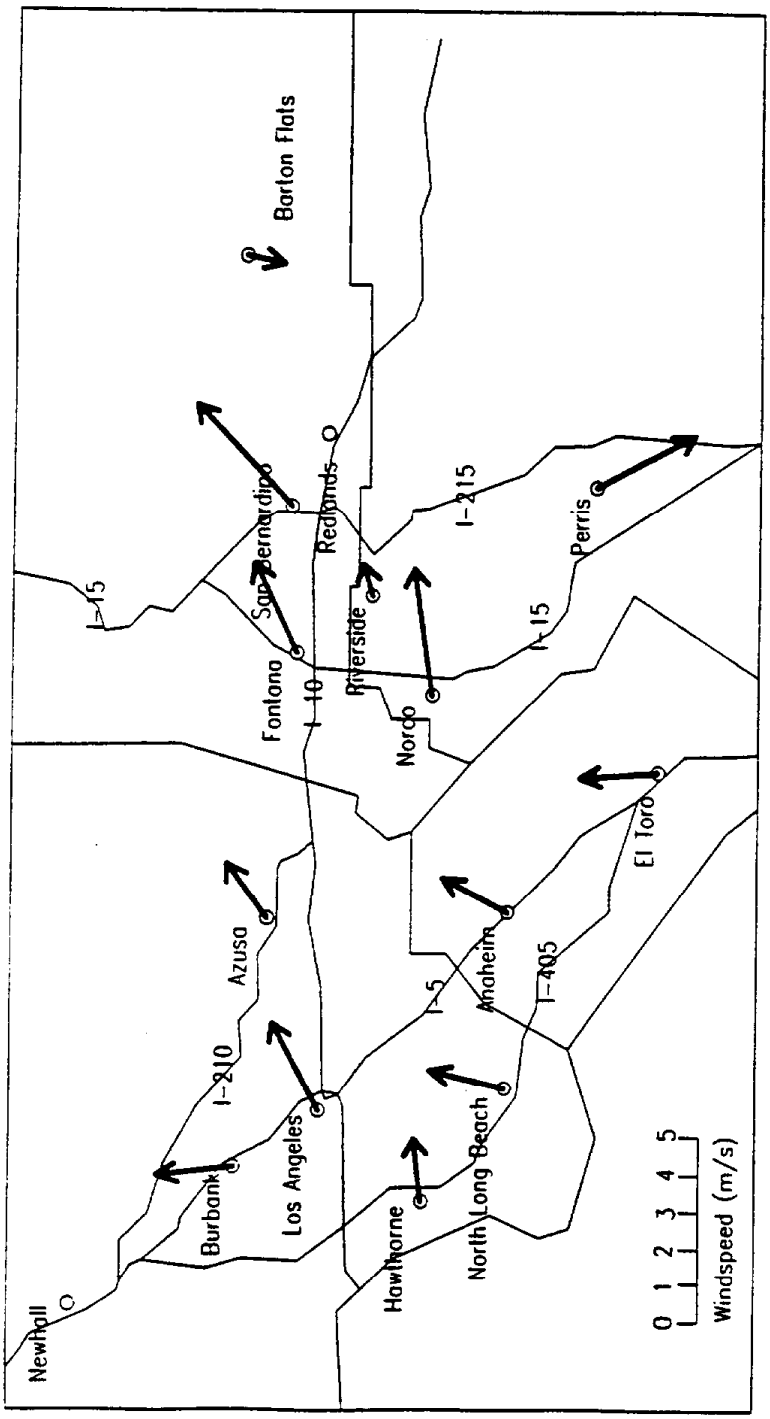

Barton Flats
I-15
San Bernardino
Redlands
I-215
Perris
Fontana
I-10
Riverside
I-15
Norco
El Toro
Azusa
I-210
I-5
Anaheim
I-405
Burbank
Los Angeles
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 18:00

Figure 51

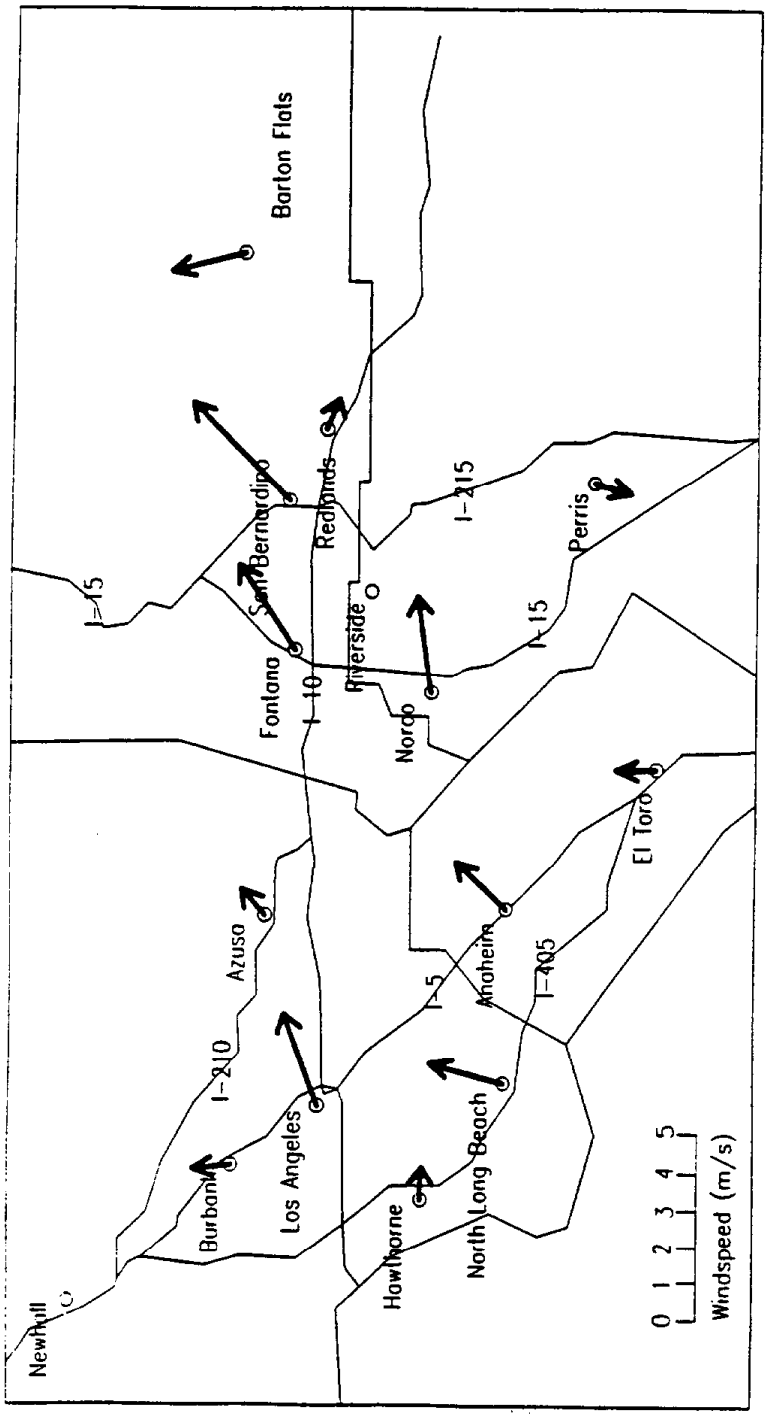
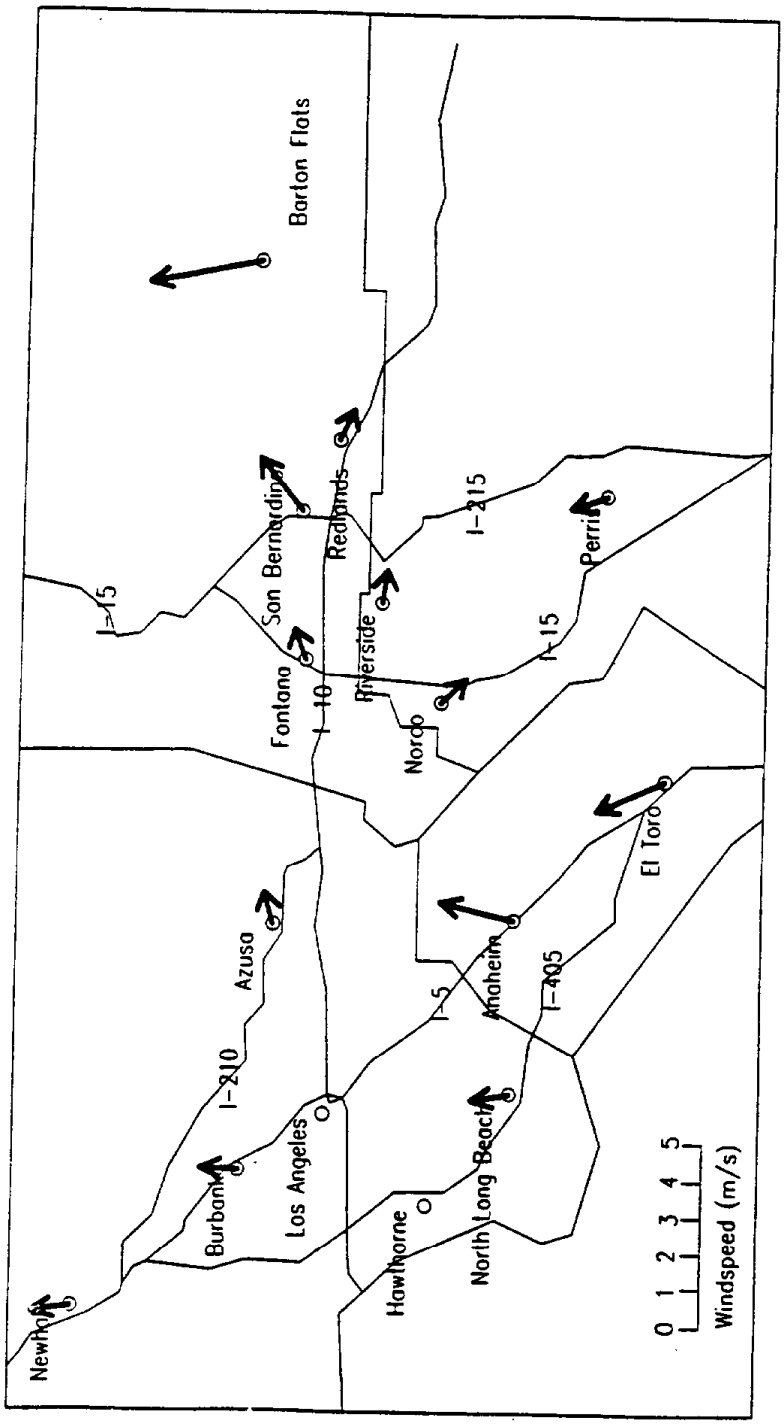

Barton Flats
I-15
San Bernardino
Redlands
I-215
Perris
Fontana
I-10
Riverside
Norco
I-15
El Toro
Azusa
I-210
I-5
Anaheim
I-405
Burbank
Los Angeles
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 19:00

Figure 52


Barton Flats
I-15
San Bernardino
Redlands
I-215
Perris
Fontana
I-10
Riverside
I-15
Norco
Azusa
I-210
Burbank
Los Angeles
I-5
Anaheim
I-405
El Toro
Hawthorne
North Long Beach
Newhall
0 1 2 3 4 5
Windspeed (m/s)
July 23, 1993 22:00

CONCLUSIONS

Ozone is the most frequently-found reactive compound ant it attains daytime hourly peaks exceeding 200 ppb at Barton Flats.

Wet deposition is non-acidic, with pH normally exceeding 5.5. The lowest value measured was 4.3 with less than 1 inch of precipitation. Sulfate and nitrate concentrations are neutralized by ammonium.

Suspended particles are non-acidic. Measured ammonium is completely explained by the presence of ammonium sulfate and ammonium nitrate.

Sulfate is not a major component of suspended particles at Barton Flats, with concentrations that rarely exceed 3 $\mu g/m^3$

Particle nitrate is high during summer and fall, with daytime concentrations often exceeding 10 $\mu g/m^3$.

Nitric acid is the most significant acidic species, achieving afternoon concentrations exceeding 6 $\mu g/m^3$. (Measurements may by negatively biased by up to 50%).

Winds at Barton Flats indicate distinct up and down valley flows during all seasons except winter. Up-valley flows correspond to transport from the South Coast Air Basin.

2. Atmospheric Deposition in California Forests: Results from Branch Washing and Process-Level Modeling. Dr. George Taylor, University of Nevada and Dr. Andrzej Bytnerowicz, USDA Forest Service.

DR. GEORGE TAYLOR: University of Nevada

We have just finished hearing about the atmospheric chemistry at Barton Flats, and I am going to talk about the effects of atmospheric pollutants on the forest ecosystem with respect to soils and forest trees. For those that are interested in plant physiology and ecology, atmospheric chemistry is an important parameter. However, we have to know what portion of what the compounds in the atmosphere actually reacts with the plant canopy or the forest soil. I want to talk about how we translate the information that John Watson, Judy Chow, and others have on atmospheric chemistry to provide the input to those addressing the health of the forest system, whether it be forest trees or soil systems. It is not a trivial effort to estimate deposition. We developed two different techniques independently and then merged them together to compare the degree to which they agree for dry deposition at the Barton Flats site. One is a bottom-up technique using branch washing, which was based upon events within the forest canopy. That work was done by Andrzej Bytnerowicz at the Forest Service Lab. The second technique used a process level model (which is a "big leaf" model), and I will talk about that. The objective was simply to estimate the input of the acidifying substances into the forest system. The two techniques are not identical; they have different assumptions, but the hope is that by doing two independent techniques, we can get some sense of the uncertainty in our measurements. Andrzej is going to talk first, and I will follow with the process level model.

DR. ANDRZEJ BYTNEROWICZ: USDA Forest Service

Thank you very much for a good introduction. I would like to also acknowledge the help of Mark Fenn and Robert Glaubig from our laboratory who helped me put all the data together and also helped prepare some of the slides (Fig. 1).

John Watson showed the location of the site (Fig. 2), and this is our study area. We have three flux measurement sites in the Barton Flats area. Site 1 is a monitoring station, and John presented data from this site. Site 2 is a tower in the forest, and I will show mainly results from that site. There is also a third site, however, no results from that site will be presented in my talk. We looked at deposition of ions at these three different sites, and we have been doing an intensive study at site 2 on the vertical distribution of concentrations and deposition of gases and particles (Fig. 3). There is a sampling tower more than 30 meters tall. I measured concentrations of gases by using the annular denuder system developed by Possanzini and modified later by Legge at four different levels: the top of the canopy at 30 m, and at lower levels of 12 meters, 26 meters, and 29 meters. We measured concentrations of

pollutants, and determined nitrate, ammonium, and sulfate deposition of ions to branches using a branch washing technique. I should mention that the tower was also used for other purposes. You will be hearing later from Pat Temple about measurements of gas exchange by trees at different levels on the canopy. I used part of his findings for calculations of the internal uptake of gaseous pollutants by plants. A summary of the methods that we used is shown on figure 4.

First, we determined concentrations of nitrogen, gases and particles. Then we looked at the compound fluxes through a vertical gradient and also a horizontal gradient. We did measurements on the tower and repeated measurements in sites 1, 2, and 3. We also analyzed through fall on a horizontal gradient. I will show some results of that which will confirm our findings with the branch washing technique. With the measurement of wet deposition (I am not going to present a lot of data on that, but it will be included in our summary) we did calculations of atmospheric deposition on the forest site level. I will show later some comparisons with other sites in California.

I would like to show you some results of the air chemistry on the tower. Figure 5 shows nitric acid in micrograms per cubic meter during the 1993 season. I chose the 1993 season because we have the best data set for this particular year. We also have data from 1992 and 1994 and, in general, the figures agree with the measurements from 1993. The 24-hour average concentrations of nitric acid were approaching 5 micrograms per cubic meter. We did not find a gradient of air pollution concentrations on the tower. In most of the cases, the values were quite similar.

The situation changes if we look at the fluxes of various ions (Fig. 7). We placed ponderosa pine seedlings at four levels of the tower because we were not always able to reach the branches of mature trees adjacent to the tower. On some occasions, we were doing inter-comparisons, by measuring deposition at top levels where we were able to reach the branch of the mature tree and from the seedlings. For our calculations, we included some corrections. The units are in micrograms per meter square per hour. Standard deviation is included in the bar graphs. We always saw a very steep gradient. The highest deposition flux was always at the top of the tower. This was important for us because in calculating deposition velocity values for various chemical species, we wanted to know what was happening within the canopy of this particular forest. I must mention that mixed conifers in Barton Flats are different from those reported from the eastern United States or Europe. Barton Flats is located in a very non-uniform terrain and very often there are gaps in the canopy. Ammonium flux behaved similarly as nitrate flux, and the higher deposition always occurs at the top of the tower (Fig. 8). We measured deposition fluxes also at the monitoring station and at the bottom of the tower. Figure 9 presents nitrate deposition during the intensive period of our study, July 23-30, 1993. Similarly for ammonium (Fig. 10), the highest deposition occurs on the top of the tower. Figure 11 is an example of a comparison between seedlings and mature trees and it shows nitrate during the intensive period of our

study. We worked with three major tree components in the area, Ponderosa pine, black oak, and white fir. For calculating fluxes for fir and oak we extrapolated results for Ponderosa pine seedling. For ammonium the results from the intensive study for the seedling and mature pine, black oak, and white fir trees are presented (Fig. 12).

Figure 13 presents my attempt to calculate conductance of nitric acid in Ponderosa pine branches on a vertical gradient. Using different kinds of calculations, basically dividing a flux by the concentration of different levels from the tower and subtracting portions which were attributed to particulate nitrate, I calculated deposition velocity values at four different levels of the tower. We see that in some cases the deposition velocity values were quite high, about 3.5 cm per second. In the majority of cases we had deposition velocity values somewhere in the area of 1 cm per second. Because these values differ at various heights of the canopy, future attempts to model air pollution intake in mixed coniferous forests should take this into account.

Figure 14 is a summary of my calculations from branch washing. In general, we assumed that we had two seasons: polluted and unpolluted ones. The polluted season included April 15 to October 15, and the unpolluted season the rest of the year. We calculated total dry deposition by including washable nitrate from the foliage (taken from the foliage washing), and washable nitrate from the branches. Unfortunately, we did not have information on LAI (leaf area indices) from California and therefore I had to use data from the Colorado Rockies obtained from Dr. Mike Arbaugh. We similarly calculated dry deposition of ammonium both for foliage and for branches. Then I calculated internal uptake of nitric acid, ammonia, and NO_2, making different assumptions based on the conductivity for these gases calculated from the trees gas exchange data. Explanation of all of my calculations is included in the supplementary material (see appendix 1). There is not enough time to go through all my calculations now, so I am showing only the final result. Figure 14 shows the total dry deposition at site 2 expressed as grams of nitrogen per hectare per year for the pine, the oak, and the fir. We obtained about 3.2 kilograms or 3,282 grams of nitrogen. A major portion of that was in a form of washable deposition. The internal uptake of the gas phase nitrogen was only a small portion. The highest deposition occurred on the oak. This was somewhat surprising because oak has foliage only during the part of the season, while pine and fir are evergreen.

Figure 15 presents the calculated total nitrogen deposition at site 2, during the 1993 season and is expressed as grams of nitrogen per hectare per year including wet deposition measurements. In order to calculate total deposition, I needed a measure of the surface area at this forest which is called leaf area index. We used two methods to collect these data; one was litter for analysis and another was the ceptometer method. With the litter fall, which is a more reliable method, we measured a leaf area index 1.89. With the other method we found a value of 3.8, and these two values were used for my

calculations. The lower estimate of total nitrogen deposition was about 5 kilograms per hectare per year and a high estimate approached about 9 kilograms per hectare per year. When deposition of nitrate in the San Bernardino forest was studied, Barton Flats was our main site, but we also did our measurements in different parts of the mountain. One of them was Camp Paivika, a highly polluted part of the San Bernardino mountains. We used two techniques for wet deposition collection. We had deposition collectors located to collect both wet and dry deposition, and we also had collectors which were only open during the wet events. Our comparisons show that Barton Flats is in the middle of the air pollution gradient (Fig. 17). If you look at the results of our measurements for native pines using the branch washing technique, the fluxes that we measured in the eastern Brook Lake, eastern Sierra Nevada, Emerald Lake, and western Sierra Nevada are between 6 and 25 micrograms per square meter per hour. At Barton Flats we are in the range 25 to 130 and the average is about 50 μg in $m^{-2}h^{-1}$. Tanbark Flat in the San Gabriel Mountains had very high deposition values. Camp Paivika, the site which I showed for the wet deposition in winter, was a highly polluted site. The values for Camp Osceola, which is right behind our Barton Flats site, are still very close to the values determined in the western Sierra Nevada.

Now I want to discuss some recent data from Bob Glaubig (Fig. 18). Here, calculated deposition of metals at Barton Flats. The deposition for the 189 day polluted season in 1993 is shown in kilograms per hectare per 189 days. Calcium is close to 5 kilograms. For total nitrogen, my own calculations and Bob's differ by about +/- 10%. For the polluted part of the season, just as for dry deposition, the value was about 4. The sulfur analysis basically confirms what John was saying; sulfur is relatively unimportant and has much lower values than in the eastern U.S.

The conclusions are shown in figure 19. There was no clear vertical gradient of nitric acid and ammonia in the plant canopy. There was a strong vertical gradient of nitrate and ammonium ion fluxes which is probably due to differences in wind speed. We have to analyze our methodological data from the tower where we have these data. Barton Flats is an intermediate air pollution site on the west-east gradient of the San Bernardino mountains. Differences in deposition fluxes to various tree species were present. Deposition of nitrogen at Barton Flats was mostly in a dry form and about 80% was attributed to dry deposition. The foliage rinsing technique can be used as a test of measuring dry depositions. The principle of this method is very similar to through-fall method, and in some situations, it is easier to use.

Q (AUDIENCE) I think some of the concentration numbers you presented in the beginning are high.

A (DR. BYTNEROWICZ) The concentrations were quite high. Concentrations of nitric acid and ammonia were elevated compared to some of the locations in California. Deposition flux values for nitrate and ammonium were about three or four times higher at the top than at the bottom of the tree canopy.

Q (AUDIENCE) I have a question on methodology. What is the basis for the distinction between internal uptake, the stomatal intake, and that which is retained by some chemical procedure?

A (DR. BYTNEROWICZ) For the gases we assume that they are taken up by the plants through stomata and that includes nitric acid vapor. For nitric acid, we used to believe that it penetrated through the cuticle. Other control studies showed that stomatal uptake of nitric acid vapor was also important. Stomatal uptake is the main mechanism for of uptake ammonia, NO_2, and ozone. Using gas exchange data (specifically exchange of water vapor between the plants and the air) and using some equations, I can calculate internal uptake of these gases. This is explained Appendix I.

Figure 1

Atmospheric Deposition of Nitrogen Compounds to a Mixed Conifer Forest Stand

Andrzej Bytnerowicz, Mark Fenn and Robert Glaubig

USDA Forest Service
Pacific Southwest Research Station
Riverside, California

Figure 2

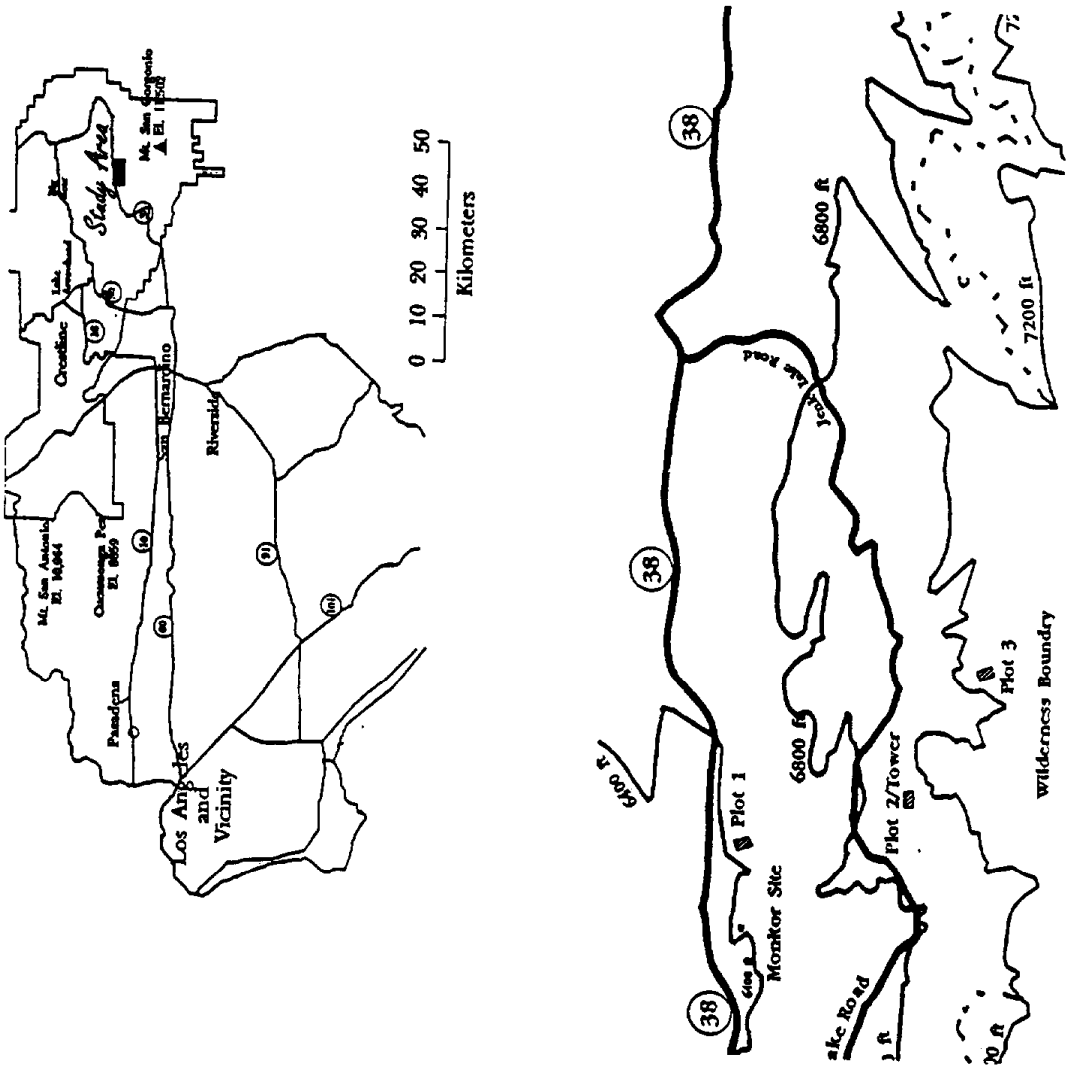
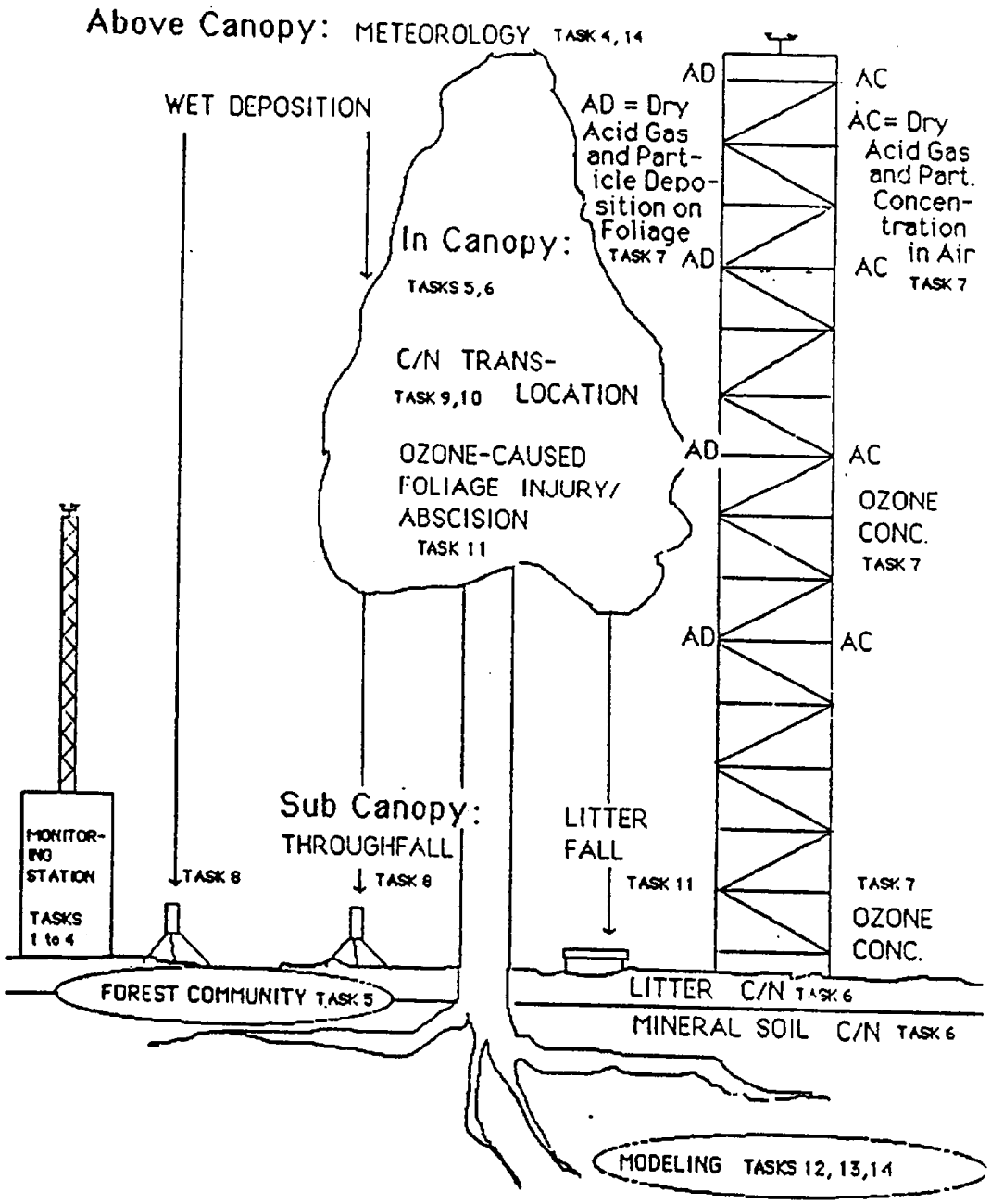

Study Area
Los Angeles and Vicinity
Pasadena
San Bernardino
Riverside
Ontario
0 10 20 30 40 50
Kilometers
38
Monitor Site
Plot 1
Plot 2/Tower
Plot 3
6800 ft
7200 ft
Wilderness Boundry

Figure 3



Hybrid diagram showing tasks, sites and "systems".

Figure 4

Methods

- determination of concentrations of N gases and particle with annular denuder systems on a canopy vertical gradient

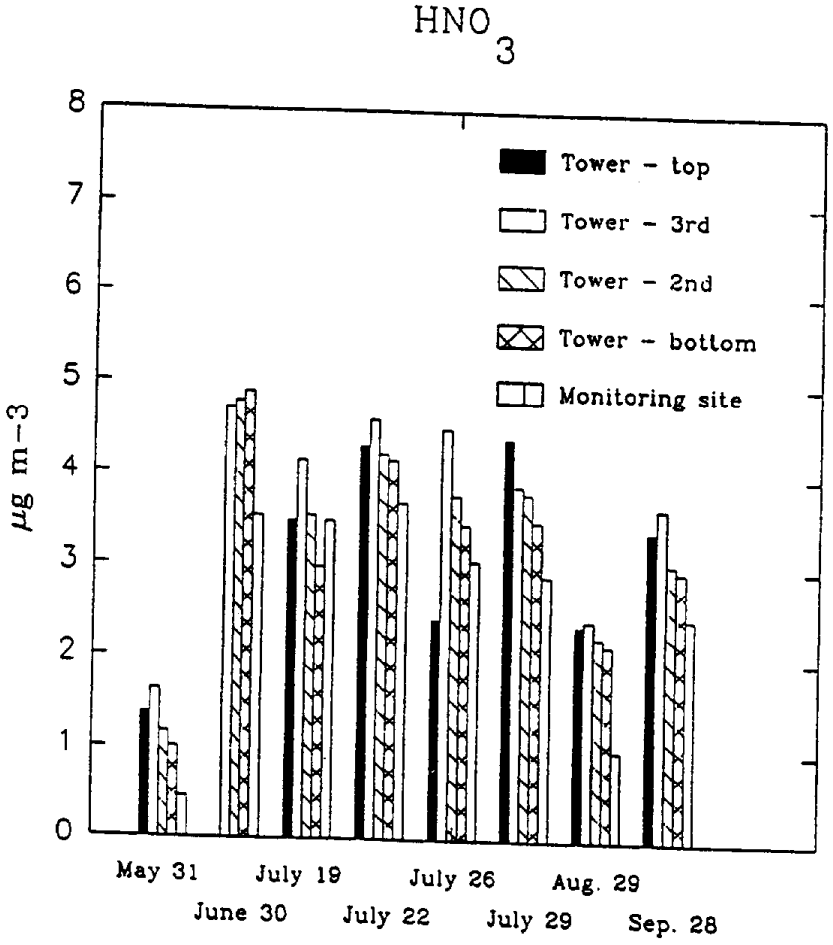
- determination of fluxes of ions on a vertical and horizontal gradients using foliage rinsing technique

- analysis of throughfall on a horizontal gradient

- determination of wet deposition (rain, snow and fog)

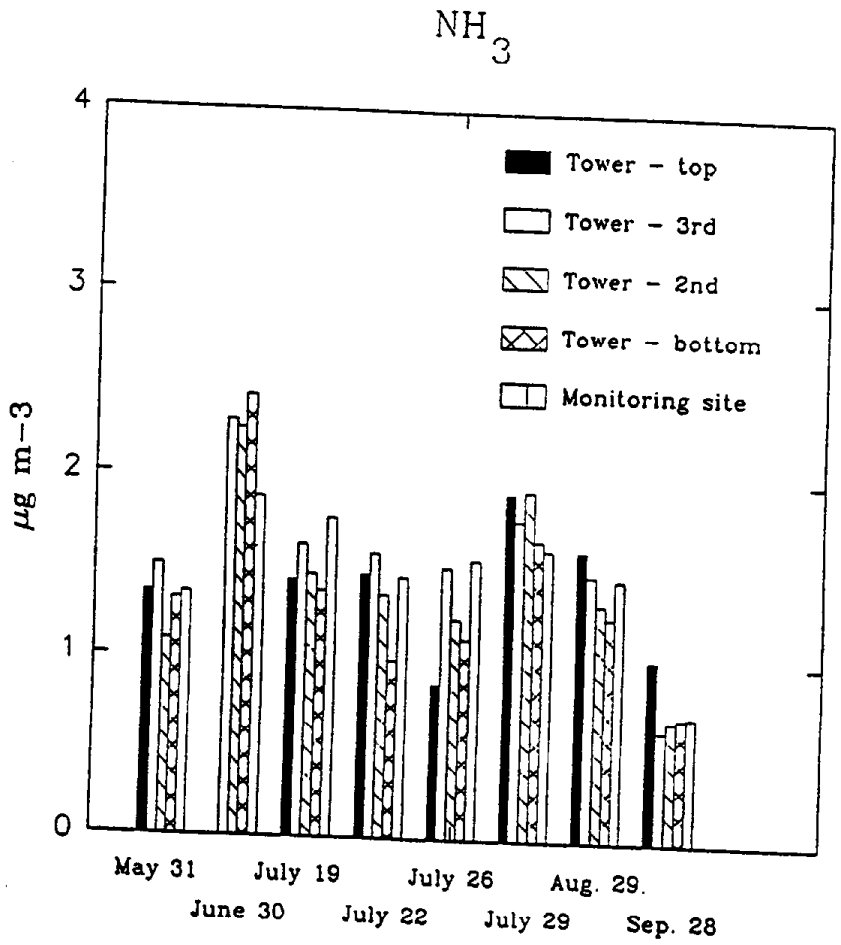
- calculation of atmospheric deposition at a forest site level

Figure 5

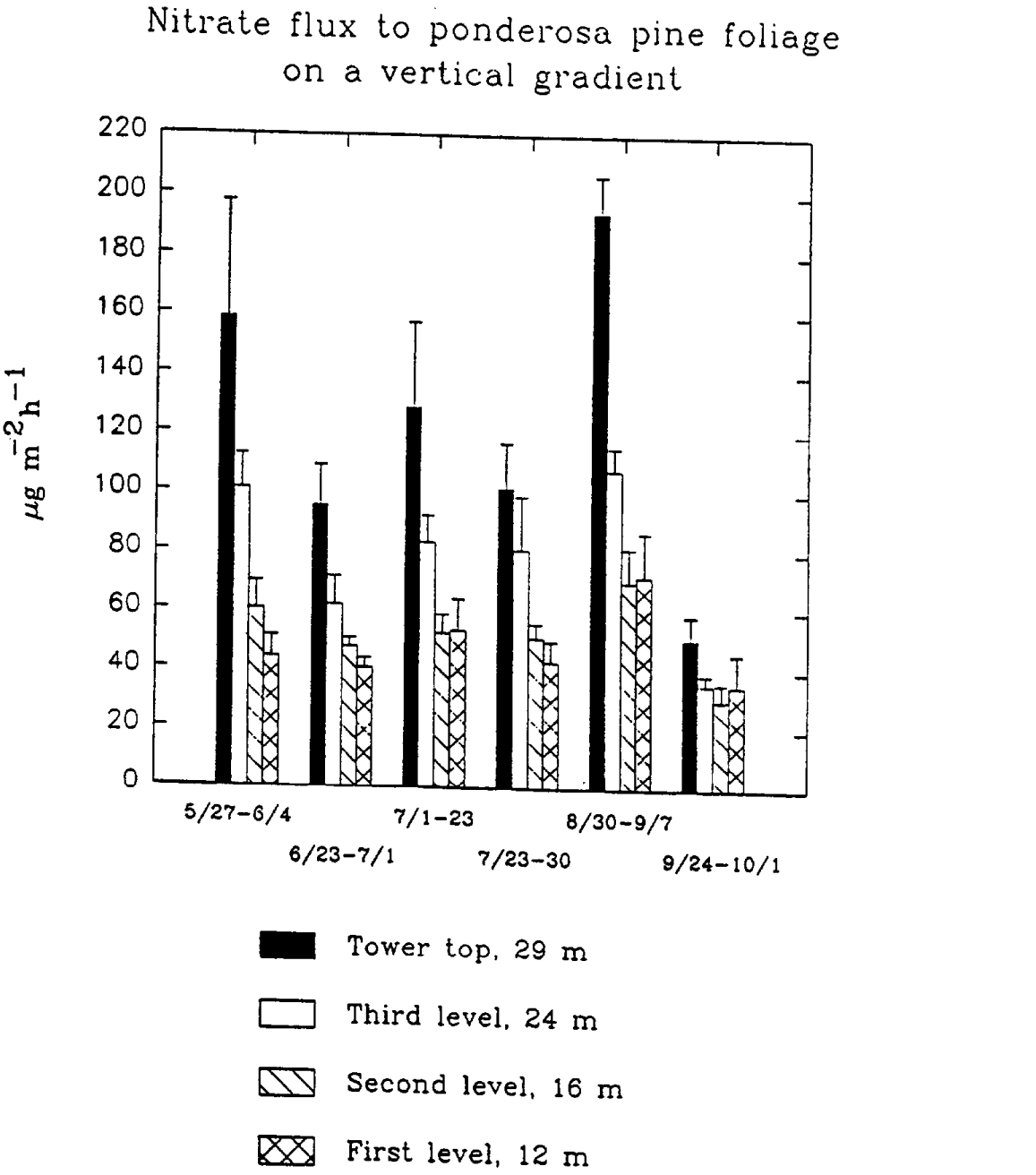


Concentration of HNO_3 vapor during the 1993 polluted season at different heights on the tower (Plot 2) and the monitoring site (Plot 1).

Figure 6

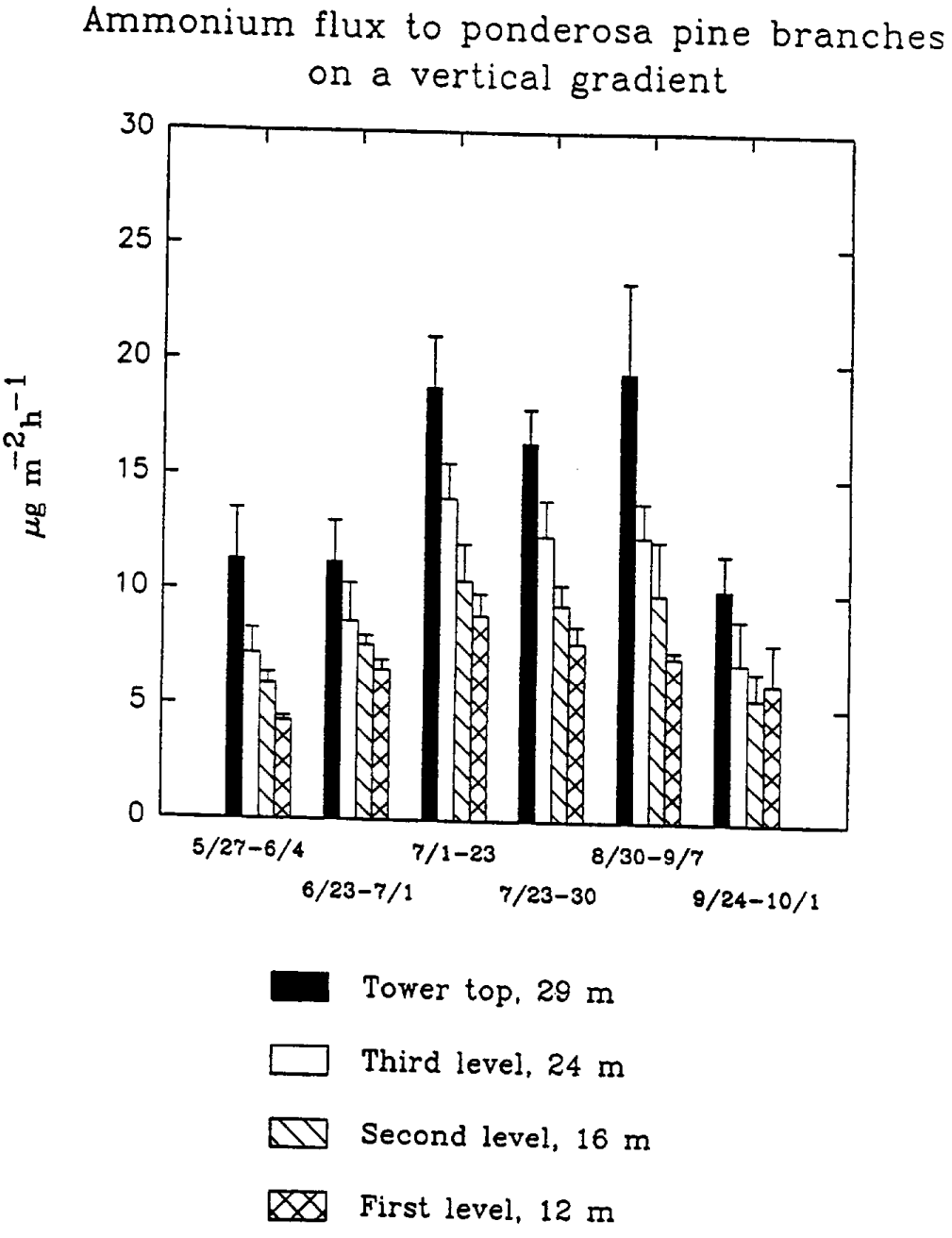


Concentrations of NH_3 during the 1993 polluted season at different heights on the tower and the monitoring site.

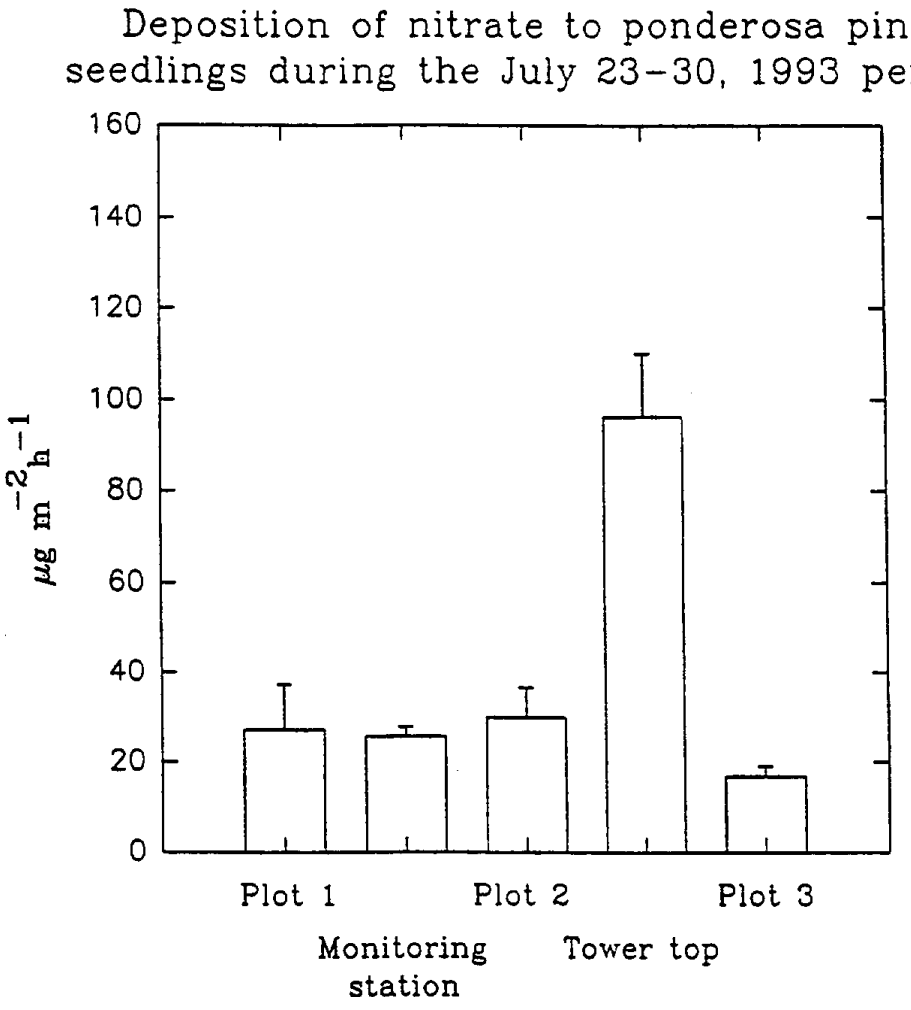


NO_3^- deposition flux to foliage of ponderosa pine seedlings on a tower.

Figure 8

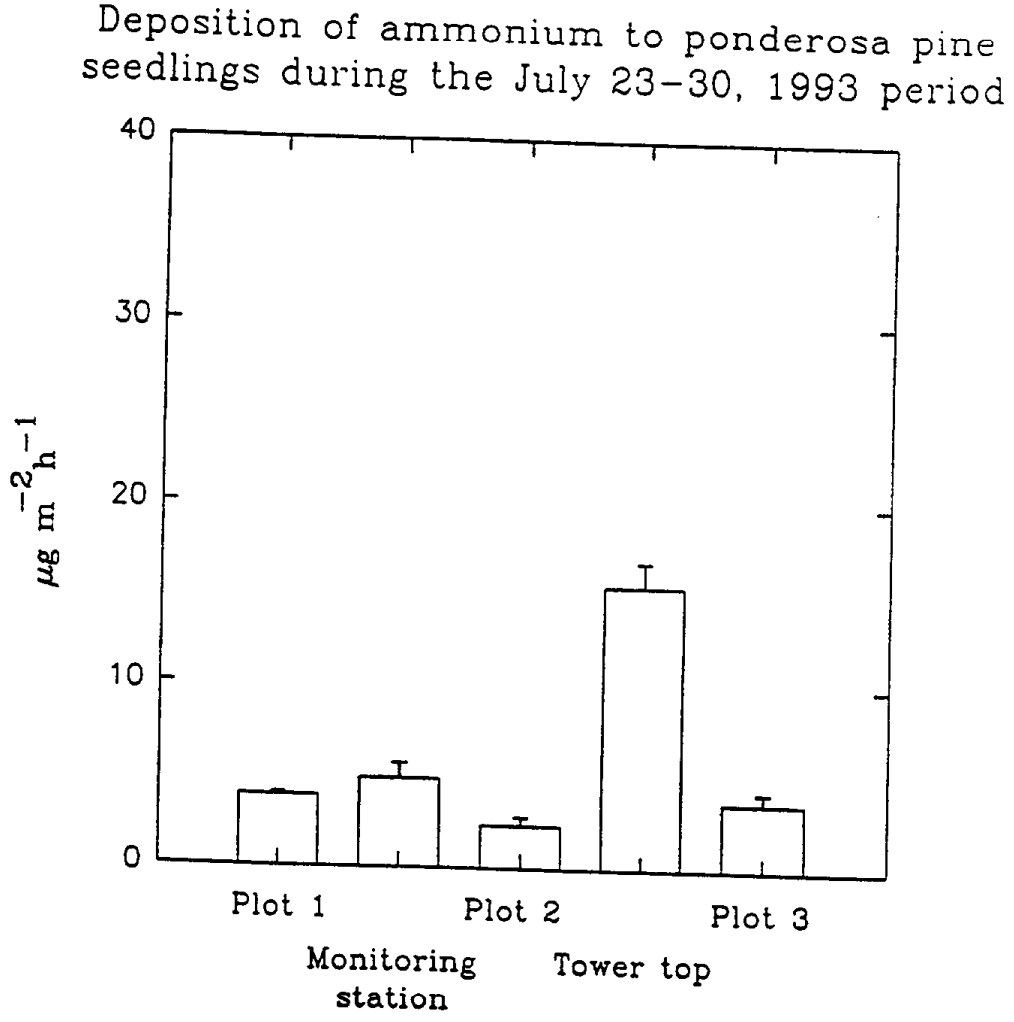


NH_4^+ deposition flux to foliage of ponderosa pine seedlings on a tower.



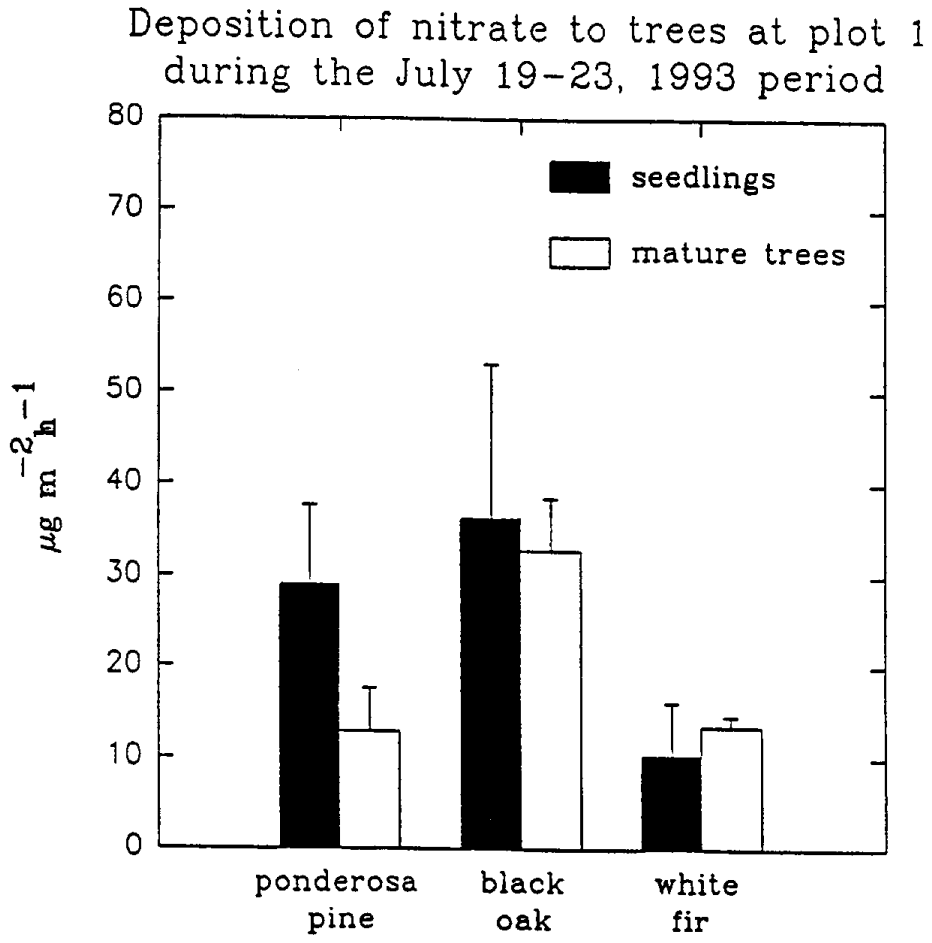
Deposition of NO_3^- to foliage of ponderosa pine seedlings at the forest floor level during the July 23 - 30, 1993 intensive study.

Figure 10

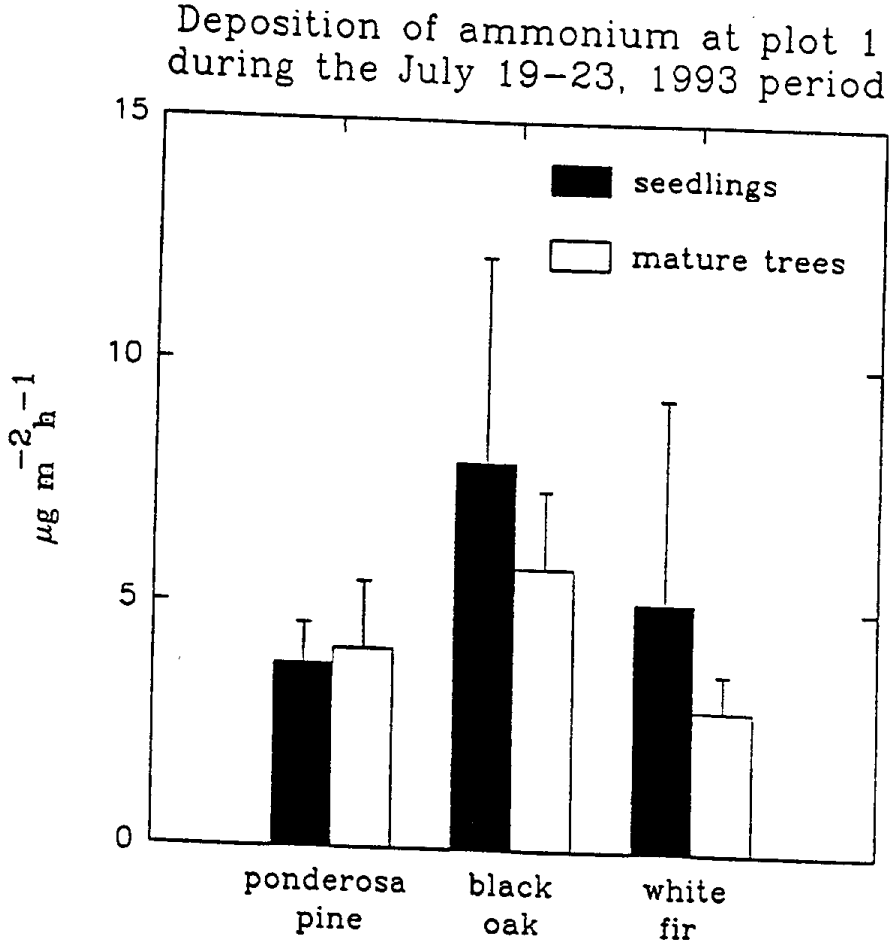


Deposition of NH_4^+ to foliage of ponderosa pine seedlings at the forest floor level during the July 23 - 30, 1993 intensive study.

Figure 11

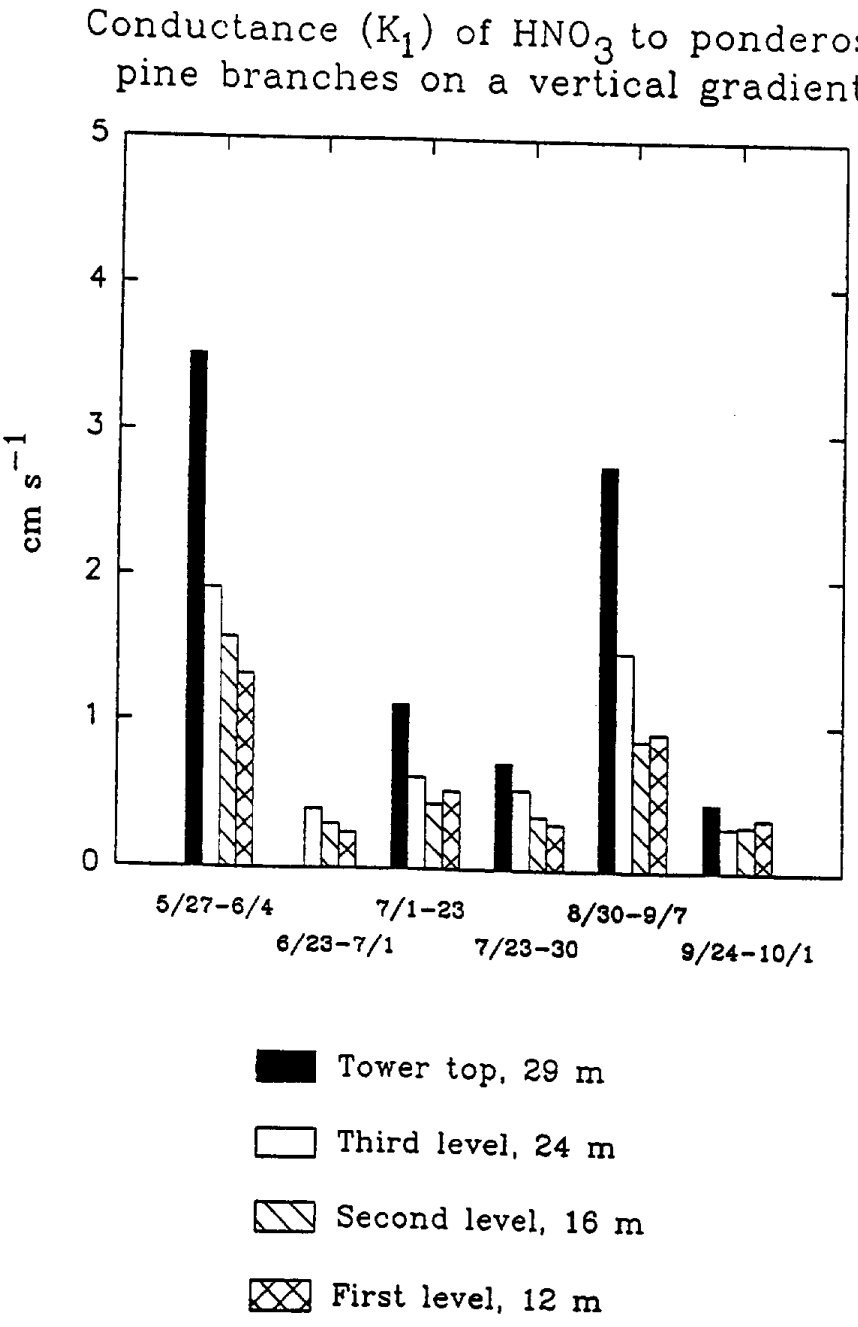


Comparison of NO_3^- deposition to foliage of mature trees vs. seedlings of various species at plot 1 during the July 19 - 23, 1993 intensive study.



Comparison of NH_4^+ deposition to foliage of mature trees vs. seedlings of various species at plot 1 during the July 19 - 23, 1993 intensive study.

Figure 13



Estimated conductance (K_1) of HNO_3 to ponderosa pine foliage for different height on the tower during the 1993 polluted season.

Figure 14

Nitrogen dry deposition to trees at Plot 2, Barton Flats, SBNF, during the 1993 season (g N ha^{-1} yr^{-1}) assuming LAI = 1.89.

Parameter	Pine	Oak	Fir	Total
NO_3 washable, foliage	313	834	250	1397
NO_3 washable, branches	111	345	186	642
NH_4 washable, foliage	208	318	114	640
NH_4 washable, branches	74	142	85	301
HNO_3 stomatal	9	26	22	57
NH_3 stomatal	27	77	64	168
NO_2 stomatal	13	32	32	77
Total	755	1774	753	3282

Figure 15

Calculated total nitrogen deposition at Plot 2 during the 1993 season (g N ha^{-1} yr^{-1}) - summary.

Parameter	Foliage rinsing (LAI=1.89)	Foliage rinsing (LAI=3.82)
NO_3 washable	2039 (2000 throughfall)	4121
NH_4 washable	941 (1000 throughfall)	1902
HNO_3 stomatal	57	115
NH_3 stomatal	168	340
NO_2 stomatal	77	156
Rain, summer	420	420
Rain+snow, winter	110	110
Ground	1423	1423
Total	5235 (5255)	8587

Figure 16

Winter Deposition of Nitrate in the SBNF

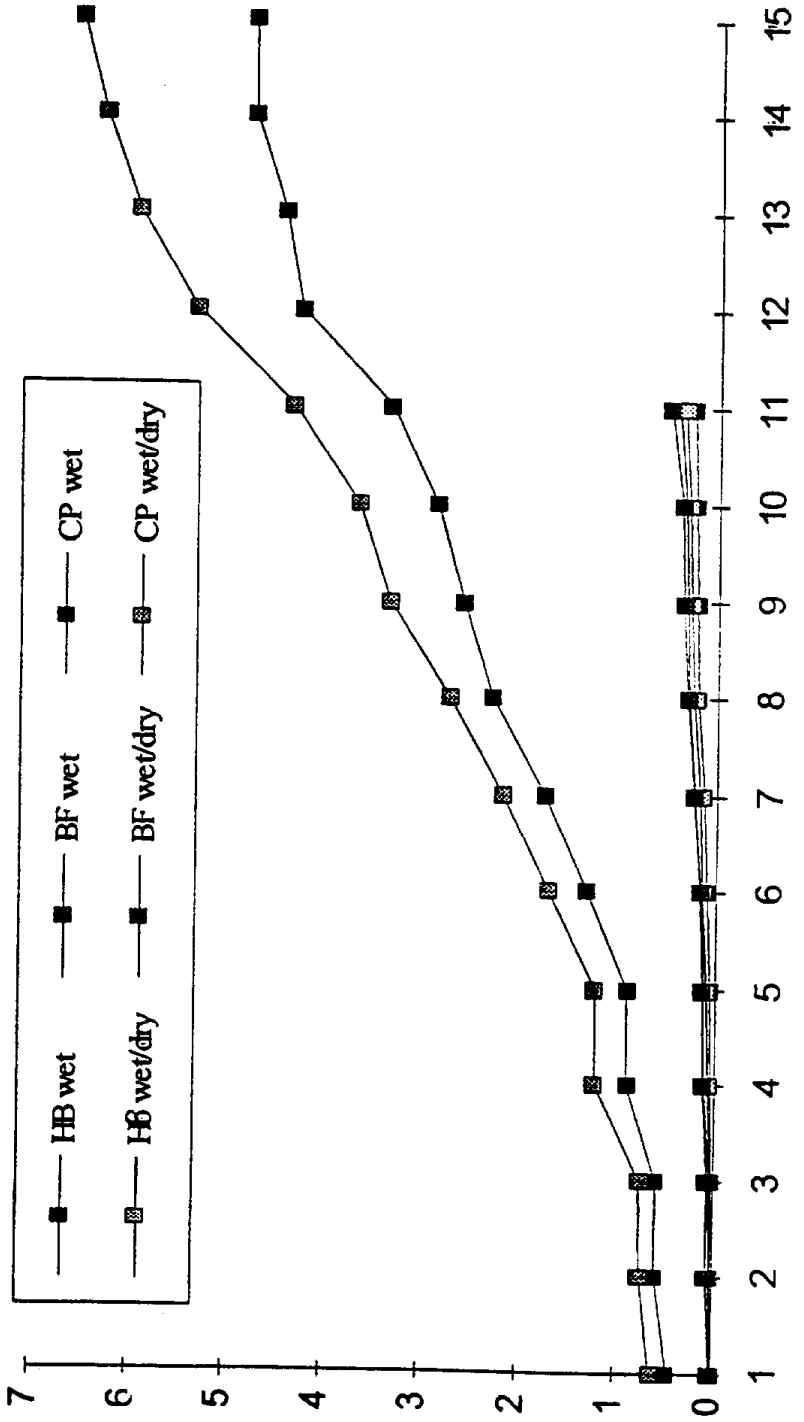


Figure 17

Deposition fluxes of NO_3^- to native trees in California determined with a foliage rinsing technique (A. Bytnerowicz and M. Fenn, 1995, in preparation).

Location	Species	NO_3^- deposition ($ug\ m^{-2}\ h^{-1}$)	Estimated annual dry deposition ($kg\ N\ ha^{-1}$)
Eastern Brook Lake, E. Sierras	Pinus albicaulis, P. contorta	6 (average)	0.5
Emerald Lake, W. Sierras	P. contorta, P. monticola	25 (average)	
Barton Flats, SBNF	P. ponderosa, Abies contorta, Quercus kelloggii	25-130 (range)	5-9
HNO_3 cuvette study	P. ponderosa, Q. kelloggii	100-600	
Tanbark Flat, San Gabriel Mountains	Ceanothus crassifolius	80-420 (range)	20-35
Camp Paivika, SBNF	P. ponderosa	180 (average)	29
Camp Osceola, SBNF	P. ponderosa	42 (average)	6
Whitaker Forest, W. Sierras	P. ponderosa	5-20 (range)	1.0-1.5

Figure 18

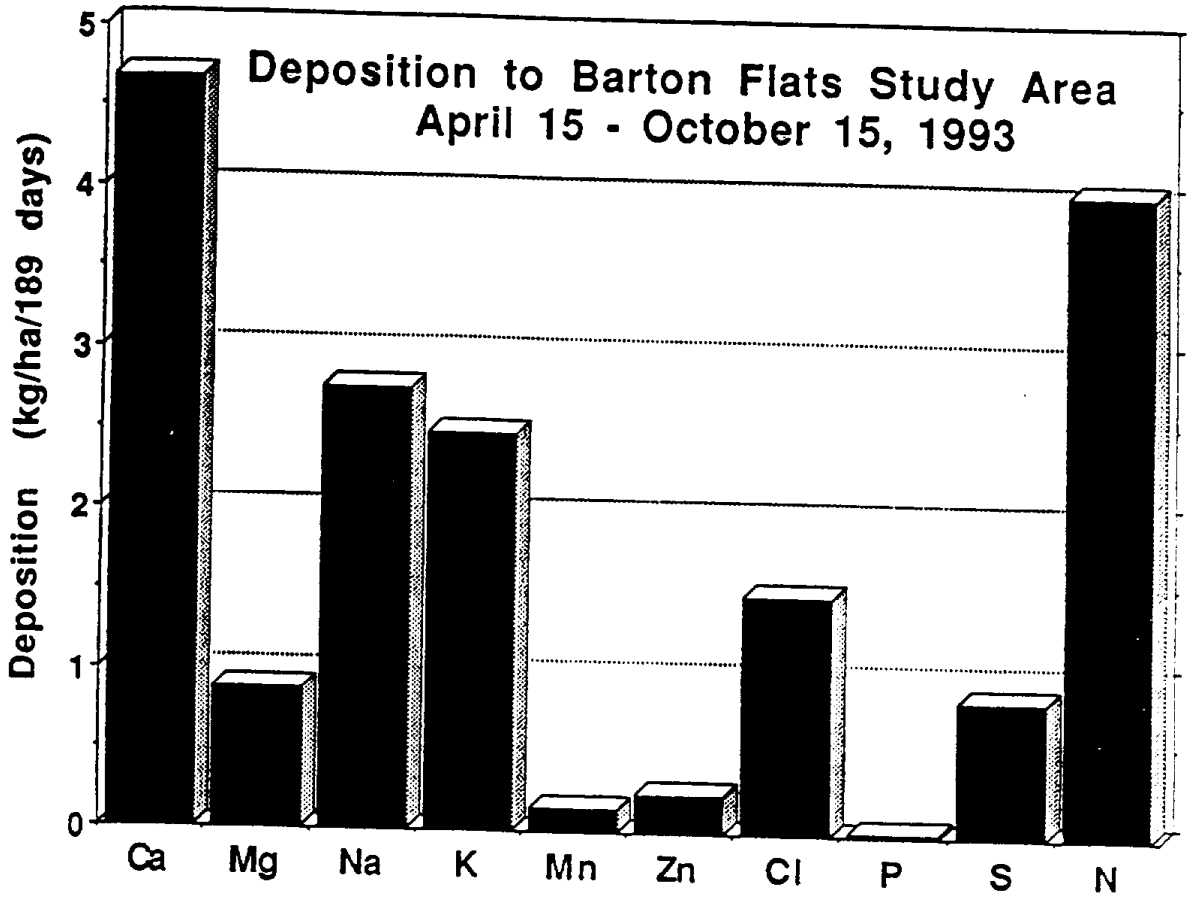

Deposition to Barton Flats Study Area
April 15 - October 15, 1993
Deposition (kg/ha/189 days)
0
1
2
3
4
5
Ca
Mg
Na
K
Mn
Zn
Cl
P
S
N

Figure 19

Conclusions

- no clear vertical gradient of HNO_3 and NH_3 in plant canopy was present

- strong vertical gradients of NO_3^- and NH_4^+ fluxes occurred (probably due to differences in wind speed)

- Barton Flats is an intermediate N pollution site on the W-E gradient throughout the San Bernardino Mountains

- differences in deposition fluxes to various tree species were found

- deposition of N at Barton Flats was mostly in a dry form (approximately 80%)

- foliage rinsing technique gave very similar results to the throughfall analysis

DR. GEORGE TAYLOR: University of Nevada

As you remember, John Watson had a lot of data that were developed to characterize a variety of chemical species in the atmosphere. We had the job to translating that information to compare that with the analysis Andrzej Bytnerowicz was doing (Fig. 1). Andrzej was doing a bottom-up approach to try to estimate the deposition of nitrogen, sulfur, and various cations to the system. The analysis task that we had was, in a complementary sense, to use all of John's data and build a model so that we can simulate the input and then compare the two estimates. As Andrzej indicated, I also want to acknowledge that there were a lot of people who contributed to this effort.

There were several steps in this effort as shown in figure 2. The first step was to take the big leaf model, a model that has been in existence for over a decade, and use it to develop input at the forest stand level. This is not a regional grid model but rather an individual stand level, so we could get estimates in terms of kilograms of nitrogen, sulfur, or whatever compound per hectare. Then you pick a time frame, be it a season, a day, a year, or a decade, and you can analyze whatever you want. We used the big leaf model, and then determined parameters for that model, because it had not been used in the western United States. It had largely been used in the eastern forests. We had to parameterize it on an individual species basis for ponderosa pine, white fir, and black oak, which are the principle component species of the stand. This was done on a physiological level. These data would be quite commonly used by plant physiologists. Andrzej was talking about a stomatal component. That is a physiological term. From the individual tree level, with the data Andrzej had, we scale up to the landscape level on a per hectare basis. Finally, we had to parameterize the model for a number of chemical species: sulfur dioxide, nitrogen dioxide, nitric acid vapor, ammonia, and ozone. The parameterization has to be on a chemical specific basis. The chemicals behave quite differently within the plant canopy, and I think Andrzej showed you some of that information. We then simulated dry deposition on an hourly time step, and we calculated the mass of the particular species that was deposited per hectare per hour. We then extrapolated in time from there. You will see some of the calculations. Then, we summarized those data for the principle dry deposited species. The easy ones were sulfur dioxide and ozone.

The real beast that is probably driving the system is the cumulative input of the nitrogen species. In this case, we are only concerned about the nitrogen as it serves species in the landscape in order for the ecologist to subsequently predict the effect on the system. They do not really care about anything other than how much of the nitrogen actually enters the forest floor, that is why we are focusing upon the nitrogen component. We then compared the deposition of sulfur and nitrogen, and we have all the other species as well. Anything that John collected, we simulated in the model, but I am going to focus here on sulfur, nitrogen, and ozone. Of course ozone wet deposition is not a significant phenomenon for

plant physiology. We will compare the sulfur and nitrogen inputs, both in wet and dry, and then we are going to talk a little bit about the uncertainty in the estimate by comparing our numbers with those Andrzej had. Remember we are starting from the bottom up on this individual species.

The leaf is the platform by which these materials are removed (Fig. 3), and the leaf is a dynamic unit. It is not monotonic with respect to the exchange of trace gases at that surface. There is deposition on the exterior. That is what Andrzej was referring to as the washable portion of these leaves. Now the question is whether there is another deposited surface that is on the leaf interior, and is it different for black oak or Ponderosa pine? In some cases, the interior is the predominant site of deposition for gases. The way you model this is to simulate the flux of those gases based on a model of water vapor flux. We have been doing water vapor models in the physiological community for three decades, so we have a pretty good handle on understanding the dynamics of water. The model simulates the loss of water from the needle coming out through the leaf interior. For other gases, we will predict the behavior by an analogy to the water vapor. Again, there are a lot of data that we can use to derive those transfer equations. The whole model is based upon water, and we estimated the influx of the gas into the leaf interior based upon the analogy to water vapor efflux. We model deposition using an analog resistance model. We calculate resistances in deposition to the leaf cuticle, and, based on the atmosphere concentrations that John provides, then calculate uptake in the leaf material. Andrzej was referring to the stomatal uptake. You model that on a gas specific basis, and you model it for each plant species individually. The big leaf model was developed largely out of Bruce Hicks' laboratory in concert with a number of other people. It is a series of resistances, some operating in parallel, some operating in series. We begin with the concentration of the species in the atmosphere. The model calculates an aerodynamic resistance above the canopy based upon wind speed and wind direction and canopy characteristics and then estimates a concentration at the canopy itself. We calculate an individual leaf boundary layer of resistance, and while most people would assume this is negligible; it is definitely not. For some species it is fairly important. We then calculate a concentration at the surface of the leaf in the micrometer layer. Then we have the actual reactive surface of the cuticle. We then use the analogy based upon the concentrations of the gases in air. We have an internal biochemical parameter. There are additional components in the model that we do not use, because, as Andrzej commented, we do not know how important the actual non-foliage surfaces are. Very few studies of this have ever been done. For example, we have a litter layer versus an open forest floor with largely rock or soil. How much is being deposited to that? We do not have the numbers to parameterize that. When it has been done, largely for eastern forests, it is a fairly small component. We just assumed that these components were not large. You can add whatever components you want; for example you can put a lichen layer in the forest.

The sum of all of those is the plant canopy resistance. The inverse of that is called the deposition velocity, measured in centimeters per second. The model generates a deposition velocity for each species for each hour. If John gives me the concentration, and I have the deposition velocity, we multiply the two together, and we have the deposition. That is the whole principle behind the model.

I now want to give you a sense of the model results. I am going to start with ozone (Fig. 4). Remember ozone decomposes, so you are not accumulating it, but it is important because it reacts as it is deposited. Figure 4 gives you an example of the numbers that we are getting out the big leaf model for white fir. Ozone deposition is in micromoles of ozone per meter square per hour, and this is on leaf surface area, not on a hectare of forest area. This figure is for the growing season in 1992. Early in the day we saw very low values, then they begin to ramp up, and then drop off in the late afternoon. If you remember, John noted his ozone values tended to peak in the late afternoon. We saw roughly the same thing in terms of deposition. Without going back through the data I cannot tell you whether that is all a function of the atmospheric component or whether the stomata are also opening much wider in the late afternoon. In essence, the pattern we see across all species is this tremendous pulsing. The marked pulsing occurs in all species during the growing season (Fig. 5) and during the middle of the day. Remember most of John's concentration data showed the concentration higher in the summer than in the winter. He also showed concentrations higher during the day than at night. The plant, then, is superimposing its physiology on top of the variation in atmospheric concentration.

Figure 6 shows the annual ozone uptake for the species calculated and summed over the duration of the time period for Ponderosa pine, white fir, and black oak in micromoles per meter square per hour. The physiology is important because we have a pretty good idea at what level of uptake you begin to see physiological effects, and we have differences in uptake between the species. Remember, those species are all seeing the same ozone concentration, so differences are a function of their physiology. There is a greater or lesser velocity between the species. We will come back to that ozone information later on.

We did the same analysis for sulfur (Fig. 7), and Andrzej showed you two different examples. One calculation was done with a leaf area index of 1.9. There is an alternative leaf area index of 3.8. For sulfur, if you want to get the result for the higher leaf area index, roughly multiply the values by 2. This is on a basis of kilograms per hectare per year. I changed units because sulfur is a conserved species, not an ephemeral species like ozone, so we are really concerned about the cumulative addition of sulfur. This is the amount of sulfur that is added from sulfur dioxide, however the data are expressed as kilograms of S not of SO_2. The values here are all around 0.1 kilograms of S per hectare per year. The highest values we saw are close to 1 kilogram of S per hectare per year if we use the higher leaf area index in the system, and that is still a fairly small value. As far as sulfur is concerned, this is not a number to be overly concerned about.

We have concurrent numbers, again from John, that give us the values for sulfur in wet deposition (Fig. 8). The values we have for wet deposition are around about 1.6 kilograms per hectare per year. Remember, the maximum value for sulfur input that I get from dry deposition is about 1 kilogram per hectare per year, so wet deposition exceeds dry deposition for sulfur dioxide.

The biggest difficulty we have for the system is the nitrogen inputs. I will show you the simple part first. Figure 9 shows the nitrogen input in wet deposition. It is the sibling graph to the one for sulfur, and the values again are calculated from John's information. In general, wet deposition of nitrate numbers are around 2-2½ kilograms per hectare per year. Nitrogen wet deposition is not the big player; it is fairly modest. The key problem that we have is one John alluded to; the nitrogen species here in figure 10. The analysis is shown here in terms of gas base concentration in micrograms per meter cubed for the dormant season which are the first two bars, and for the growing season which are the next two bars. As John showed and I summarized, the growing season numbers are characteristically much greater than the dormant season. If you look at differences between day and night, it is dramatic in some cases. For example, the differences for nitric acid vapor and for ammonia are large, but the difference is not so great for NO_2. It makes a lot of difference between day and night because concentration at the surface of the canopy differs radically. I need to now estimate nitrogen input just like I did for every thing else using the big leaf model.

We will start with the easiest nitrogen species NO_2, which everybody was assuming was important a decade ago (Fig. 11). These are the inputs of nitrogen in terms of NO_2 for the three species. We are using the higher leaf area index for the canopy, and everything else will use the higher leaf area index. The end deposition in terms of kilograms of N per hectare per year range from about 0.25 up to about 0.3. The maximum you can get in terms of nitrogen inputs from NO_2 is something slightly less than 1 kilogram per hectare per year, and that is less than the wet deposition. It is not a large component, and I would not be overly concerned about it. It is, however, a major component in terms of atmospheric concentration.

Now we get into the two difficult species, nitric acid vapor and ammonia. These are the data that John gave us for nitric acid vapor concentrations by month beginning in 1991, 1992, and 1993 (Fig. 12). They are mean values, and they range from a high of close to 2.5 down to almost non-detectable. I want to translate that information into deposition into the system, and that is done in Figure 13. A lot of the technical details are missing in generating these estimates, and I cannot go over them here, but the bottom line is estimated for each species on a per hectare basis per year. Nitrogen deposition as it comes in from nitric acid vapor ranges from about 2.65 for Ponderosa pine and about 2.5 for white fir and black oak, and the combination of those is about 7.5 to 8 kilograms of nitrogen per hectare per year that comes in as nitric acid vapor. Remember, NO_2 deposition is roughly about 1 kilogram per hectare per year.

The mean monthly concentrations ammonium in the system turns out to be the most difficult problem (Fig. 14). Ammonia concentration varied from about almost 4 micrograms per meter cubed down to values close to non-detectable. In trying to develop the analysis, you must look to the literature to get information to parameterize the model. We have great information on sulfur dioxide, great information on nitric acid vapor, and good information on NO_2. The amount of information we have on ammonia is not the best in the world relative to understanding the activity of the surface, and we were constrained by the information we had. Figure 15 shows the deposition velocities that the model generated. Remember, these are the numbers that the model generated based upon water vapor. Figure 15 is during the growing season, April 1991, and is for white fir. This will be multiplied by the concentrations from the previous graph to estimate deposition. Deposition velocity at the surface of the canopy goes up quite a bit with a maximum around 0.55 centimeters per second and then it drops off. That is a function of the reactivity of the surface of the leaf. There is a lot of uncertainty of how we parameterize that number, but we did use numbers justified by the available literature. Most of those data are from Europe and agricultural feed blocks are largely the source. We developed numbers for ammonia in terms of kilograms per hectare per year (Fig. 16). The values again differ between species and this is a species specific characteristic. They vary from about 1.1 kilograms per hectare per year for Ponderosa pine down to about 0.75 for white fir and then up again close to 1 for black oak. We see a total somewhere close to 3 kilograms per hectare per year coming into the system as ammonia.

In summary (Figs. 17-19) the dry deposition of sulfur is SO_2, based upon the estimate we have using the leaf area index, is about 1.2 kilograms of acid per hectare per year (Fig. 17). The wet deposition is at 1.6 kilograms per hectare per year. The ratio of dry sulfur to wet sulfur is about 0.75, so the bulk of the sulfur that is coming in is a wet form. 43% of the total sulfur is coming in as dry deposition. That is not much sulfur, and ecologically, it is not a concern.

Mean ozone deposition is analyzed at the leaf level (Fig. 17). The uptakes that we see vary between species. Ponderosa pine is about 8 micromoles per square meter per hour. This is a leaf area measurement, not a stand level measurement. White fir is about 4, and black oak is about 7. Those values are equal to or greater than the threshold you would predict for physiological effects based upon the existing literature.

For nitrogen deposition (Fig. 18), we are switching back to the stand level units, not leaf area specific levels. Dry nitrogen uptake, the accumulation of all of those nitrogen species is about 12 kilograms per hectare per year. Dry nitrogen comes in the following forms: about 8 for nitric acid vapor, about 3 for ammonia, about 1-1.4 for nitrogen dioxide. Wet deposition is about 2.3 kilograms per hectare per year. Most of what comes into the system is nitric acid vapor. The ratio of dry to wet deposition is about 5, and dry nitrogen deposition is about 84% of total nitrogen inputs in the system.

The total input we estimate is 14.2 kilograms per hectare per year. I would just like to add that we tend to isolate these statements and when we are thinking about nitrogen; we do not think about sulfur or the other chemical species. There may well be interactions in the toxic effects of these compounds, for example between ozone and nitrogen.

Where are there uncertainties in these numbers (Fig. 19)? We do not have any extensive cloud water input data on these stands. Paul or Andrzej may have sone information to add, but the data I have shown do not include cloud water inputs. The ammonia deposition number I derived from information largely in the European literature and parameterized for the model. We are probably conservative on the ammonium estimate; the ammonium may be higher but not lower than our estimate. It is difficult to estimate ammonia, because there are hardly any data available.

I suspect we should also consider return of compounds to the atmosphere. We have talked only about inputs to the system. Any system that is saturated with nitrogen or has nitrogen inputs accumulating over time, is also likely to be losing some of that nitrogen back to the atmosphere. We have no way of characterizing that. I could model it if I had the numbers, and I suspect that there is significant export from the system, not going through the water flux, but going out through the atmosphere. You see this if you put too much nitrogen on an agricultural field. Nitrogen is exported out into the atmosphere. So, we have a conservative estimate of the nitrogen deposition, and there is uncertainty about the possible interactive effects on nitrogen in those species that are sensitive to ozone.

Q DR. MAUTZ: Is exposure of the cuticle to reactive gases deposited there marked by particular reactions?

A (DR. TAYLOR) Yes, it clearly is, but the data are not something we put in the big leaf model, and it is not a data set one would feel really comfortable about. For example, people in the UK have shown that there is an interaction between ammonia and sulfur dioxide, so that when those compounds co-occur there appears to be a reaction that accelerates the uptake. No one really knows what that is, but it appears to be an acid-base chemical reaction. It happens, but we do not put it into the model, because we do not have enough information, and the data we do have are not on the California species. What happens on that surface is a big issue right now, and there is no consistent hypothesis that I would yet be willing to put into a model. It could be one of those uncertainty factors that Ralph talked about.

A DR. KLEINMAN Is it reasonable to assume that there is no significant uptake from particle species?

A (DR. TAYLOR) We have particle species in the model. That is part of the effort. The model incorporates wind speed and wind direction, and we used curvilinear relationships for particle

deposition. I have the data, and it is a trivial input relative to the other sources that are in the canopy, but nevertheless we include it. There is a particle cut on the big leaf model that handles sulfates, nitrates, and ammonium. All of that input is a surface deposition, which is to say it is a cuticular deposition.

Figure 1

Atmospheric Dry Deposition in California Forests: Results from Branch Washing and Process-Level Modeling

Andrzej Bytnerowicz[1] and George Taylor[2]

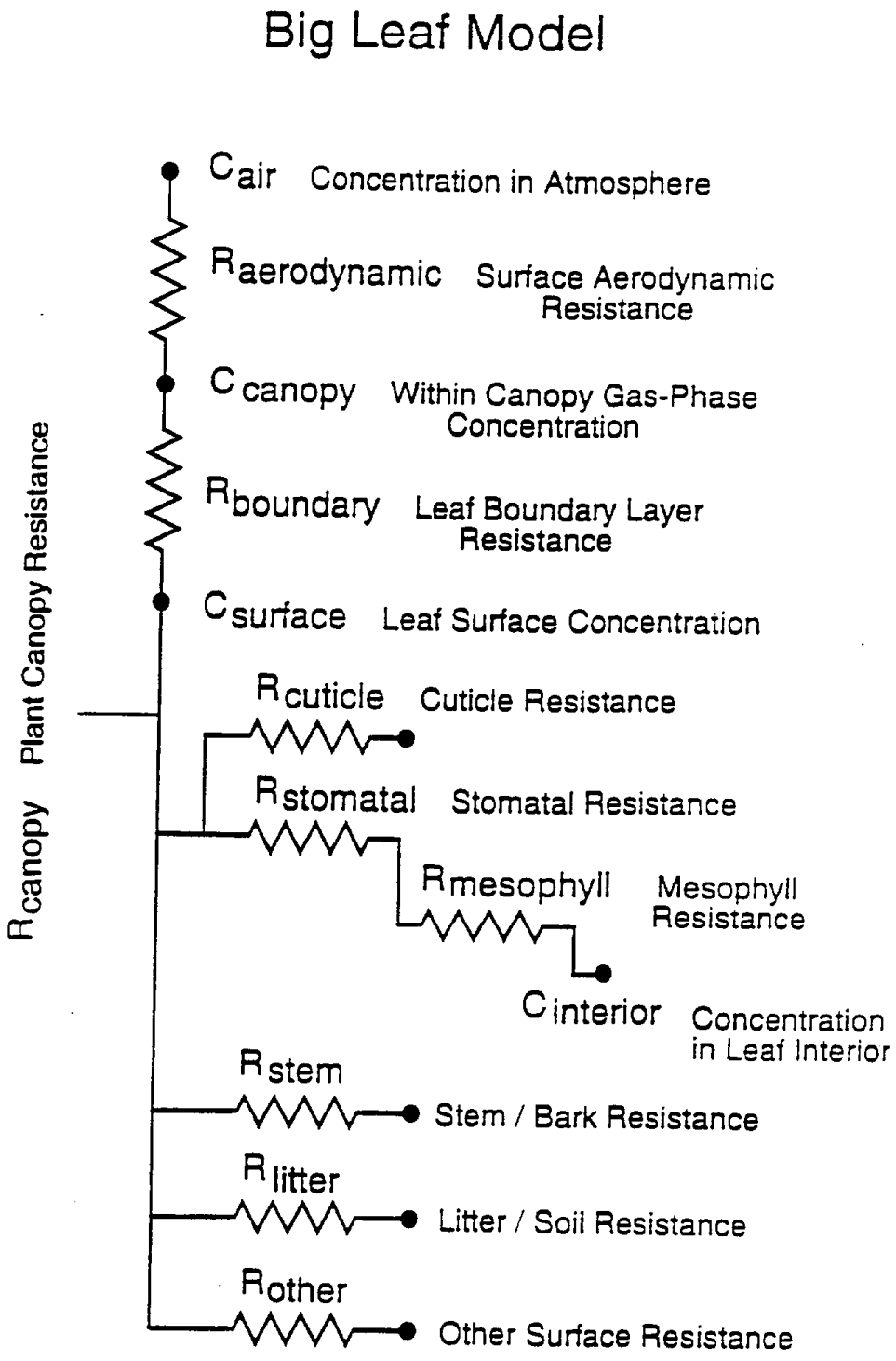
[1] US-Forest Service
[2] University of Nevada, Reno

Figure 2

Activities

- Δ Parameterize the Big-Leaf Model at the Leaf and Canopy Level
  - by tree species (Ponderosa Pine, White Fir and Black Oak)
  - by forest landscape (hectare)
  - by chemical species (SO_2, NO_2, HNO_3, NH_3 and O_3)
- Δ Simulate Dry Deposition on Hourly Time Step
- Δ Summarize Data for Dry Deposition of Principal Chemical Species
  - nitrogen ($\sum$(N-HNO_3 + N-NO_2 + N-NH_3))
  - sulfur (S-SO_2)
  - ozone (O_3)
- Δ Compare Deposition of S and N from Wet and Dry Processes
- Δ Address Uncertainty in Estimate of Dry Deposition

Figure 3



Schematic diagram showing the array of resistances operating within the Big Leaf Model, which is used to simulate pollutant gas deposition to plant canopies (adapted from Baldocchi et al. 1987).

Figure 4

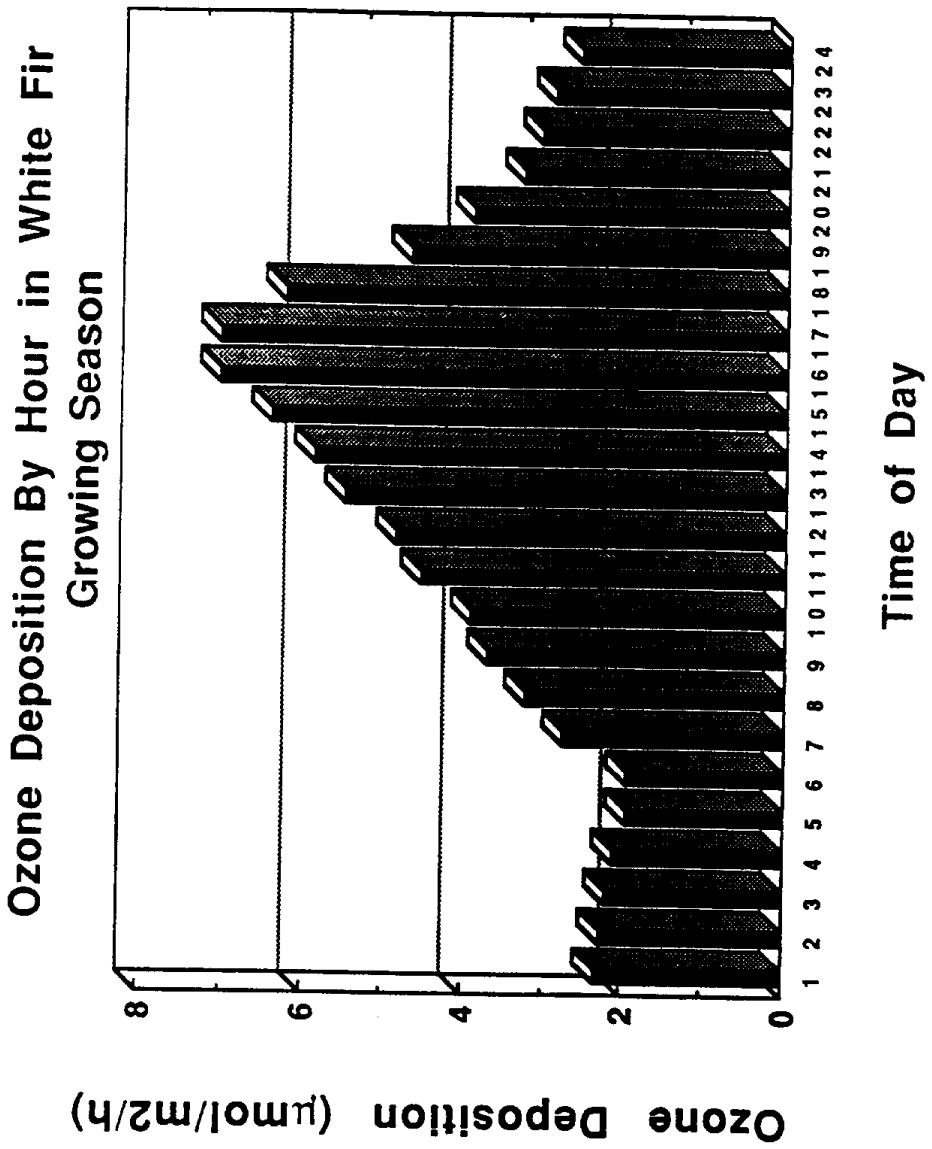

Ozone Deposition By Hour in White Fir
Growing Season
Ozone Deposition (µmol/m2/h)
0
2
4
6
8
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Time of Day

Figure 5

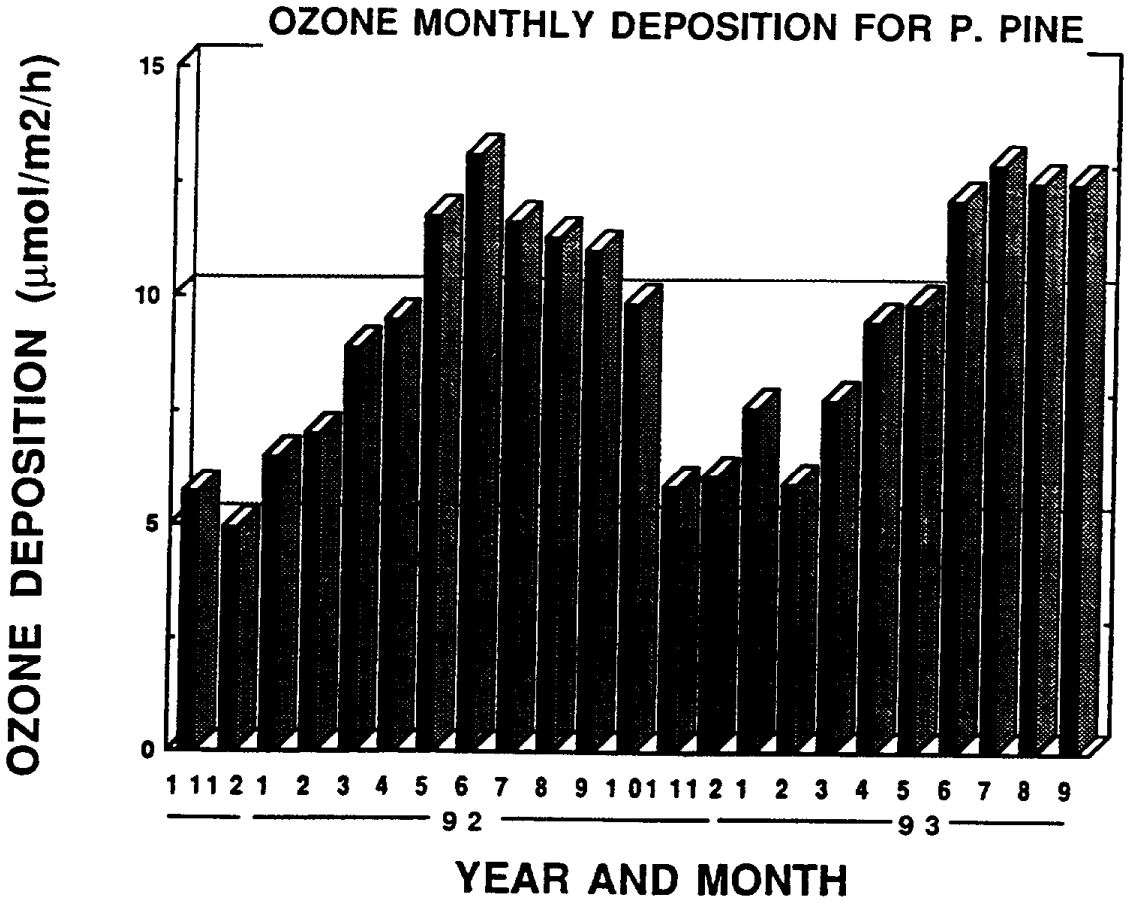

OZONE MONTHLY DEPOSITION FOR P. PINE
OZONE DEPOSITION (µmol/m2/h)
15
10
5
0
1 11 2 1 2 3 4 5 6 7 8 9 10 11 12 1 2 3 4 5 6 7 8 9
92
93
YEAR AND MONTH

Figure 6

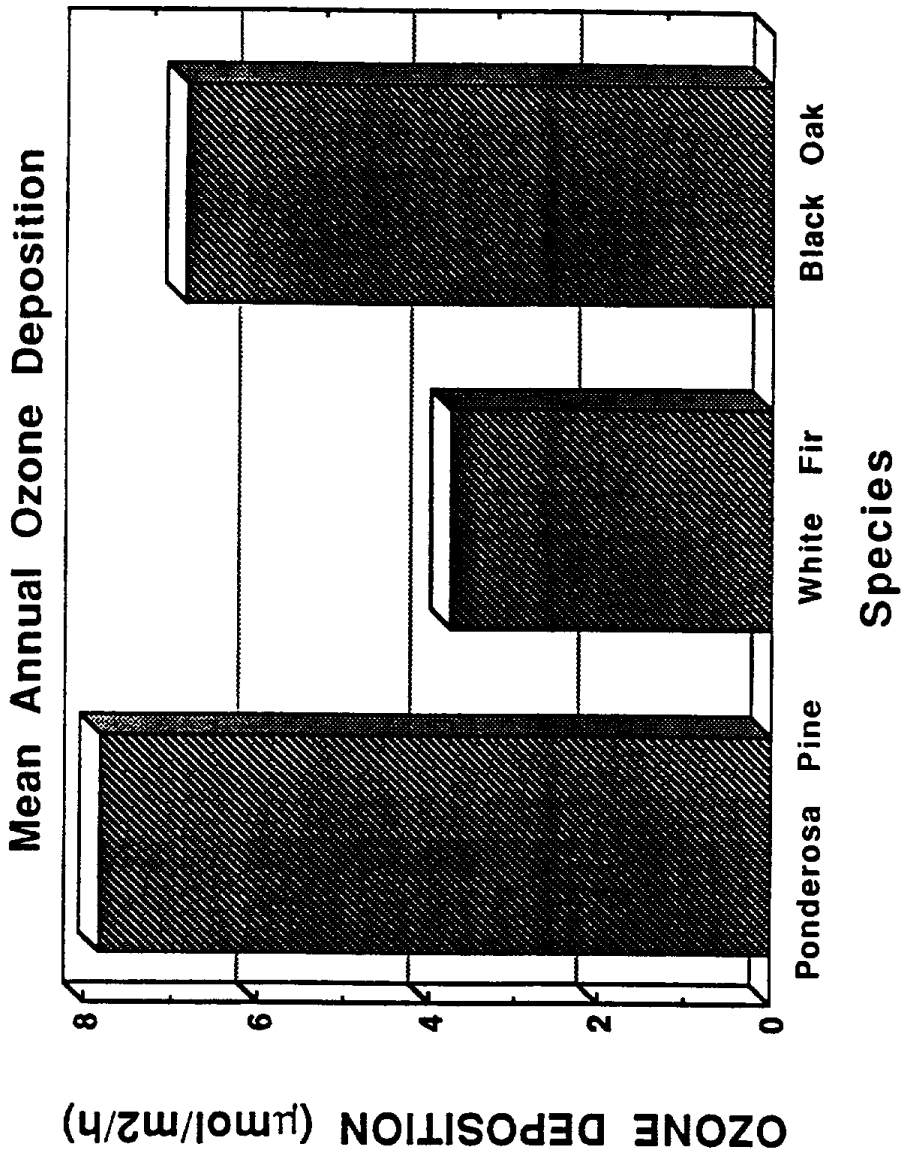

Mean Annual Ozone Deposition
OZONE DEPOSITION (µmol/m2/h)
0
2
4
6
8
Ponderosa Pine
White Fir
Black Oak
Species

Figure 7

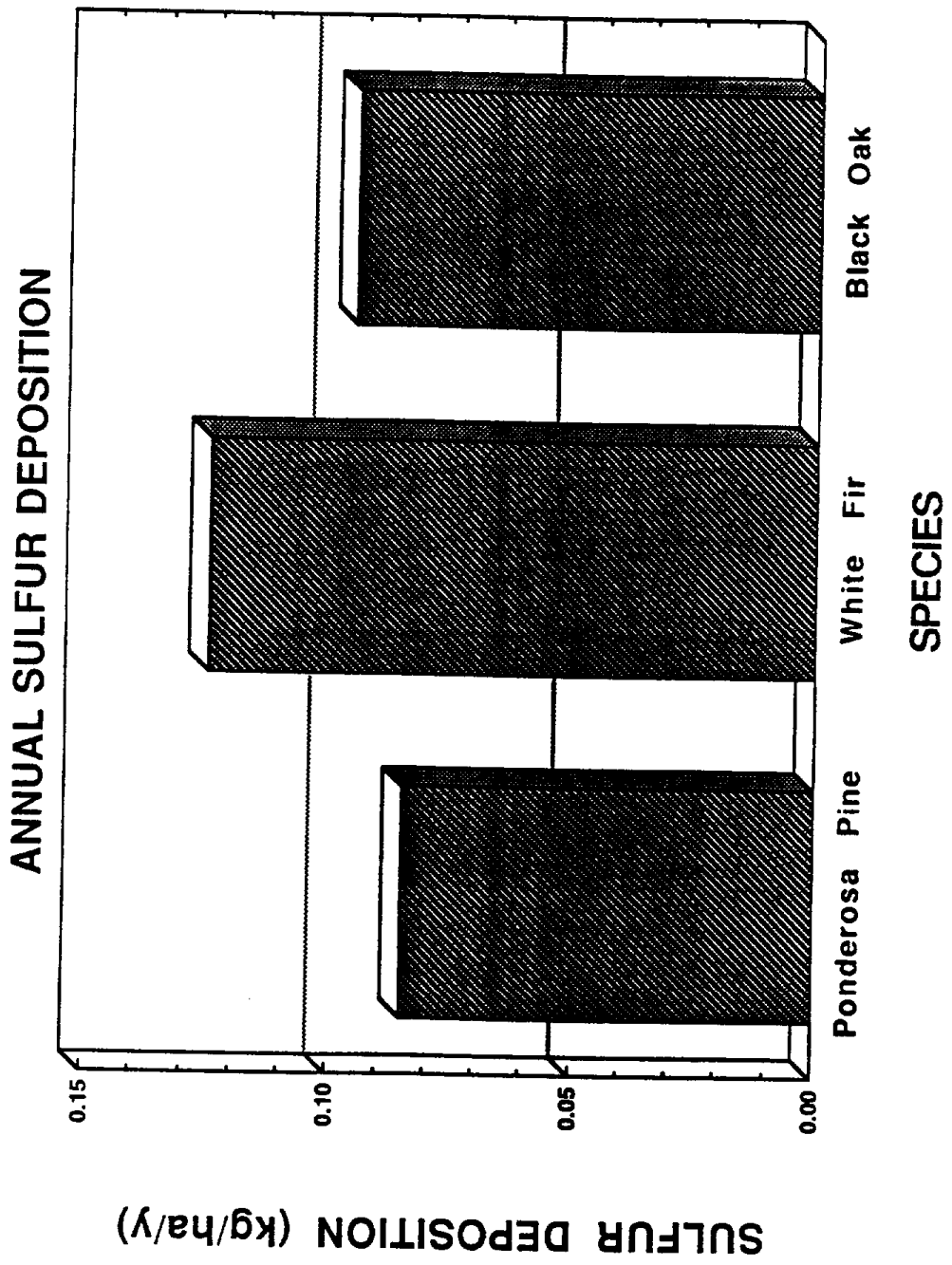

ANNUAL SULFUR DEPOSITION
SULFUR DEPOSITION (kg/ha/y)
0.15
0.10
0.05
0.00
Ponderosa Pine
White Fir
Black Oak
SPECIES

Figure 8

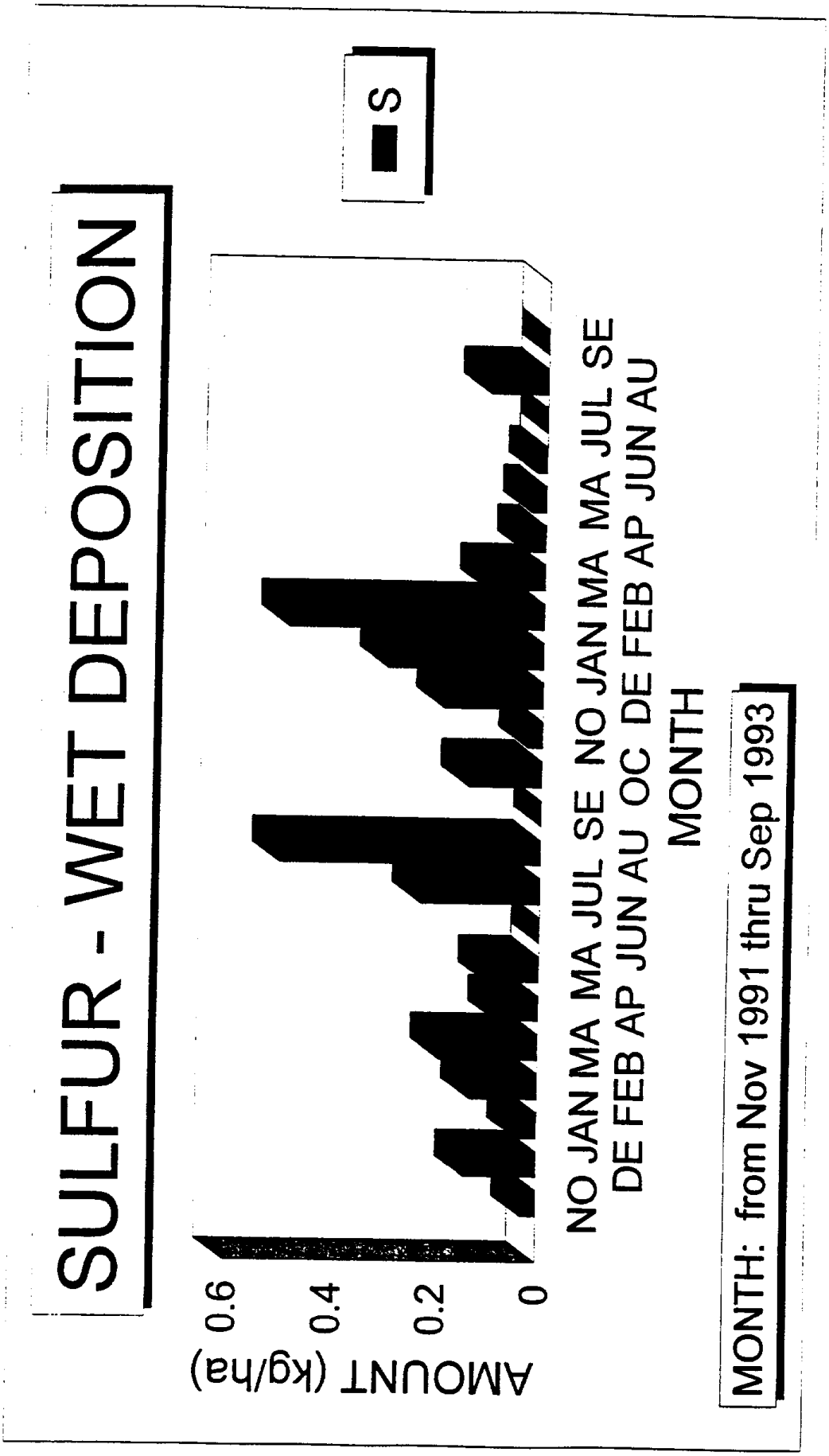

SULFUR - WET DEPOSITION
S
AMOUNT (kg/ha)
0.6
0.4
0.2
0
NO JAN MA MA JUL SE NO JAN MA MA JUL SE
DE FEB AP JUN AU OC DE FEB AP JUN AU
MONTH
MONTH: from Nov 1991 thru Sep 1993

Figure 9

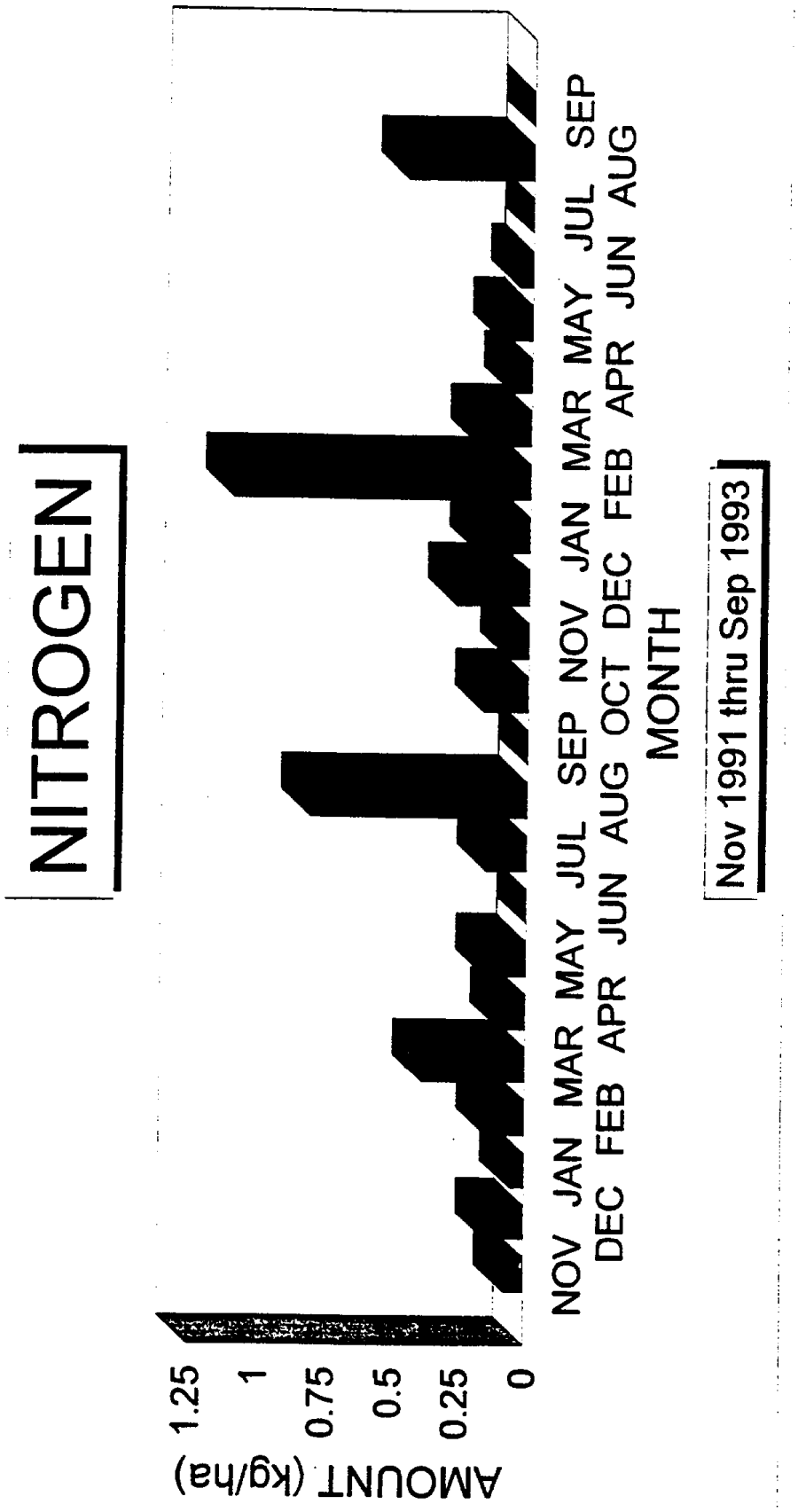

NITROGEN
AMOUNT (kg/ha)
1.25
1
0.75
0.5
0.25
0
NOV JAN MAR MAY JUL SEP NOV JAN MAR MAY JUL SEP
DEC FEB APR JUN AUG OCT DEC FEB APR JUN AUG
MONTH
Nov 1991 thru Sep 1993

Figure 10

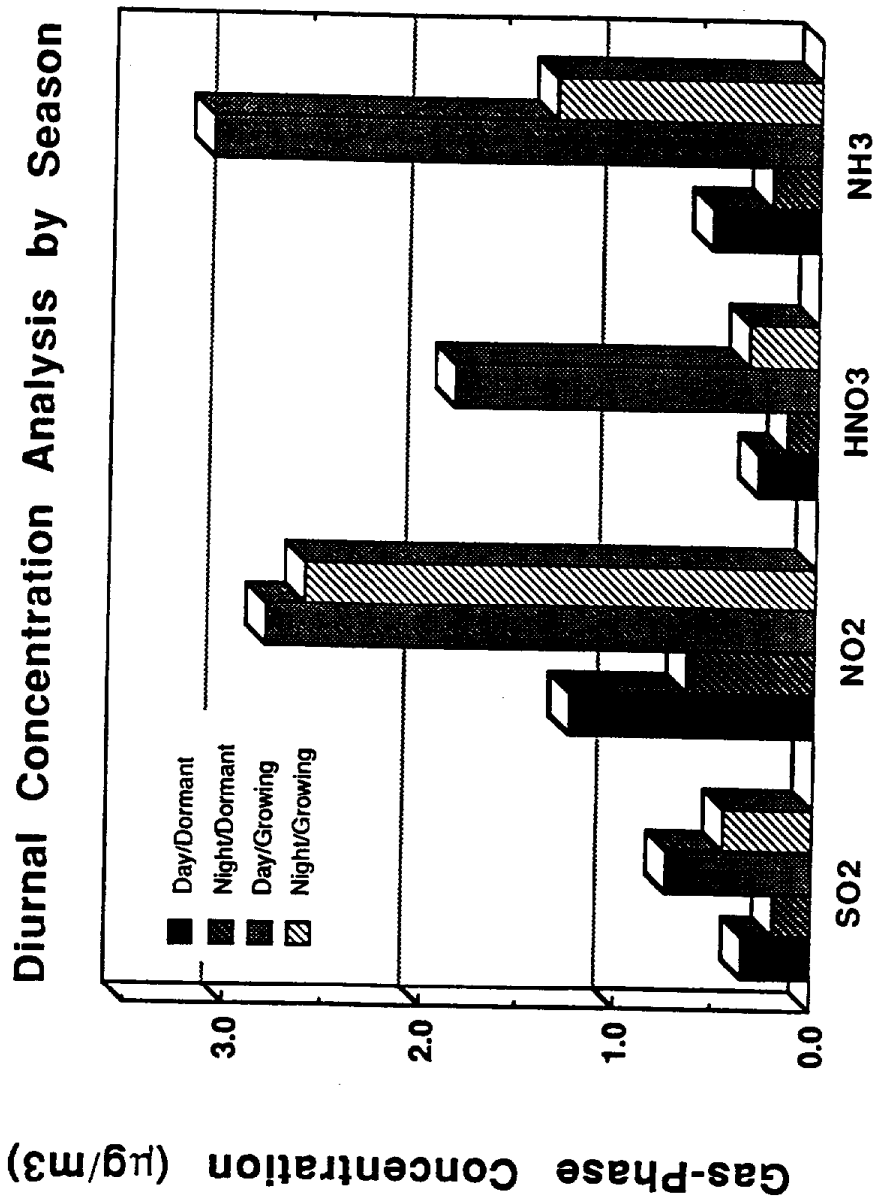

Diurnal Concentration Analysis by Season
Day/Dormant
Night/Dormant
Day/Growing
Night/Growing
3.0
2.0
1.0
0.0
SO2
NO2
HNO3
NH3
Gas-Phase Concentration (µg/m3)

Figure 11

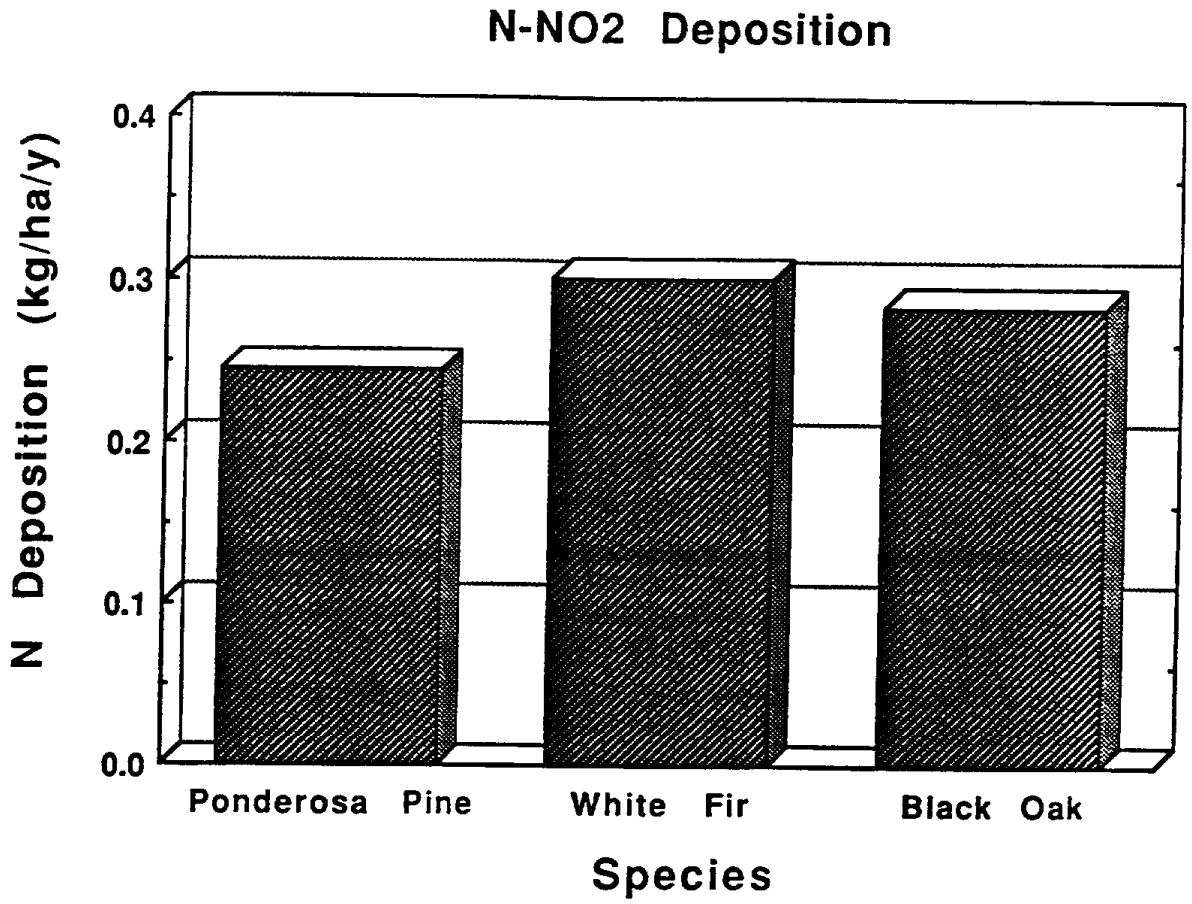

N-NO2 Deposition
N Deposition (kg/ha/y)
0.4
0.3
0.2
0.1
0.0
Ponderosa Pine
White Fir
Black Oak
Species

Figure 12

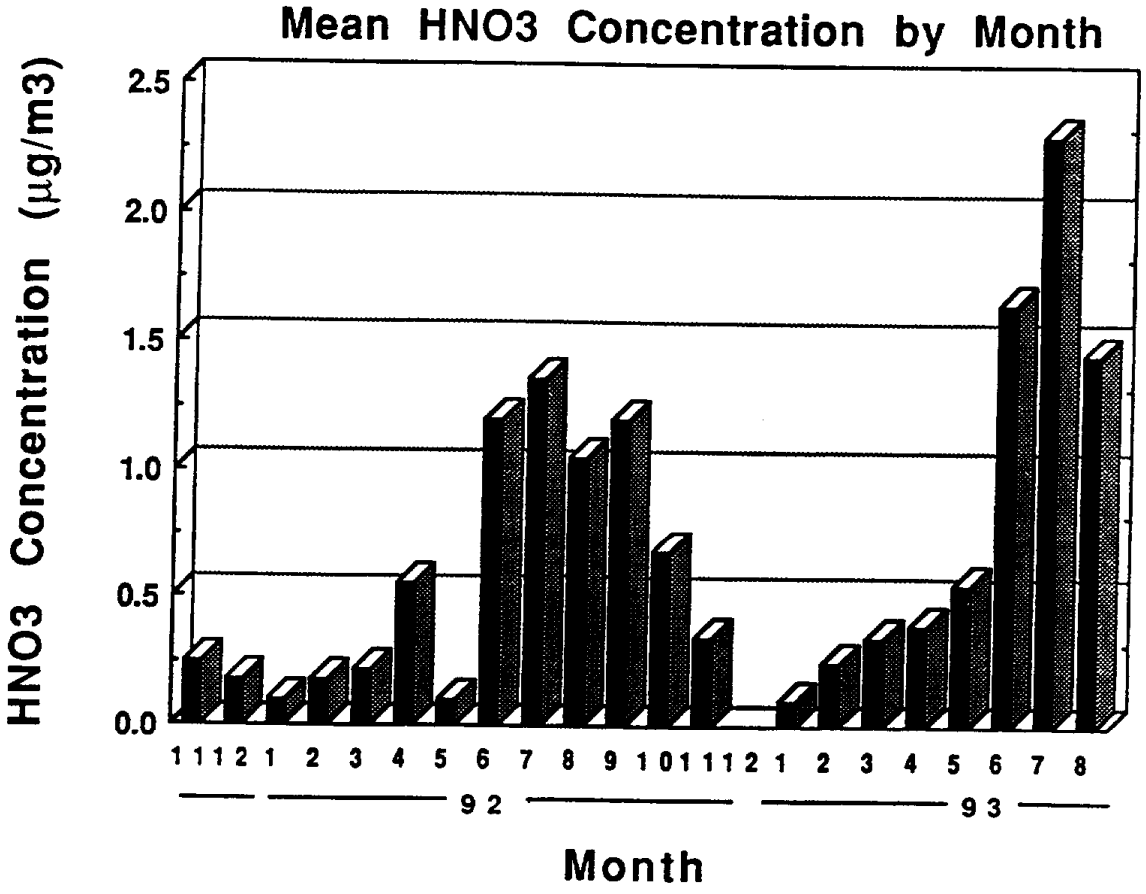

Mean HNO3 Concentration by Month
HNO3 Concentration (µg/m3)
2.5
2.0
1.5
1.0
0.5
0.0
11 12 1 2 3 4 5 6 7 8 9 10 11 12 1 2 3 4 5 6 7 8
92
93
Month

Figure 13

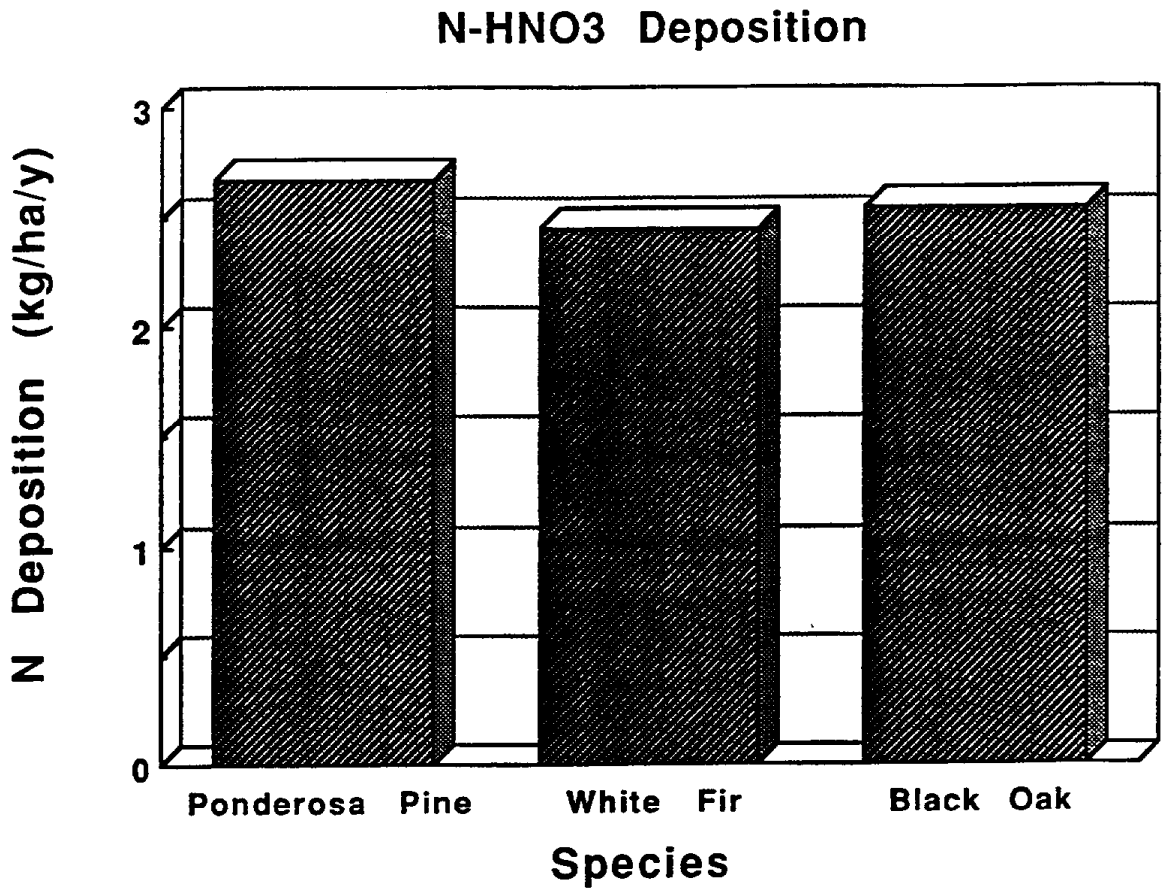

N-HNO3 Deposition
N Deposition (kg/ha/y)
3
2
1
0
Ponderosa Pine
White Fir
Black Oak
Species

Figure 14

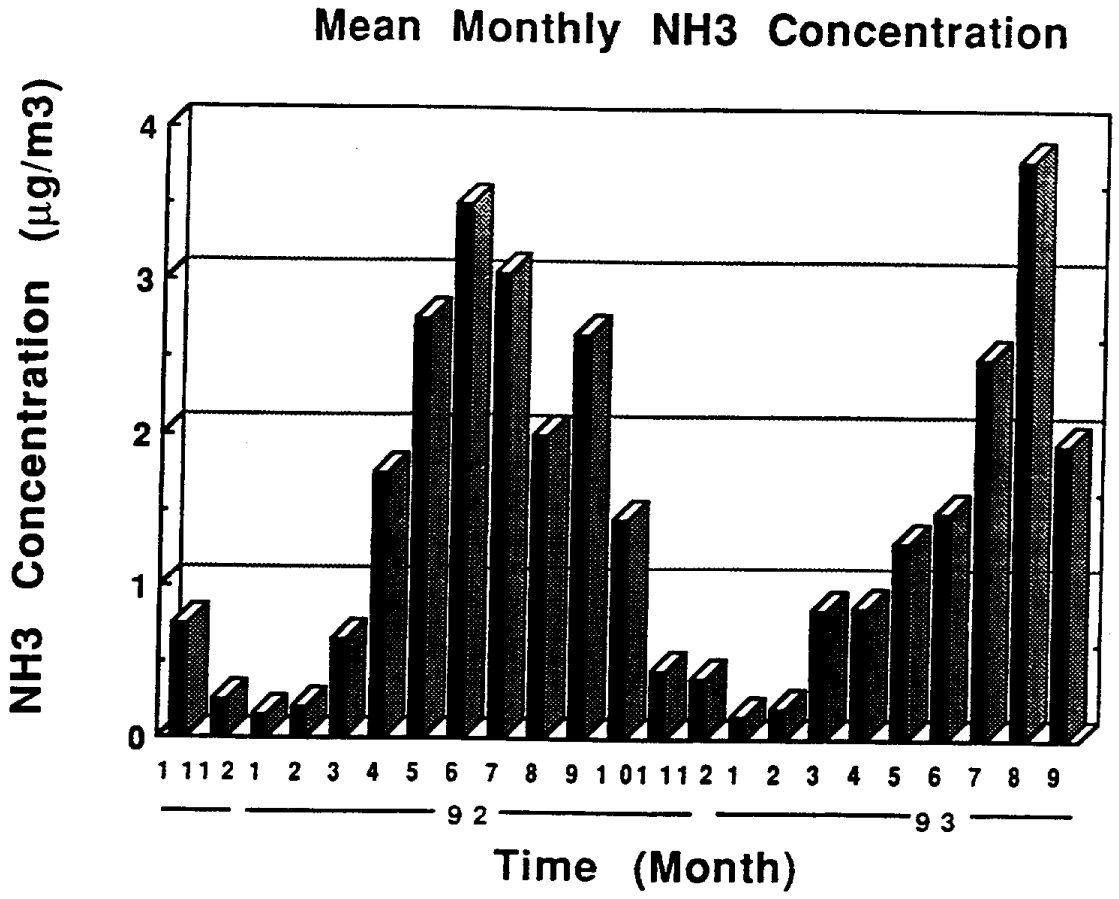

Mean Monthly NH3 Concentration
NH3 Concentration (µg/m3)
0
1
2
3
4
11 12 1 2 3 4 5 6 7 8 9 10 11 12 1 2 3 4 5 6 7 8 9
92
93
Time (Month)

Figure 15

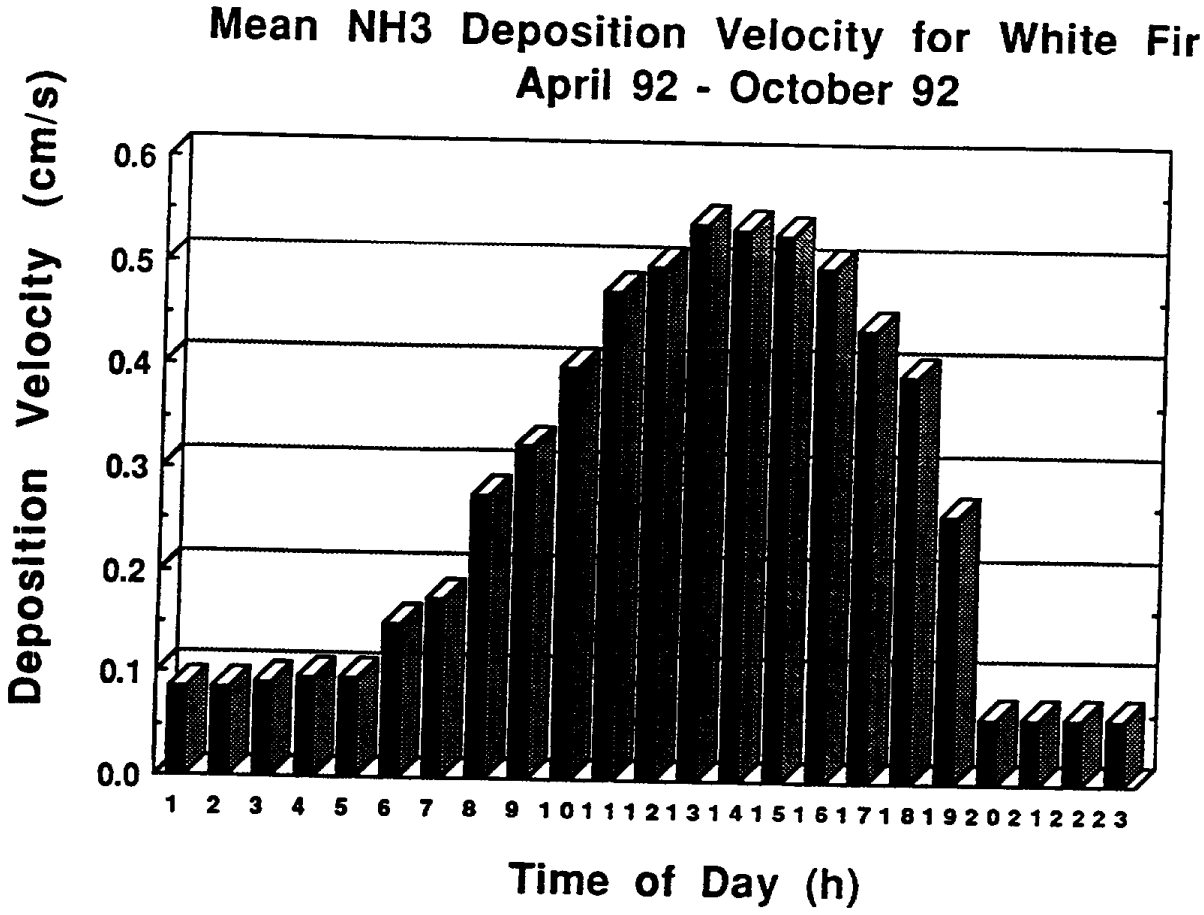

Mean NH3 Deposition Velocity for White Fir
April 92 - October 92
Deposition Velocity (cm/s)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
Time of Day (h)

Figure 16

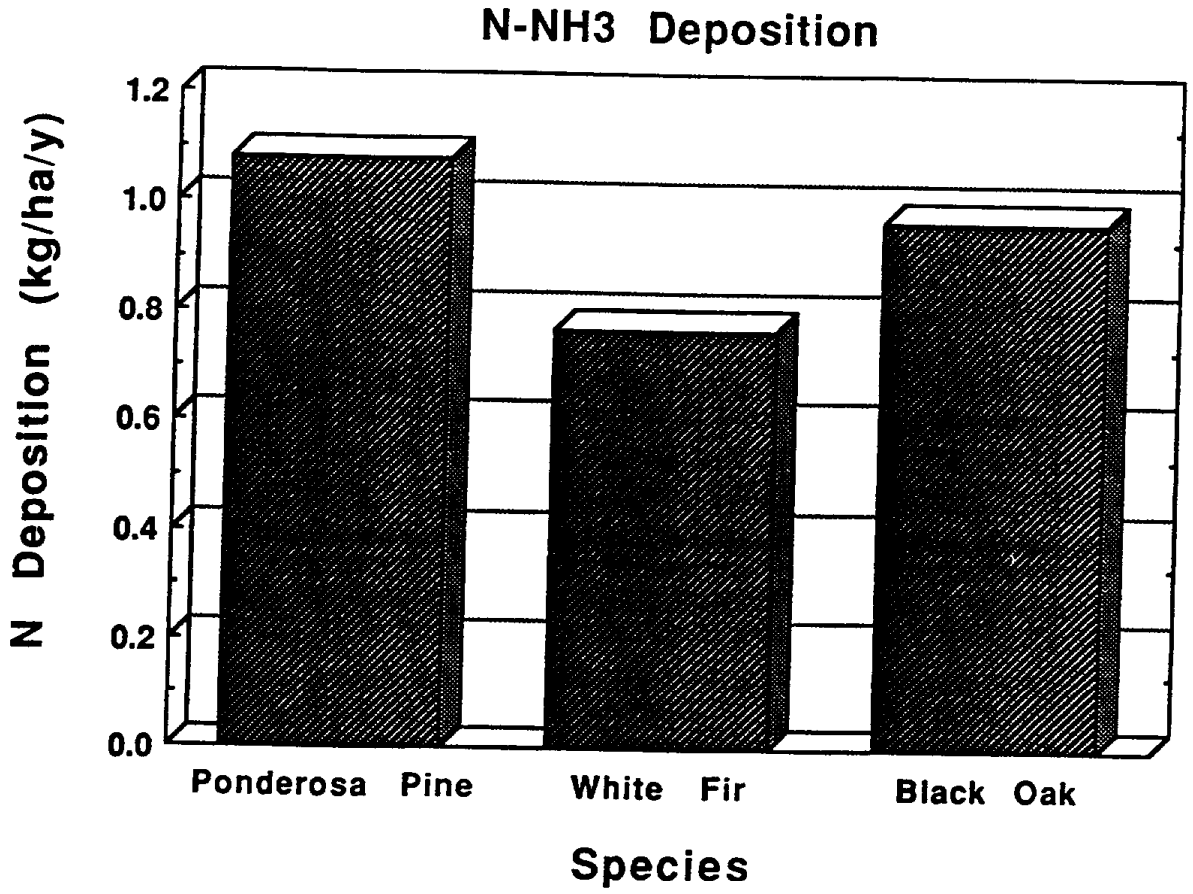

N-NH3 Deposition
N Deposition (kg/ha/y)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Ponderosa Pine
White Fir
Black Oak
Species

Figure 17

SUMMARY

Δ Sulfur Deposition (stand level)

- Dry S-SO2 Deposition = 1.2 kg/ha/y
- Wet S Deposition = 1.6 kg/ha/y

- Dry S/Wet S Deposition = 0.75
- Dry S/Total S Deposition = 0.43

Δ Mean Ozone Deposition (leaf level)

- O3 Deposition/Uptake for Ponderosa Pine = 7.8 μmol/m2/h
- O3 Deposition/Uptake for White Fir = 3.7 μmol/m2/h
- O3 Deposition/Uptake for Black Oak = 6.8 μmol/m2/h

- O3 Deposition >> threshold for physiological and growth effects

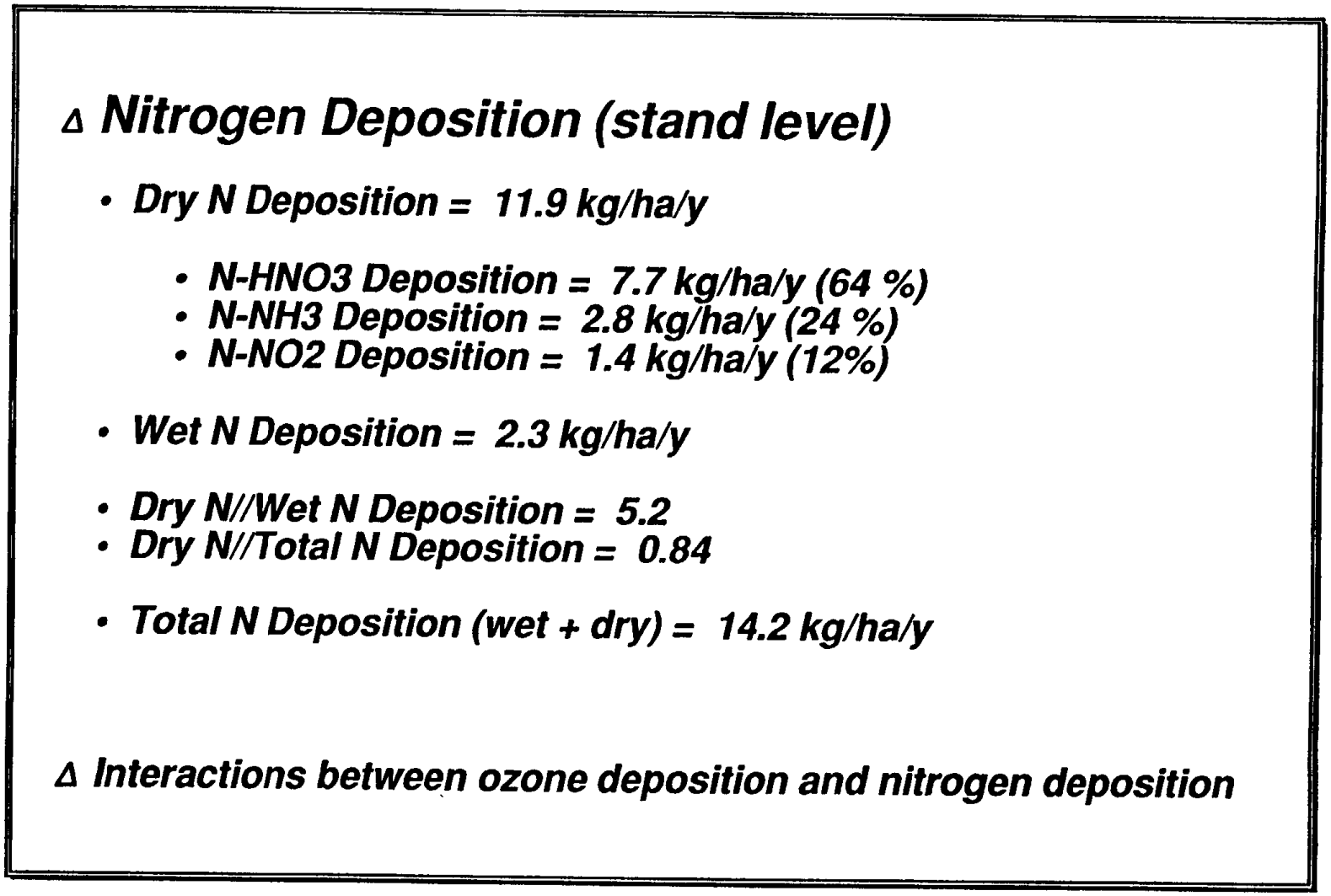

Δ Nitrogen Deposition (stand level)
• Dry N Deposition = 11.9 kg/ha/y
• N-HNO3 Deposition = 7.7 kg/ha/y (64 %)
• N-NH3 Deposition = 2.8 kg/ha/y (24 %)
• N-NO2 Deposition = 1.4 kg/ha/y (12%)
• Wet N Deposition = 2.3 kg/ha/y
• Dry N//Wet N Deposition = 5.2
• Dry N//Total N Deposition = 0.84
• Total N Deposition (wet + dry) = 14.2 kg/ha/y
Δ Interactions between ozone deposition and nitrogen deposition

Figure 18

Figure 19

Uncertainty

- Δ Cloud Water Deposition (Low volume, high enrichment)
- Δ NH3 Deposition
  - processes controlling deposition, uptake and metabolism at the leaf level
  - parameterization of the Big-Leaf Model by species
- Δ Re-Emission/Re-Suspension of Dry-Deposited Nitrogen
- Δ Conservative Estimate of Nitrogen Deposition
- Δ Ozone Interaction with Nitrogen: Physiology and Growth of At-Risk Species

DR. BRENT TAKEMOTO, Moderator: Air Resources Board

The afternoon session will focus on the effects of air pollutants on vegetation, and the presentations will be by Dr. Pat Temple at UC Riverside and Dr. Mark Fenn who is at the US Forest Service in Riverside. Subsequent to those presentations will be a talk given by Dr. Dale Johnson at the Desert Research Institute and Dr. Mark Poth at the US Forest Service. They will look more closely at field work they have done with soil as well as modeling results for what is known as the nutrient cycling model. I would like to have Mark Fenn first and then Pat Temple talk about air pollution effects on tree health.

3. Air Pollution Effects on Tree Health. Dr. Mark Fenn, USDA Forest Service, and Dr. Patrick Temple, SAPRC, UC Riverside.

DR. MARK FENN: USDA FOREST SERVICE

I will be talking about direct injury to foliage of pines from air pollution. There are obviously a number of factors that can impact tree health, forest health, and productivity, and multiple stress interactions are involved. Mount San Gorgonio in the San Gorgonio Wilderness, is a protected wilderness area that is influenced by air pollution impacts. From the tower in plot 2 at the Barton Flats study area near the San Gorgonio Wilderness ozone damage to Ponderosa pines can be seen with healthier trees close by. One kind of damage to the Ponderosa pine needles is, a symptom known as winter fleck, and it is found throughout California and also in other parts of the country. Its cause is not exactly known, but it is very widespread. It is found on the upper surface of the foliage, but on the lower surfaces, you do not see this kind of damage. The classic ozone injury pattern on conifer needles is yellow mottling in Ponderosa and Jeffrey pine. Often there is a mix of both types of injury symptoms on the same foliage. Winter fleck is found not only in air polluted areas but also in many forests throughout California and other areas.

Q (AUDIENCE) What does it do other than discolor? What is the problem to the tree?

A (DR. FENN) What you see with the discoloring is simply an obvious symptom to the naked eye. If you look at the tissue level, there is a lot of damage to the cells and tissue, and of course ozone damage is well known to actively cause the foliage to fall off from the tree prematurely. Winter fleck obviously has an impact on total photosynthesis and tree growth, because the tree is losing tissue. This winter fleck is found over large areas and only occurs in foliage that has been exposed to at least one winter. I want to point out that there is a variable number of needle whorls that are still retained on the branch. As the needles age, they tend to fall off. In healthy trees that are not stressed by drought

or air pollution, needles are often retained at up to 5-6 years or sometimes longer. If you have an exposure to ozone, however, foliage loss can occur in needles as young as two years, and it really has a large impact on the tree.

Figure 1 shows the percent of branches with these winter flecking symptoms on the foliage from three plots, two in the Sierra Nevada and one at Barton Flats. These trees which were exposed to relatively high ozone. The second data set is from the three northern California sites in the Sierra Nevada that do not have high air pollution exposure. You can see that the winter fleck injury symptoms are more prevalent at the high pollution sites compared with the low pollution exposure sites. This is the first time that we suspected there was a direct relationship between air pollution exposure and winter flecking. One hypothesis is that exposure to various air pollutants, ozone, acids, and possibly UVB radiation, may predispose needles to greater winter fleck injuries.

I would now like to describe the ozone injury index which has recently been developed. Part of this project, called the Forest Ozone Response Study is sponsored by the ARB as well as the National Park Service and U.S. Forest Service. There are the four major components of the ozone injury index (Fig. 2) whorl retention, chlorotic mottle, needle length, and percent live crown. Below are the weighting factors used for these four components. The greater weight factors (40 percent) are for the mottle and whorl retention, and 10 percent weight factors are assigned to the needle length and percent of live crown components. This index combines these four components and ranges from 0-100 with 0 being no injury.

Figure 3 shows some data in the San Bernardino Mountains across an air pollution gradient from Angeles Oaks to Barton Flats to Heart Bar, which is an eastern site with lower air pollution exposure. As you can see, the ozone injury index decreases as exposure to ozone decreases. The Barton Flats site is in the middle part of this gradient.

If you look at ozone injury index over time (Fig. 4 from 1991 to 1994), at the three Barton Flats study plots, you can see there is a general increase in ozone injury during this three-year period at plot 1, plot 2, and plot 3. We attribute this increase in ozone injury to increasing water availability throughout these three years as compared to the previous several years of drought there. Pat Temple will talk about that in greater detail. Basal area increase over 1991 to 1994 is shown in the three plots (Fig. 5) for the three major over story species, Ponderosa pine, Jeffrey pine, and black oak.

Q (AUDIENCE) What does basal area mean?

A (DR. FENN) Basal area is a measure of the cross-section area of the tree trunk. You can imagine if you cut off the tree and looked at the cross sectional area, that the increase in diameter and area of the tree with growth trunk is a good measure stand growth.

The main point in this figure is that Ponderosa pine shows a much lower percent increase over

this three-year period compared to white fir and black oak. This phenomenon is found not just in polluted areas, but throughout the state. It results largely because of fire suppression, because white fir and oak species commonly found in the mixed conifer forest thrive when fire is absent. Because fire has been suppressed over many decades now, we have a greater and greater stand component of white fir. That is the main explanation for white fir's in basal area increase. A secondary explanation is that it is only moderately sensitive to ozone. However, Ponderosa pine and Jeffrey pine are much more sensitive to ozone injury and that tends to magnify this difference. Again we emphasize that we cannot consider air pollution or any type of environmental stress effect alone. You have to consider it in the context of both forest dynamics and other environmental factors.

Drought is a major stress and a determining factor in tree health, growth, and forest productivity. Figure 6 shows the 10 year running mean and also the yearly total of precipitation at Big Bear Dam, a site not far from our study sites at Barton Flats in the San Bernardino Mountains. As you can see, precipitation is highly variable. There is really no such thing as a normal precipitation year. Also, I would like to point out that there was a severe drought for several consecutive years in the late 1980s. In fact, if you look from 1980 to 1990, for about nine years there was very low precipitation in the San Bernardino mountains. I would like to show how some tree response data representing drought stress. Let us start off with Figure 7 which is the average dry weight of Ponderosa and Jeffrey pine needles by age, that is by the year the needles were formed. These data are averages of sums of five branches per tree. The numbers above the bar represent the number of trees which had annual whorls still retained on the branch. These data were collected at the end of 1991, and the important point is that if you look at the average needle weight, you see by 1989 and 1990, the consecutive drought years, the drought had quite an impact by decreasing needle biomass. By 1990, the length of needles had decreased markedly and this is quite unusual. In 1991 we had abundant rain in March and with the resumption of greater water availability, you can see the needle biomass increased greatly. However, as Pat Temple will explain, when you have greater water availability in a more normal year, the tree stomata are more open and take up a lot more ozone. When we have a great drought period here during which the stomata are not taking up as much ozone, you do not see as much ozone damage. As soon as you have a good wet year, the trees also take up a lot more ozone and you begin to see a lot more ozone injury. Thus, we have a pattern of consecutive stresses, drought stress followed by ozone stress. The bottom graph shows similar data on needle length and the bars represent the year in which we measured the needle length. In the final drought years we saw that needle length just like biomass decreases. As soon as the rain increased in 1991 and from there on, needle length has greatly increased and returned to a normal length.

Today we have heard talks on air pollution concentration, deposition values, and such questions

were raised as "but what effect did it have on the forest?" I want to focus on the relationship of concentrations of ozone to injury that we see in the pine trees. Figure 8 is one way of presenting the ozone data. This is a 12-hour average, and we have three years of data, 1992, 1993, and 1994, at Barton Flats. There is not a great deal of variation from year-to-year expressing the ozone concentration in this manner as 12-hour averages. Let us compare that to another way of expressing ozone exposure called the "sum O6 ozone index" (Fig. 9). It gives greater weight to concentrations that are higher. The index includes the cumulative hours of ozone exposure at concentrations greater than 0.06 ppm. It accentuates differences more, and these higher concentrations are more significant in terms of plant response. And you can see in June, there are much greater differences in sum 06 ozone among the years. In Figure 10 we look at the relation of this ozone exposure index and percent chlorotic mottle on the needle. Current year needles do not have very much chlorotic mottle. Chlorotic mottle is almost always found in needles that are one or two years or older. If you look at one-year-old and two-year-old needles, you can see a very strong relationship between this sum O6 ozone exposure index and the amount of chlorotic mottle. This tells us that this ozone exposure index seems to be a very good indicator of the plant response. From these data, we are now going to look further and see how well this same type of response may work for other indexes to explain ozone injury throughout the mixed conifer forests in California.

To conclude (Fig. 11), the upper surface flecking of Ponderosa and Jeffrey pine was recently found to be more prevalent in areas of more photochemical air pollution. This was not known previously, so the possible role of acidic deposition in causing this winter fleck, or causing greater winter fleck, or predisposing winter fleck is going to be investigated. The other point is that ozone symptoms were abundant in the Barton Flats area, and index of chronic injury to trees increased from 1991 to 1994. This increase in injury was related to greater precipitation in those years and higher stomatal conductance. During the drought years (Fig. 12), ozone injury was reduced due to low stomatal conductance. New needle mass was reduced with each successive year of drought, but when soil moisture and stomatal conductance was higher, ozone caused needle injury. The overall result was reduction of needle surface area because several years of drought decreased the needle length. Then we had years of greater rainfall and ozone injury caused a lot of those needles to fall, thus reducing the numbers of needles. It really makes it hard for the trees to recuperate with these sequential stresses. Lastly, the concentration-weighted ozone exposure indices were highly correlated with foliar injury. With that I will close and let Pat present his data.

Q (DR. PITTS) I have one question. I thought when we had drought years, at least after 20 years of drought, that the trees would show massive mortality. During the drought years, one of the problems is the bark beetles, and infestation of bark beetles weakens the tree. Is that right, Paul?

A (PAUL MILLER) That is right.

Q (DR. PITTS) So that being the case, I have been saying that during these drought years, we also had higher ozone levels more often. Could it be a combination of things that kill the trees? How do I explain to people that more water will kill the pine trees?

A (DR. FENN) I am not saying there is less ozone in the drought years, I am saying that the trees take up less ozone.

Q (DR. PITTS) But if you used the reduced rate the tree takes up ozone during drought and factored in the increased ozone levels, in other words measure an integrated exposure to ozone, there is a combination of effects. Is that right? Basically, can I tell people that the trees would take up less ozone, but the atmosphere has a lot more ozone, and the product of the two effects is more kills on the Ponderosa?

A (PAUL MILLER) I think the problem is fairly complex. One of the points we make is that it is possible in a drought year, because of higher ozone concentrations, that we have more ozone uptake. I do not think that is necessarily the case, and I think Pat will explain that. We are trying to look at this thing in terms of annual growth responses. When you look at one year after the other and look at the drought, the field situation is a combination of these two stresses working together, especially drought. The weaker trees that have been ozone injured are going to be the ones killed more easily by pests in this longer view.

(DR. FENN) For those that are interested in more information on that, there is a recent publication by the Forest Service on California forest health. It goes into a lot of these different issues you are talking about.

Q (AUDIENCE) I have two questions. In regard to the ozone exposure index, how are the weighting factors derived?

A (PAUL MILLER) Well these are commonly used. For example, in an ongoing EPA project dealing with ozone responses, one of the exposures often used was the sum 06 index. There are just a myriad of others that could be tested. When we first looked at the data, we decided to focus on that index as opposed to some average value.

Q (AUDIENCE) Are other weighting factors significantly different from what you used, or are they all about the same?

A (PAUL MILLER) Well, they can vary. For example, another one was to sum the number of hours over some threshold, for example 0.08 ppm.

Q (AUDIENCE) How different would the picture look if you used different weighting factors?

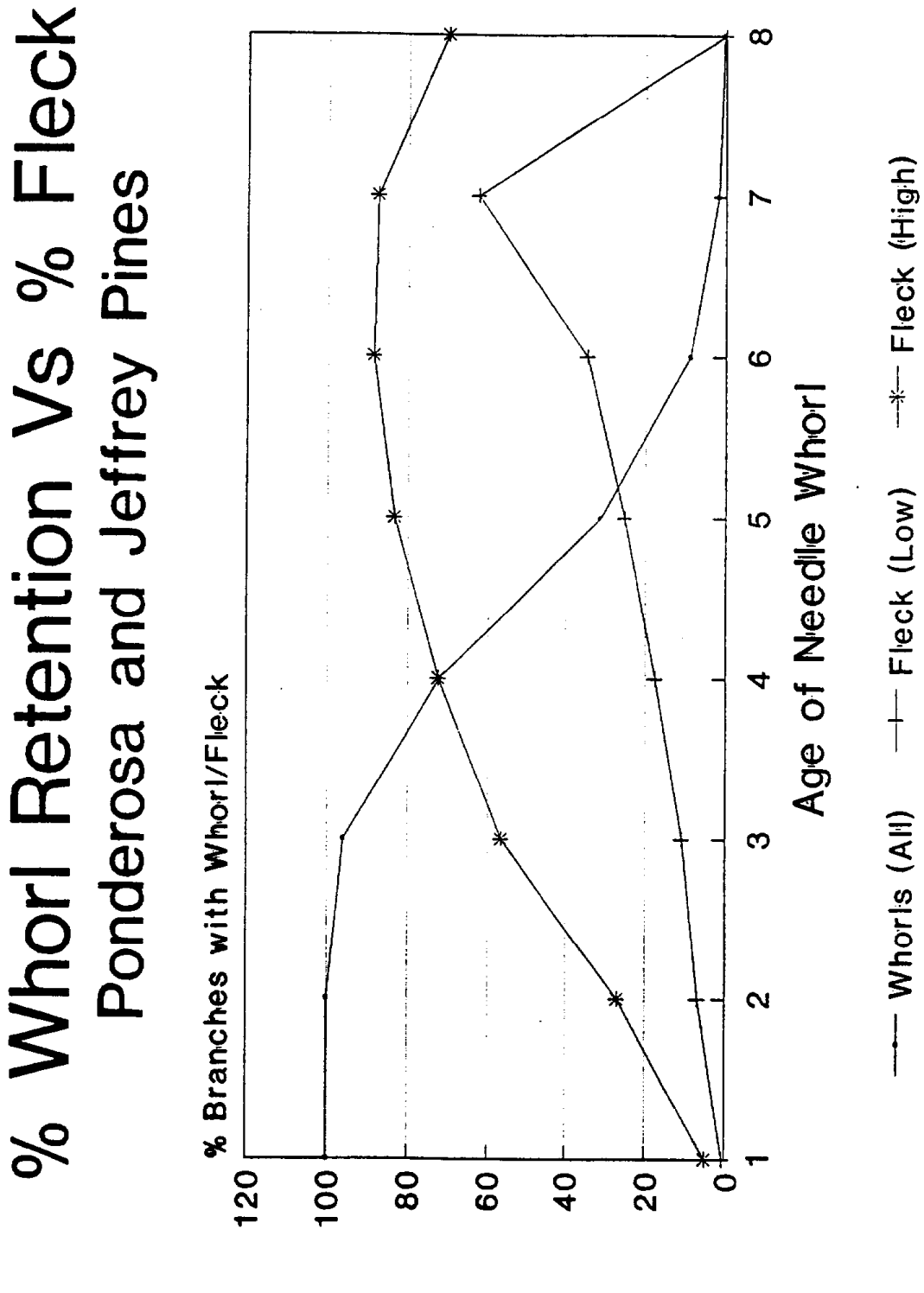
A (PAUL MILLER) Well, that is what we are trying to discover.

Q (AUDIENCE) The second question: with regard to the winter fleck, you show an increase

in flecking with years, but for both plots at year 7, it started to decrease. Why did it decrease?

A (DR. FENN) I think there is a simple answer. After 7 years, we have fewer needles in whorls left on that branch. They normally tend to undergo abscission by the time they are 4-5 years old, and if they are exposed to ozone, they are abscised before that. The needles that remain have fewer fleck symptoms in typical time course for Ponderosa and other pines. At about 3 years old, the annual whorls of foliage begin to fall off, but it depends on a lot of stress factors. If it is a really healthy tree, by year 6 or 7, the needles are mostly gone. If there is air pollution or drought stress, they are going to fall before that. I think the main point is that we were surprised to see this great increase in winter fleck in foliage that had been exposed to air pollution.

Figure 1


% Whorl Retention Vs % Fleck
Ponderosa and Jeffrey Pines
% Branches with Whorl/Fleck
120
100
80
60
40
20
0
1
2
3
4
5
6
7
8
Age of Needle Whorl
Whorls (All)
Fleck (Low)
Fleck (High)
Sierra Nevada and San Bernardinos

Ozone Injury Index (OII)

- Components:
  - * Whorl Retention (number), including needles/whorl (3 classes)
  - * Chlorotic Mottle / Whorl (6 classes)
  - * Needle Length / Whorl
  - * Percent Live Crown
- OII = WR + CM + NL + PLC
- Weighting: 40% + 40% + 10% + 10%
- Index Range 0 to 100 (0 = no injury)

Figure 3

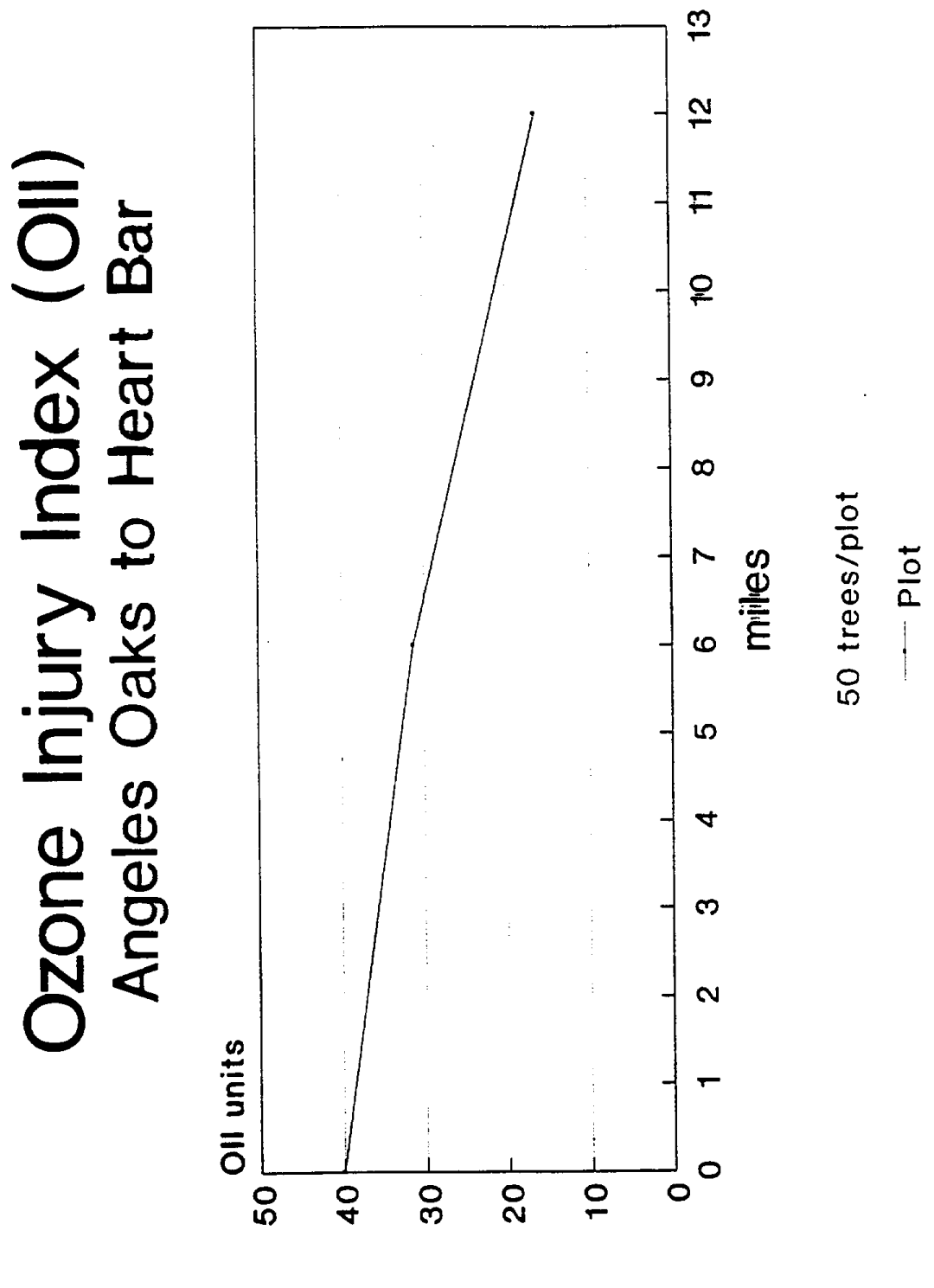

Ozone Injury Index (OII)
Angeles Oaks to Heart Bar
OII units
50
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13
miles
50 trees/plot
Plot
1994

Figure 4

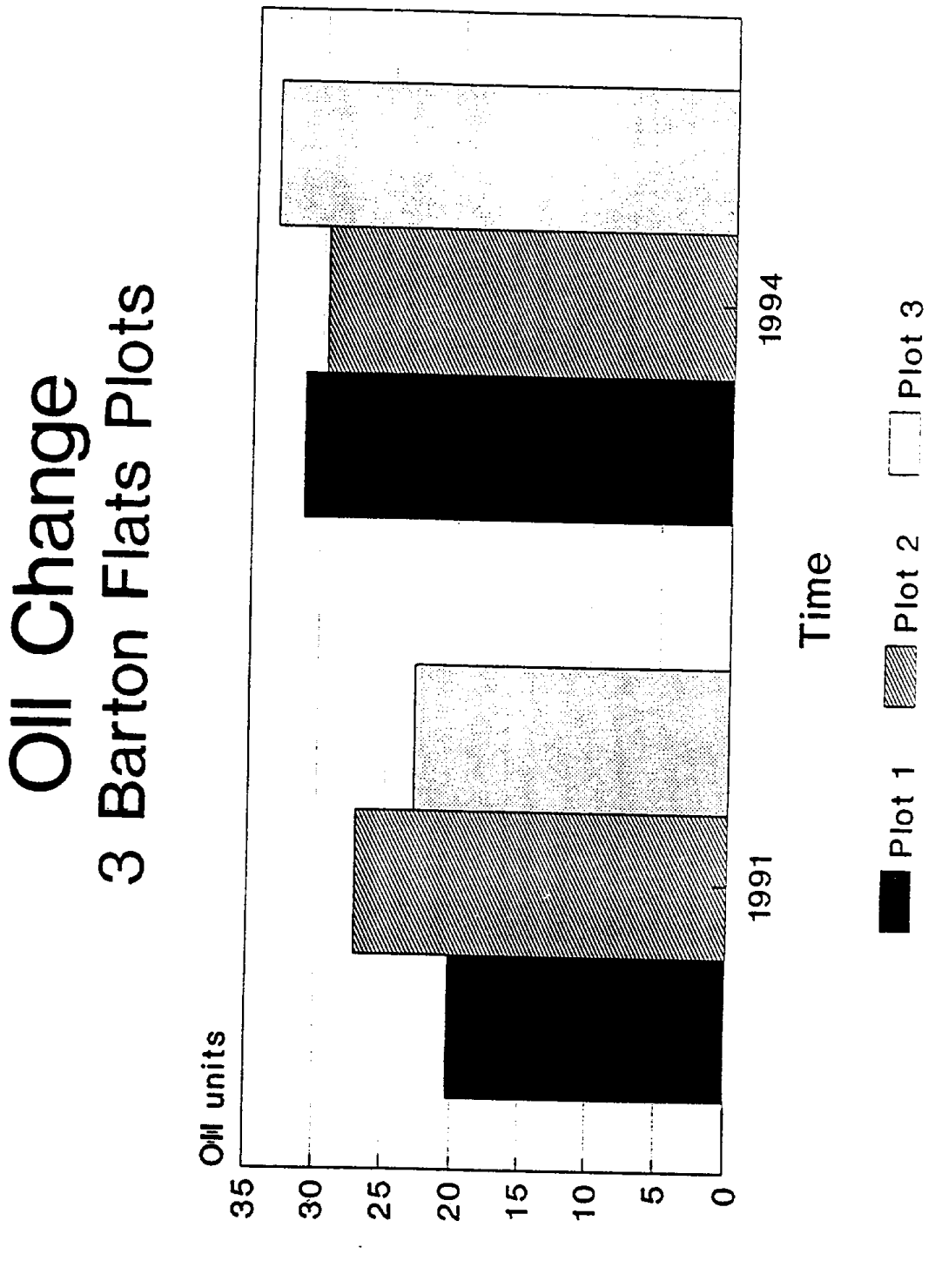

Oil Change
3 Barton Flats Plots
Oil units
35
30
25
20
15
10
5
0
1991
1994
Time
Plot 1
Plot 2
Plot 3
1991 to 1994

Figure 5

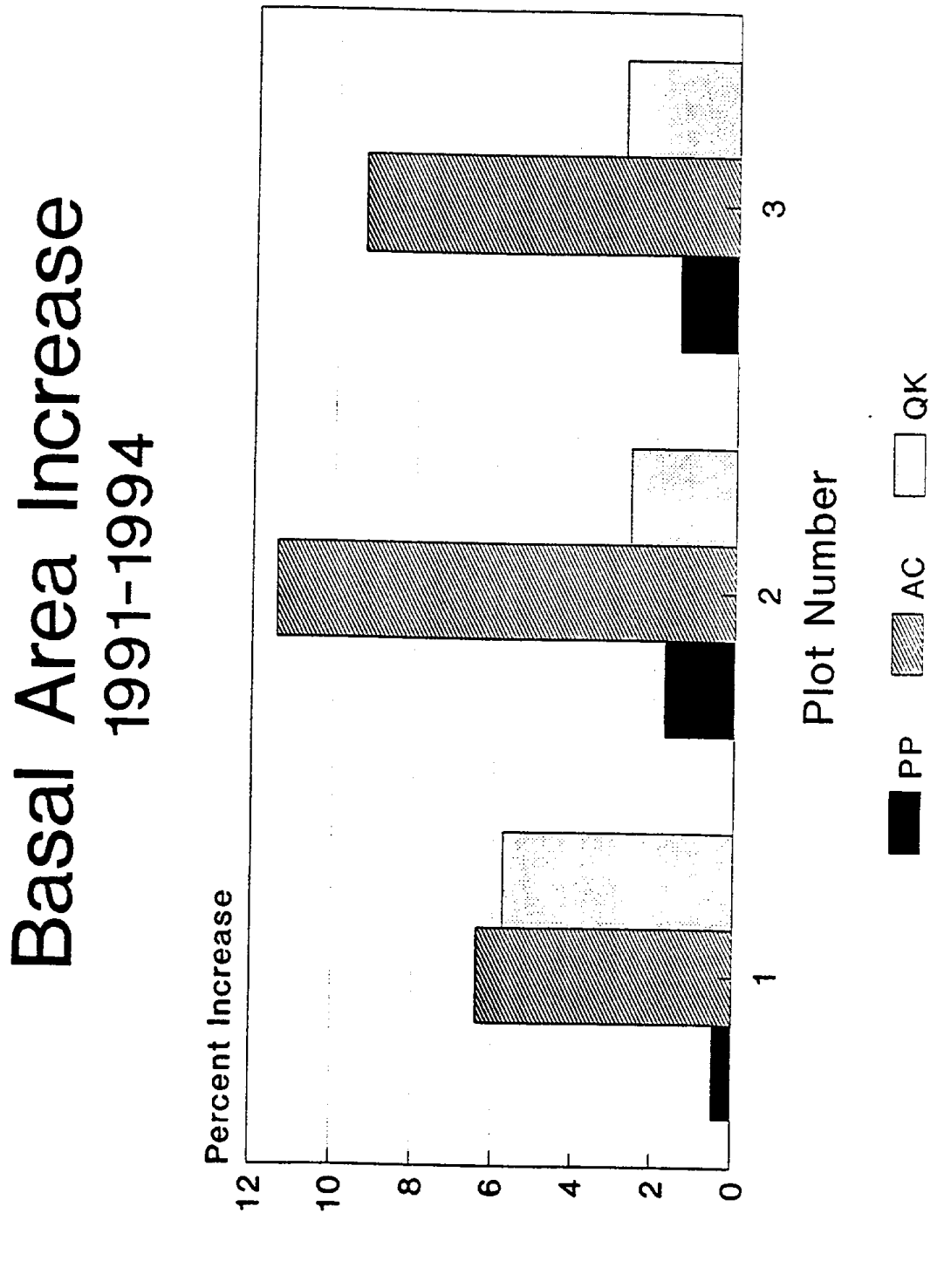
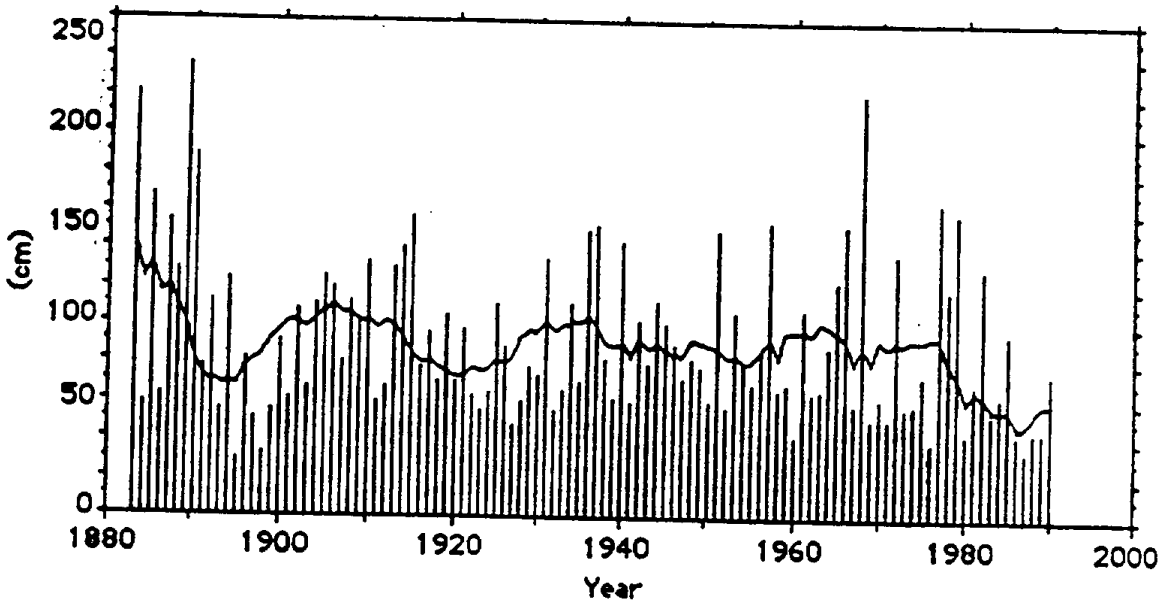

Basal Area Increase
1991-1994
Percent Increase
0
2
4
6
8
10
12
1
2
3
Plot Number
PP
AC
QK
Species in Plots

Figure 6



Precipitation record from 1883 to 1990 at Big Bear Dam, a site central to the forest vegetation monitoring plots in the San Bernardino mountains of southern California. The ten-year running mean is included.

Figure 7

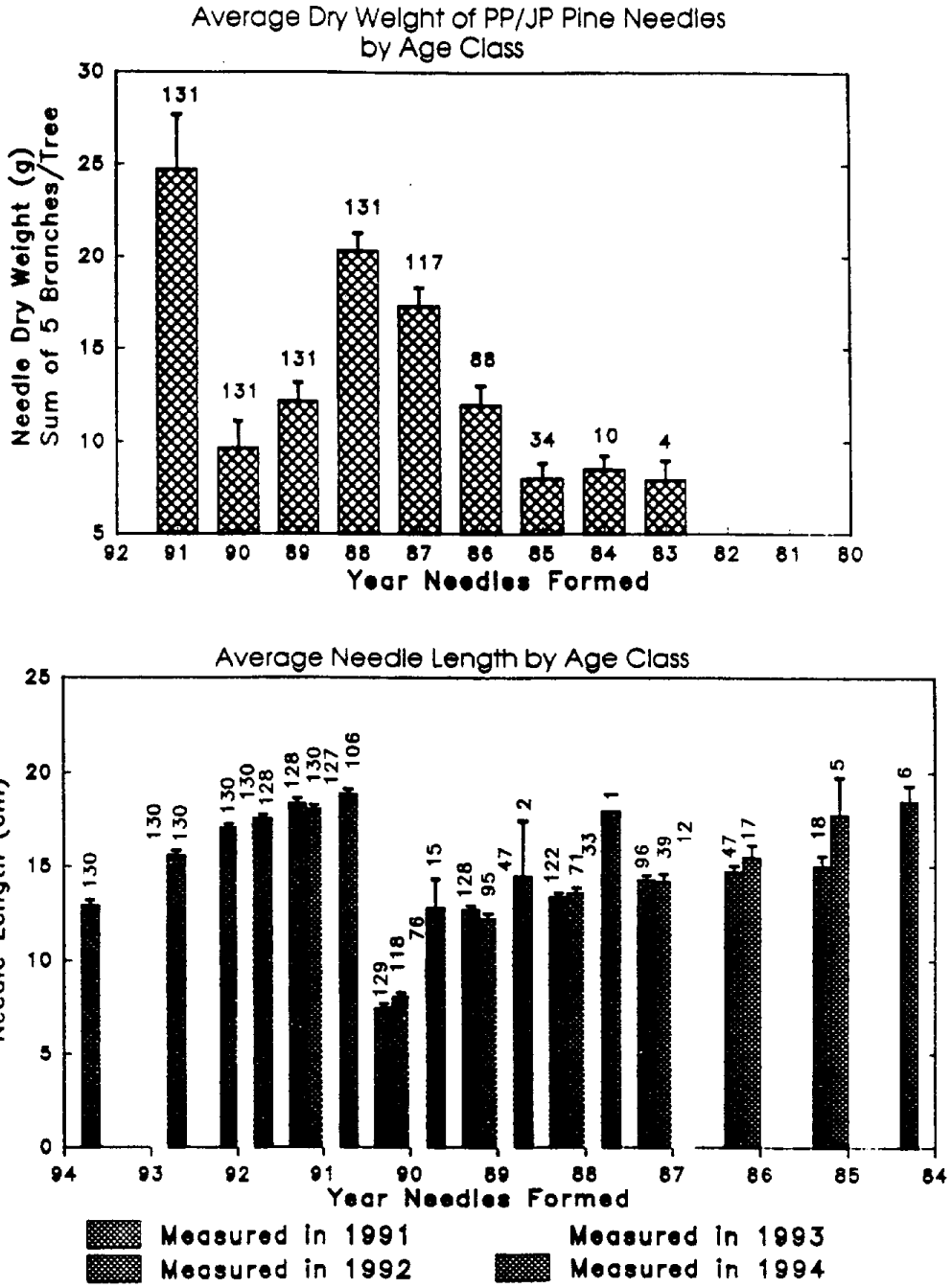

Average Dry Weight of PP/JP Pine Needles
by Age Class
Needle Dry Weight (g)
Sum of 5 Branches/Tree
30
25
20
15
10
5
131
131
131
131
117
88
34
10
4
92 91 90 89 88 87 86 85 84 83 82 81 80
Year Needles Formed
Average Needle Length by Age Class
Needle Length (cm)
25
20
15
10
5
0
130
130 130
130 130 128
128 130 127 106
129 118 76 15
128 95 47 2
122 71 33 1
96 39 12
47 17
18 5
6
94 93 92 91 90 89 88 87 86 85 84
Year Needles Formed
Measured in 1991
Measured in 1992
Measured in 1993
Measured in 1994

Figure 8

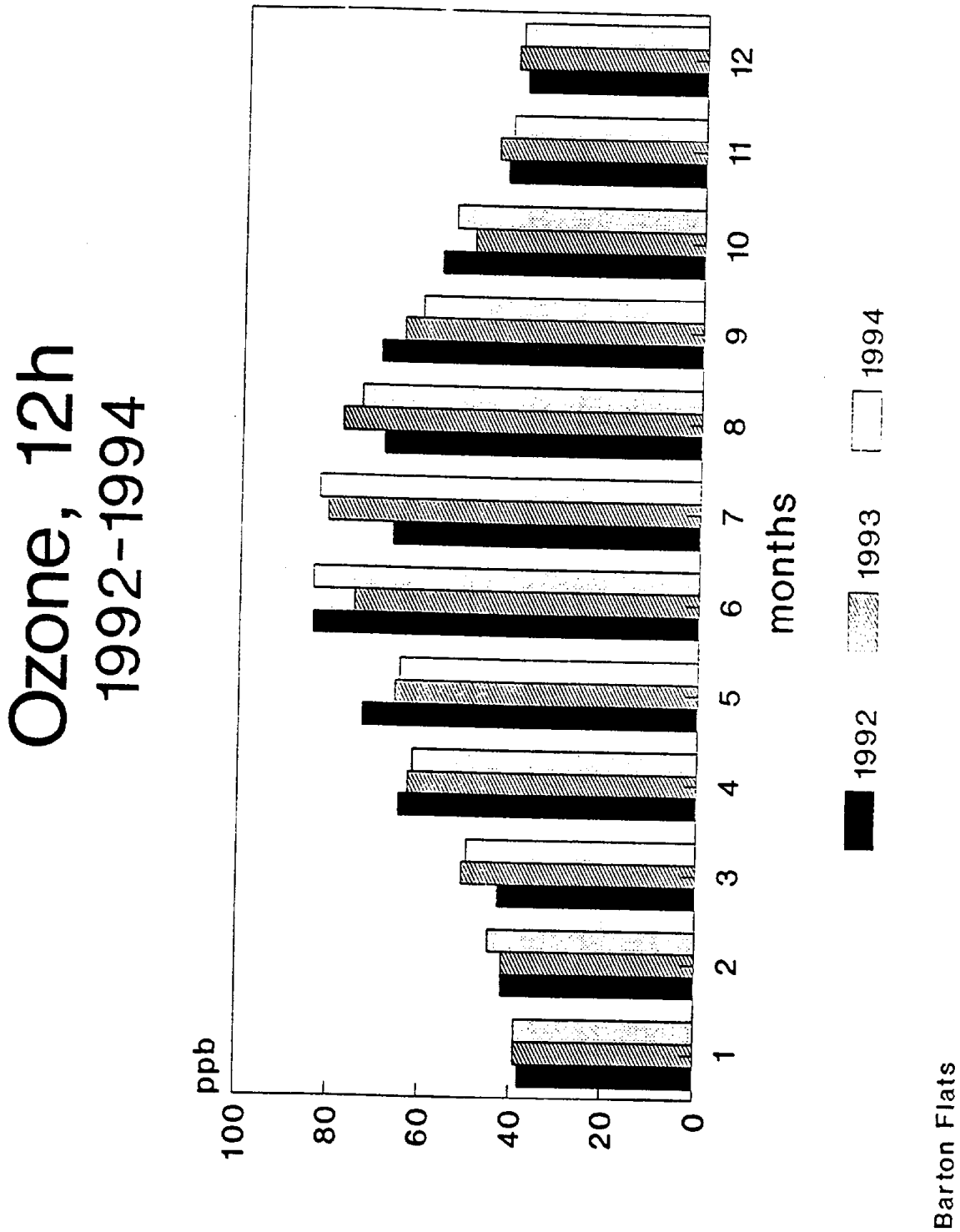

Ozone, 12h
1992-1994
ppb
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
months
1992
1993
1994
Barton Flats

Figure 9

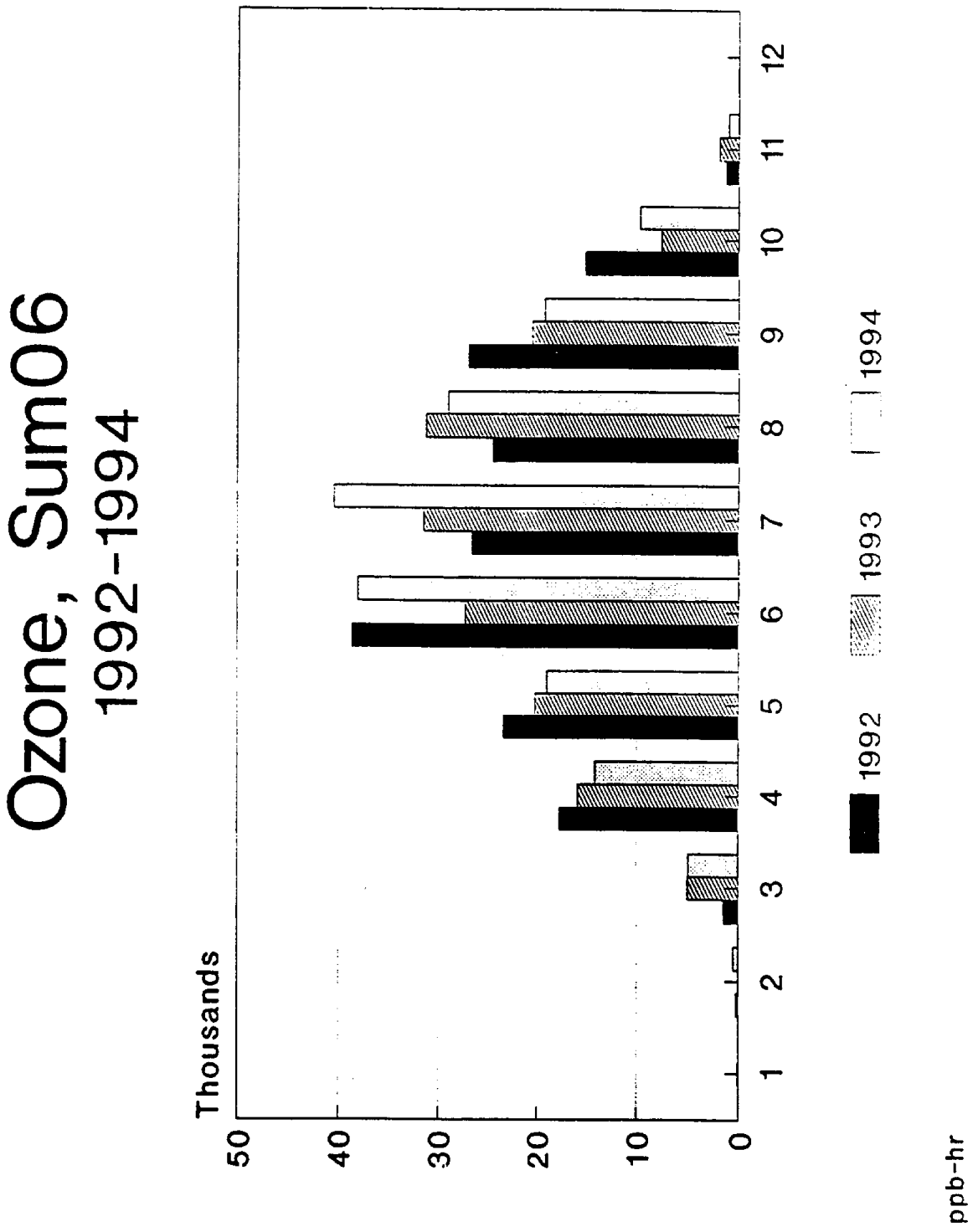
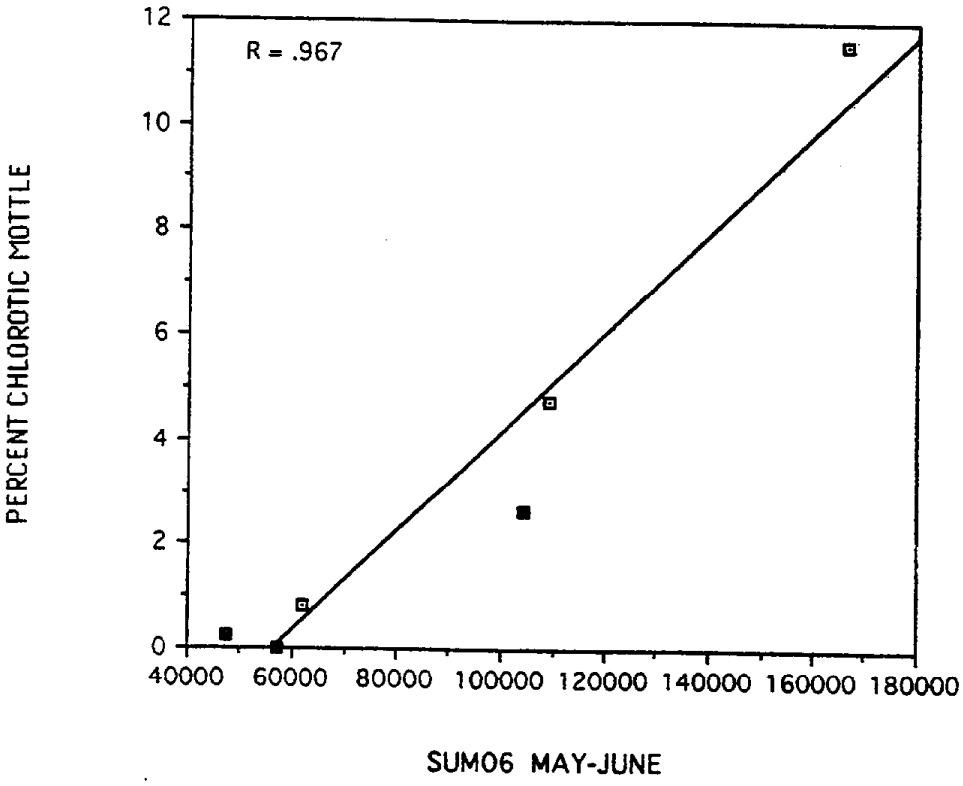

Ozone, Sum06
1992-1994
Thousands
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12
1992
1993
1994
ppb-hr

Figure 10


R = .967
PERCENT CHLOROTIC MOTTLE
SUM06 MAY-JUNE
0
2
4
6
8
10
12
40000
60000
80000
100000
120000
140000
160000
180000

Forest Ecosystems
Conclusions--Forest Health

- An upper surface flecking of ponderosa and Jeffrey pine needles that occurs only after exposure to winter weather was recently found to be more prevalent in areas with more photochemical air pollution. The possible role of acidic deposition in causing winter fleck is unknown.

- Ozone symptoms were abundant and an index of chronic injury to trees increased from 1991 to 1994.

Barton Flats Project

Figure 11

Forest Ecosystems
Conclusions--Tree Health

- During drought years ozone injury is reduced because of low stomatal conductance. New needle mass is reduced with each successive year of drought. When soil moisture is abundant ozone causes needle injury and defoliation. Thus drought and ozone act sequentially.

- Concentration-weighted ozone exposure indices are highly correlated with foliar injury.

Barton Flats Project

Summary of Forest Health Presentation: AAPP Meeting in Costa Mesa

Mark Fenn, Research Plant Pathologist

and

Paul Miller, Supervisory Research Plant Pathologist

USDA, Forest Service, Pacific Southwest Research Station, Riverside, CA

Research Objectives

This segment of the project at Barton Flats in the San Bernardino Mountains studied the condition of forest vegetation in three monitoring plots located in the vicinity of the meteorology and air quality monitoring station operated by the project. The overall intent of the work was to examine if or how, acidic dry and wet deposition interacts with ozone and climate-induced stresses to alter tree and forest health. The focus was on immediate and visible effects on foliage and short-term effects on stem growth. Other portions of the project were concerned about long-term effects mediated through changes in soil and nutrient cycling.

The specific goals were to:

A. Establish a verifiable data base characterizing tree health and forest condition.

1. Describe tree density, size composition, and species composition at each plot.

2. Describe the initial state of tree health followed by repeat evaluations of foliage and crown symptoms each year (1991-1994),

3. Describe stem growth changes of companion species from 1991 to 1994.

B. Test relationships between pollution loading and detectable changes in tree health.

1. Describe the accumulation or intensification of needle symptoms in relation to different ozone exposure indices.

2. Describe other needle symptoms not caused by known biotic agents in an attempt to discover possible relationships to acidic pollutants.

Initial Results

Descriptive Measurements -- The three monitoring plots were selected to be similar in topography and species composition. All were characterized as ponderosa-Jeffrey pine/white fir/black oak. Position and stem diameter were recorded for all stems >10 cm diameter-breast-height (dbh), for all species. Within each plot, a subsample of approximately 42 ponderosa and/or Jeffrey pines were selected for more intensive measurements. The sample resulted in 64 ponderosa pines and 66 Jeffrey pines when all three plots were counted. Additional measurements made on these trees included: tree height, percent live crown and annual measurements of needle whorl retention, chlorotic mottle symptom severity on each whorl, and needle length of each whorl.

Annual changes in tree condition were expressed as an index, called the ozone injury index (OII). This index ranges between 0 and 100 where higher values means more crown injury. The index was computed by giving 40 percent weight each to whorl retention and chlorotic mottle, and 10 percent weight each to needle length and percent live crown. The index was employed concurrently for a statewide assessment of ozone effects on ponderosa and Jeffrey pines. It was employed successfully in the Barton Flats study to show a decrease in tree injury along a 12-mile west-to-east-decreasing ozone gradient, where Barton Flats was at the mid-point, and to show an increase in tree injury from 1991 to 1994. The percent increase in basal area for all species between 1991 and 1994 ranged from <1 percent to 12 percent . White fir had the highest increase at all plots (6 to 12 percent), followed by black oak (2 to 6 percent) and ponderosa/Jeffrey pines (<2 percent). The relative growth response of these species was the same as the estimated ranking of ozone sensitivity (white fir least injured, and ponderosa/Jeffrey pines most injured). Other sources of growth data from the San Bernardino mountains agree with this finding.

Variation in the Physical Environment and Tree Response -- The long-term precipitation record for the San Bernardino mountains shows extreme annual variation with frequent clusters of consecutive years that are much lower than the long-term annual mean. We found that both annual needle whorl weight and modal length of needles in each whorl reflect moisture availability for the year in which they grew. For example, from 1988 to 1990, when years of consecutive drought were present, the length and weight of needles were reduced. At the peak of the drought in 1990, needles in that whorl were half as long and half as heavy as those in the 1988 (early drought) whorl. In 1991, both needle length and weight returned to the highest level observed because of unusually abundant spring and summer precipitation. Other studies in this project have confirmed that ozone flux to foliage is lowest when soil moisture availability is low and stomatal conductance (transpirational water loss) is low. Needles did not develop as much ozone injury in the drought years as in the recovery year following the drought (1991). Therefore, trees were attempting to respond to two stresses. Drought reduces needle mass, while ozone hastens the abscission of the needles with reduced mass (length) and injures the longer needles formed in response to more favorable moisture availability.

The summer ozone exposure looked very similar during the summer months when monthly 12-hour (daylight) averages were compared from 1992 to 1994. Accumulative expressions that favor higher concentrations, namely, the sum of hourly concentrations >60 ppb ozone, or the sum of hours >80 ppb ozone, show some distinct differences between years. The above expressions of ozone injury were also calculated separately for April through 15 June, and 16 June through August. The incremental increase in chlorotic mottle symptoms was measured for each needle whorl formed from 1992 to 1994. The regression coefficient for chlorotic mottle and number of hours >80 ppb ozone for April through 15 June was higher than for 16 June to August. This suggests that the most sensitive exposure-response relationship would emphasize the higher concentrations that occur during the April through 15 June period.

The question about the possible relationship between dry and wet acidic deposition to needle injury symptoms was investigated by carefully recording the nature and extent of all visible injury. An upper needle surface necrotic flecking is common on those needles that have been through at least one winter period. Flecking intensifies on a particular whorl with successive winters of exposure. A survey, including pines in both the Sierras and the San Bernardino mountains, shows that upper surface needle flecking is highest where photochemical oxidant air pollution is highest (using ozone concentration as a surrogate measure for expected levels of other pollutants). We have no evidence to implicate acidic deposition as a cause of upper surface needle flecking, but the circumstances suggest that some modification of the needle cuticle may be involved, which makes the epidermal tissue more vulnerable to winter conditions.

Summary

The pine/white fir/black oak forest mixture, typical of the Barton Flats area, presently shows the effects of constant exposure to ozone and sequential exposure to drought. Ozone injury to foliage increases during years with greater soil moisture availability. Stem growth measurements suggest that ponderosa and Jeffrey pine have reduced competitive ability in comparison to white fir and black oak. We cannot implicate acidic deposition in causing upper needle surface necrotic flecking on pines, but experiments should be designed to investigate the origin of this symptom, which appears to be more prevalent in regions with higher photochemical air pollution.

DR. PATRICK TEMPLE: SAPRC, U.C. RIVERSIDE

I am going to talk about the stomatal conductance model in relation to ozone exposure. The stomata are the gatekeepers for gas exchange. Ozone, nitric acid vapor, ammonia, and other gases are on the outside of the leaf, and the leaf tissues and their potential physiological responses are on the inside. How do you get those two together? Essentially, the gases outside are conducted inside through the stomata. When we talk about conductance and flux deposition, we are essentially talking about tissue exposure. It occurred to me earlier that the medical people consider whether exposed children are indoors or outdoors. A tree is always outdoors, but the tree does not necessarily respond. At night when stomata are closed, a tree will not see ozone or gaseous materials, because very little can get inside the leaf. My job over the last three years, from 1992 to 1994, was to look at stomatal conductance on an annual basis up in the Barton Flats area.

I want to first present a couple of caveats. The most important is that I was working only with a very small, very limited population of trees. Earlier, you saw the diagram of the tower and those of you who have been up there realize you can only reach one or two individual trees in that canopy and the same is true for the saplings, the seedlings, and the other populations studied. This was a very small number of individuals. I will show you the results of a large numbers of observations of stomatal conductance taken throughout the year for three populations of Jeffrey pine at 7000 feet elevation. These results also pertain to Ponderosa pines in the area. We looked at stomatal conductance beginning in 1992. At the bottom of Figure 1, I have a measure of the soil moisture at the Barton Flats site, and there are two areas where I recorded it. The circles are data taken from a clearing with bare mineral soil, and the squares represent water content in the organic layer underneath the plant canopy. Amazingly enough, there was far more water in the surface soil of this bare mineral area, and that is essentially why a lot of these pine trees germinate and grow well after a fire. In 1992, a typical year, soil water started out high and the soil water become depleted as the season progressed. Maximum conductance of these trees peaked generally around 10 o'clock in the morning, but there was a very flat diurnal curve, and the conductance generally stayed pretty high throughout the rest of the day. Only as the sun went down did you start to see a significant reduction in conductance. The important point is that the overwhelming majority of conductance in 1992 was in and around the month of June. In July, August, and September, the conductance for all of these seedlings, saplings, and canopy foliage as well declined significantly. Thus, May, June, and a bit of July, are the important times of the year. I should mention that 1992 was a good rainfall year, and there was a lot of winter precipitation. In 1994, we had a dry year, and there were almost no summer rains (Fig. 2). The soil water contents started out high, declined throughout the summer, then reached a low plateau in mid-June. Most of the water has been used up by day 150, which was around the first of June. The stomatal conductance corresponds to that. In 1994, by the middle of

June the stomata were closing down. If you had an ozone episode out there in August and September, the plants would not respond to it.

You notice I jumped from 1992 to 1994. I have to show 1993 (Fig. 3) to demonstrate how the life of a plant physiologist and ecologist out in the field can be messy. The trees did not show any kind of pattern in 1993. We had a tremendous rain event in June, and whether that influenced the conductance or not, I am not sure. 1993 was also a year of transition. Mark Fenn mentioned that we had 7-8 years of drought prior to our study at Barton Flats which began in 1992. We had the so-called "March miracle" in 1991, and there were good rains in 1992 and 1993. 1993 was a transitional year, because the trees were shifting from drought stress years to a couple of good water years. They went through a whole series of phase changes. Figure 4 gives you an example of how the leaves developed and its effects on the stomatal conductance of Ponderosa pines. This is a population of Ponderosa pines that retained different age classes of needles, and I studied a series of trees with three age classes of needles in August 1993. In this case, the trees that had three years of needle retention had the highest stomatal conductance in the one-year-old needles. The highest stomatal conductance was in the current age class of needles for those trees that had been affected by ozone or for some other reason had only two age classes of needles. The one-year-old needles had a very low level of conductance. So as the trees were affected by ozone, not only did the stomatal conductance affect the ozone response, but the ozone response in turn affected stomatal conductance adding another layer of complexity the whole system. In 1993, many of these trees were actually losing their older age classes of needles in response to ozone, and as they did, their stomatal conductance was fluctuating. That is one explanation I have for the highly variable data set in 1993.

Let us look at the ozone exposure for these trees (Fig. 5). This figure is the monthly ozone for each of the three years. 1992 was a little bit different with rain in August, and that is why the monthly mean ozone was so low, but otherwise the three years were about the same. Now let us look at how much ozone these trees actually saw. Figure 6 shows a seedling population that was growing at the base of the Barton Flats tower. It shows the ozone flux, a measure of how much ozone actually gets into the leaves of the trees for the three years of the study. About 25-30% of all the ozone uptake occurred in the month of June. If you consider May, June, and July, about 60-70% of all the ozone was taken up in these three months. If you were designing an ozone standard for trees, the annual mean would not tell you very much. If you are want to know the season of the year that most strongly affects the plant response to ozone, it would be in May, June, and July. The same pattern occurred for the saplings (Fig. 7). Figure 8 is the mature tree at the top of the canopy. Here we observed a slightly different pattern. April of 1994 showed more of a response, but in general the month of June is the peak month for absorption of ozone.

I am going to summarize all of this information in Figure 9. The mean monthly ozone for the three years of the study was about the same. Precipitation in 1994 was very low. In 1992 and 1994, the ozone flux, or the amount of ozone taken up by the trees scaled pretty much to the precipitation. In 1993, we had high precipitation, but perhaps because 1993 was the year in drought transition, we saw no correspondence between precipitation and ozone flux. I can tell you that in some years you can predict the ozone response and the amount of ozone taken up by seasonal precipitation Two out of three years we could do that, and one year we could not.

In general in wet years, the mature trees took up less ozone, so one would expect that all other things being equal that the mature trees would have less ozone response than the seedlings and saplings. In a bad year, that is in a drought year, the ozone uptake was about the same.

Q (AUDIENCE) Can you show us how the precipitation correlates with ozone? It is not apparent from the figure without some more explanation.

A (DR. TEMPLE) In 1992, precipitation was high relative to a drought year, and ozone uptake was also high. In 1994, precipitation was low and ozone uptake was also low. That was the only correlation I was making. 1993 complicates that whole pattern, because the precipitation was the same as 1992, but the ozone uptake was lower, so the relationship is complex. I interpret 1993 as a transition year in which the trees were coming out of their drought stress and moving into a more well watered phase.

Q (AUDIENCE) So there is no obvious relation to the height of the tree sampled in this obviously small area of mature trees?

A (DR. TEMPLE) Oh, yes, the saplings were about 2-3 meters high and mature trees 25 meters high.

Q (AUDIENCE) Could that explain a lot of that difference?

A (DR. TEMPLE) Your point is well taken. I did not take into account some of the concentration gradient that may exist from the top of the canopy to ground level. As Paul will tell you, on most days of the year there is quite a wind blowing through this area, and so there is a relatively small concentration gradient. Now as Andrzej said, there may be a flux gradient, but that is different from a concentration gradient. My calculations are based on no difference in concentration between the top of the canopy and the ground level. There may be a difference in flux into the leaves if there is a difference in wind speed. That is a possible complication, but it is a point well taken. The concentration appears to be the same because the canopy is very open and is probably well ventilated at most times. Paul has data to show that under stagnant conditions, you can see a gradient of 20% maximum. There is a much higher ozone concentration, 20% higher, above the canopy.

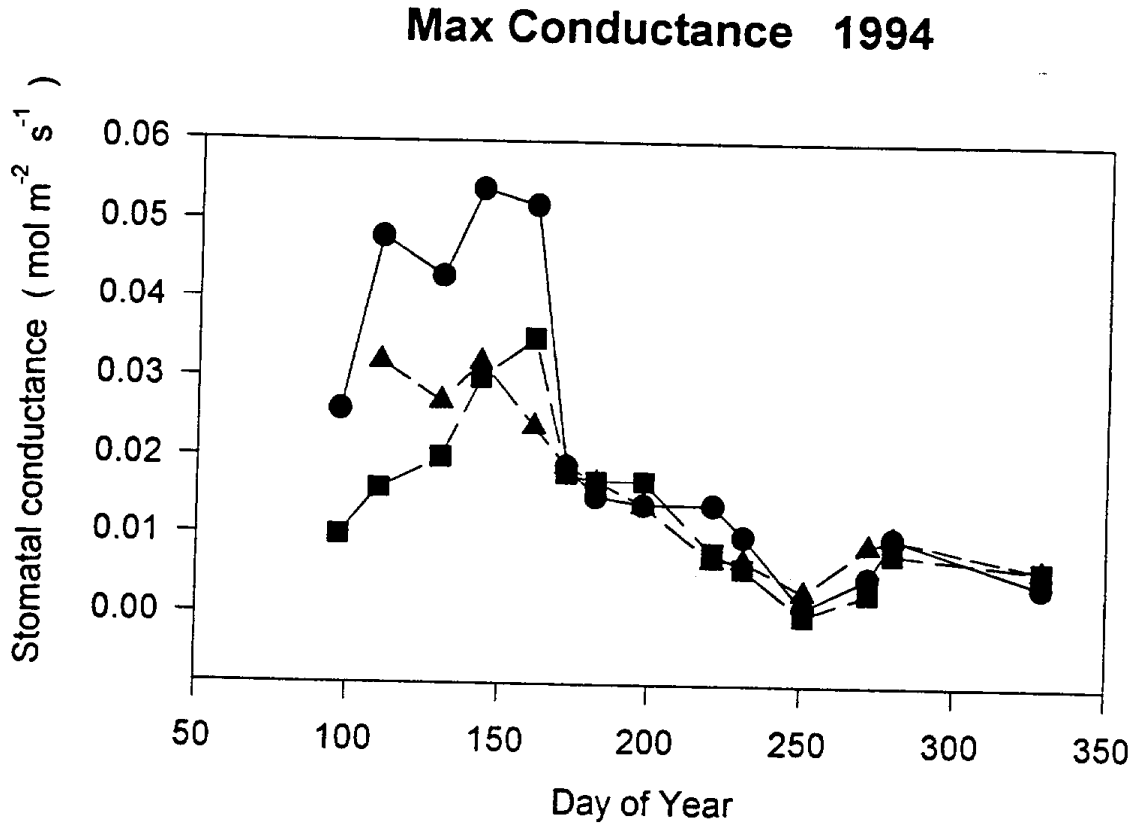
Q (AUDIENCE) Do you think if all of this was untangled you would begin to see a pretty

good correlation between increase in biomass and the ozone exposure?

A (DR. TEMPLE) If I knew enough to untangle the complexities, perhaps. There is no doubt there is a correlation between ozone uptake and the effects of that ozone on but it is a very complex scenario. We have done some studies, and Paul has been looking at this for 30 years. He can show you very clearly that there are some trees that are affected by ozone. The way we know they are affected is that they retain only two years of foliage, and a healthy Ponderosa pine should have three or maybe four years of foliage. Most trees that have ozone symptoms grow less than healthy trees. However, there may be susceptible and resistant trees growing side by side. The susceptible tree grows slower and less than the healthy tree. Yes, we can make that kind of correlation, but we need models like George's and others to sort out these complexities and to figure out the correlation between ozone exposure, ozone concentration, ozone flux, ozone dose, and ozone response.

Figure 10 outlines the conclusions of my study. I found that ozone flux was variable across the three years of the study. Ozone flux was also variable across tree age. The mature trees at the top of the canopy appeared to take in less ozone than the saplings. Most of the annual ozone flux occurs in May, June, and July. Ozone flux is a function of annual precipitation, but it is not a strong correlation in some years. Ozone flux is also controlled by foliar dynamics, as we saw in 1993 when the trees were in transition from a drought phase to a wet phase. I have been emphasizing ozone, but of course if you have an acidic component such as nitric acid vapor, or other gas phase air pollutants, they will follow a similar pathway. Pollutant flux and physiological response are controlled by stomatal conductance.

Figure 1


Max Conductance 1994
Stomatal conductance (mol m-2 s-1)
0.06
0.05
0.04
0.03
0.02
0.01
0.00
50
100
150
200
250
300
350
Day of Year

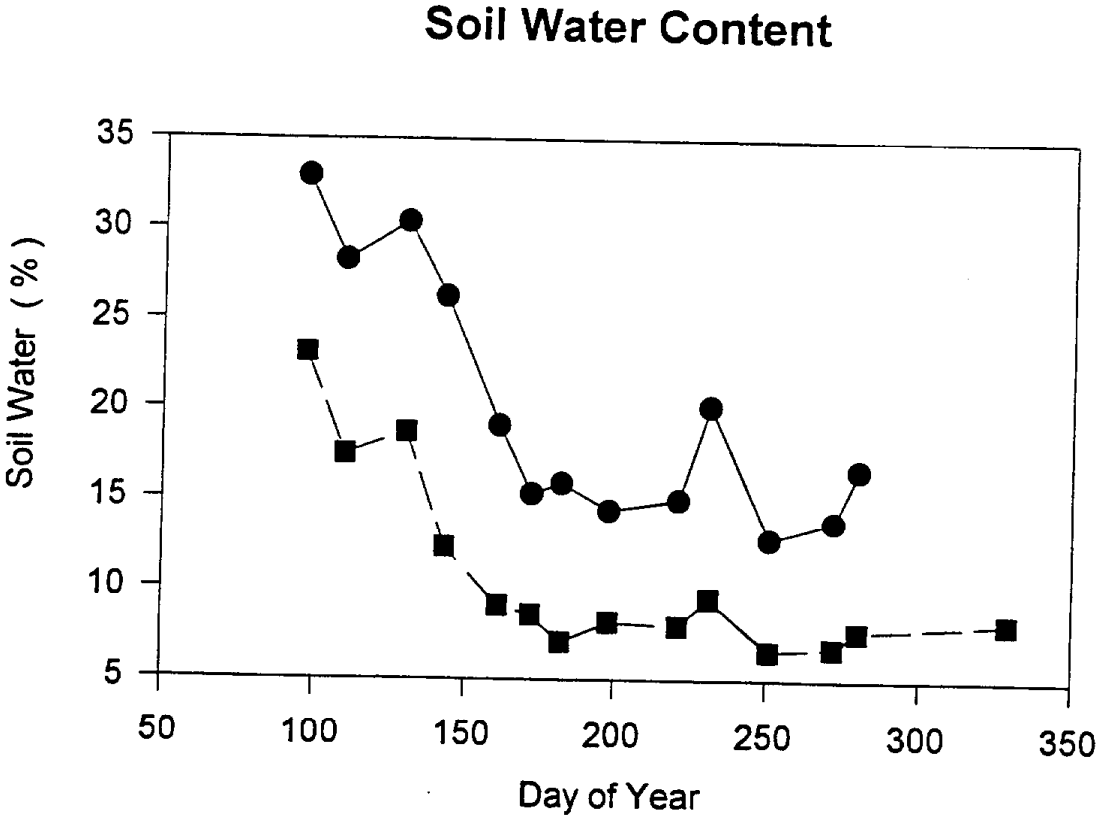
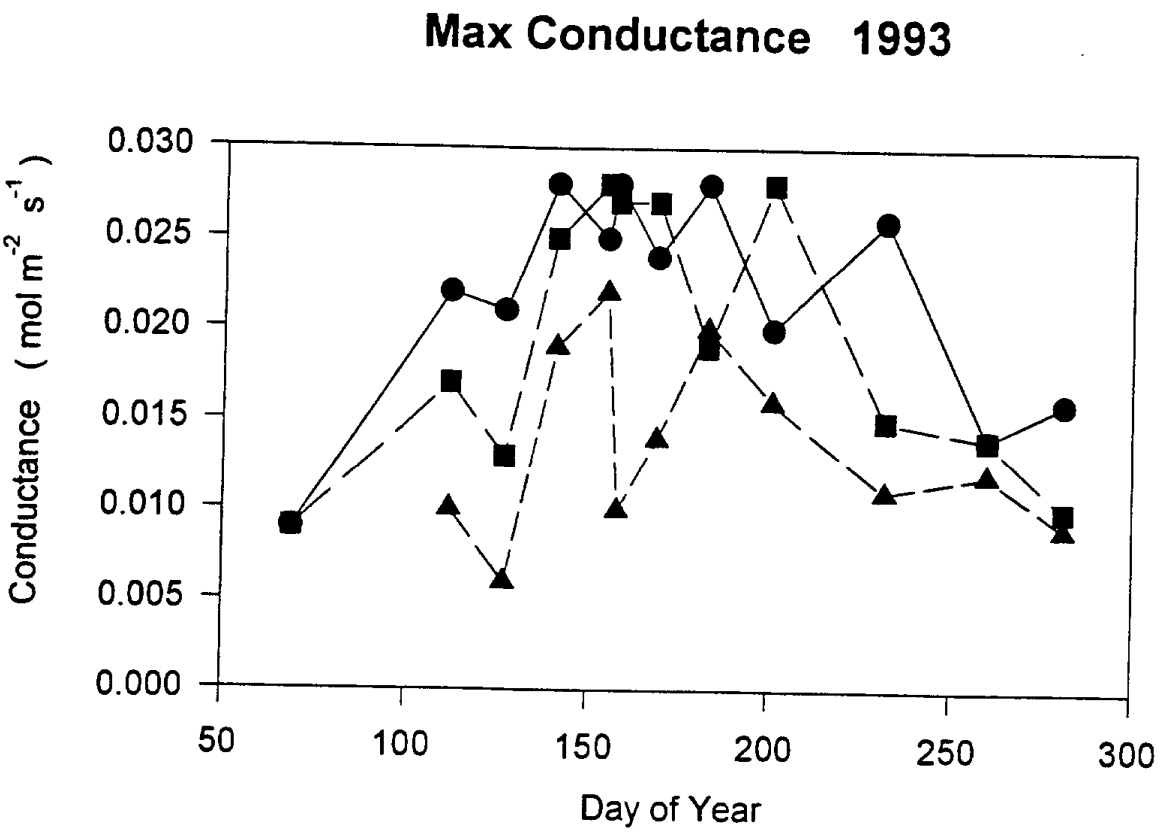

Soil Water Content
Soil Water (%)
35
30
25
20
15
10
5
50
100
150
200
250
300
350
Day of Year

Figure 2


Max Conductance 1993
Conductance (mol m-2 s-1)
0.030
0.025
0.020
0.015
0.010
0.005
0.000
50
100
150
200
250
300
Day of Year

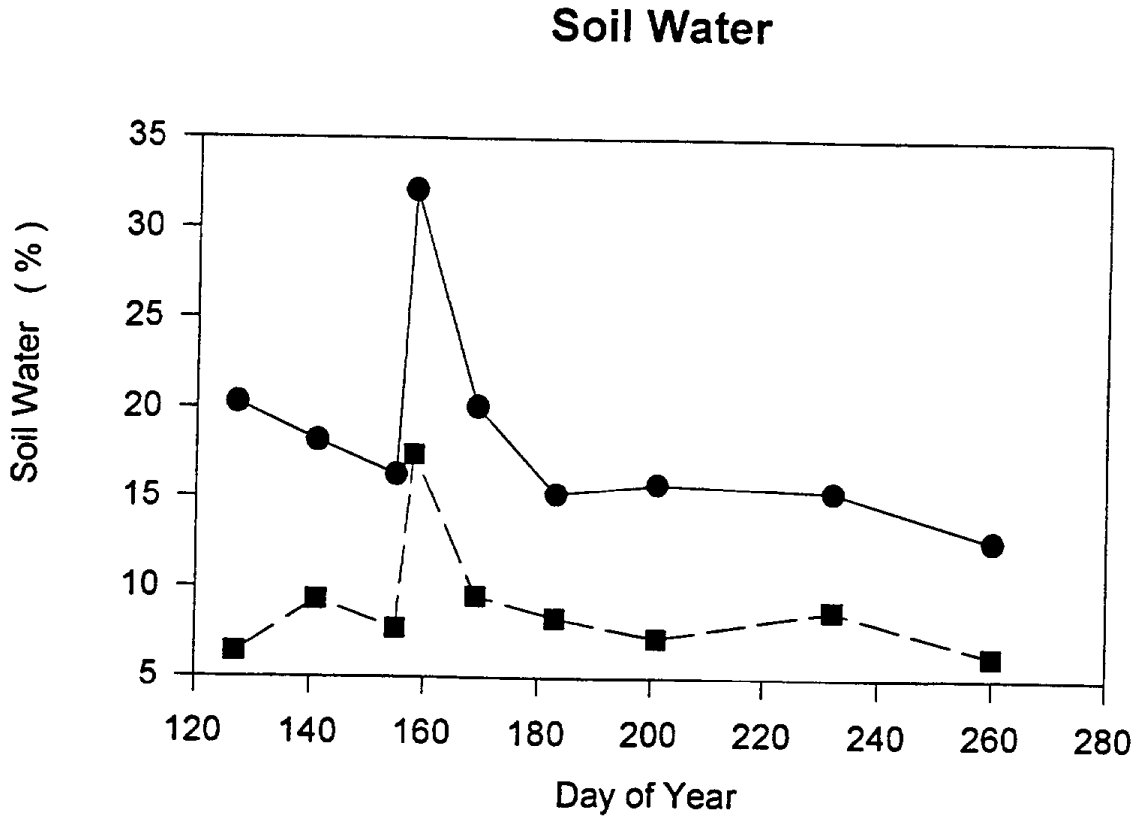
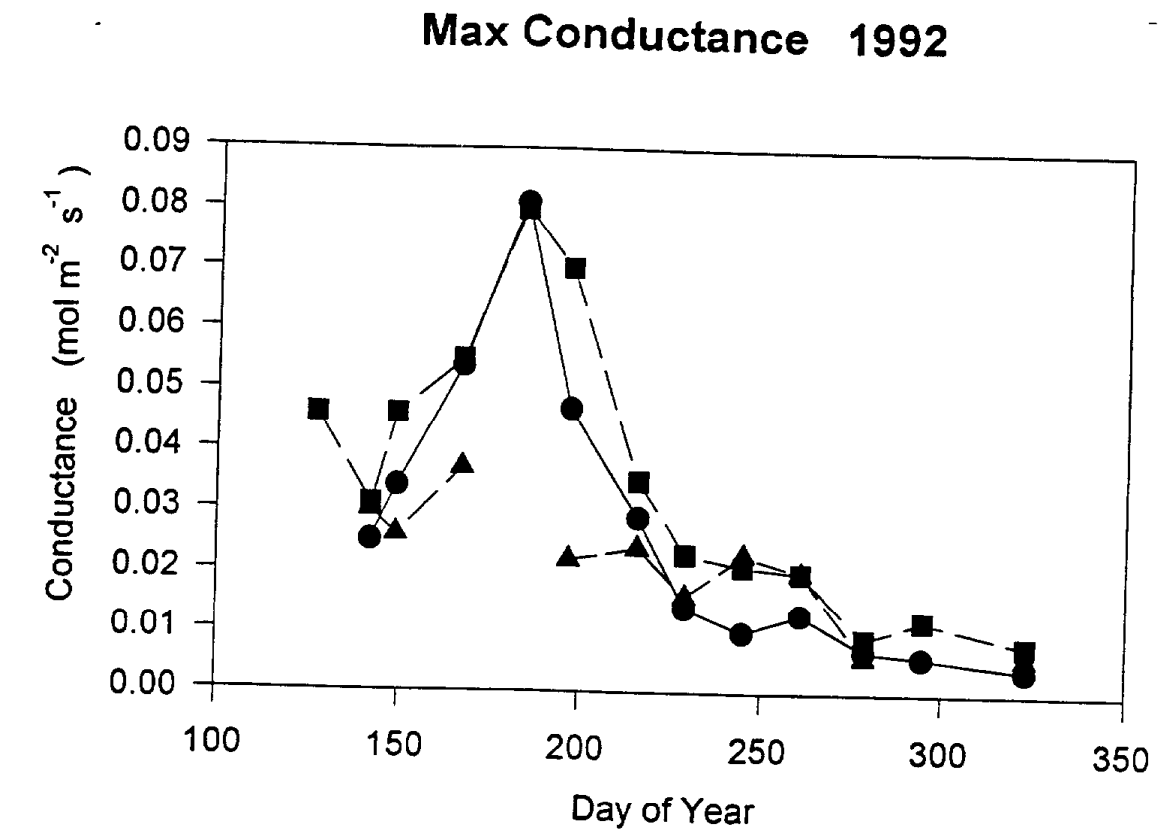
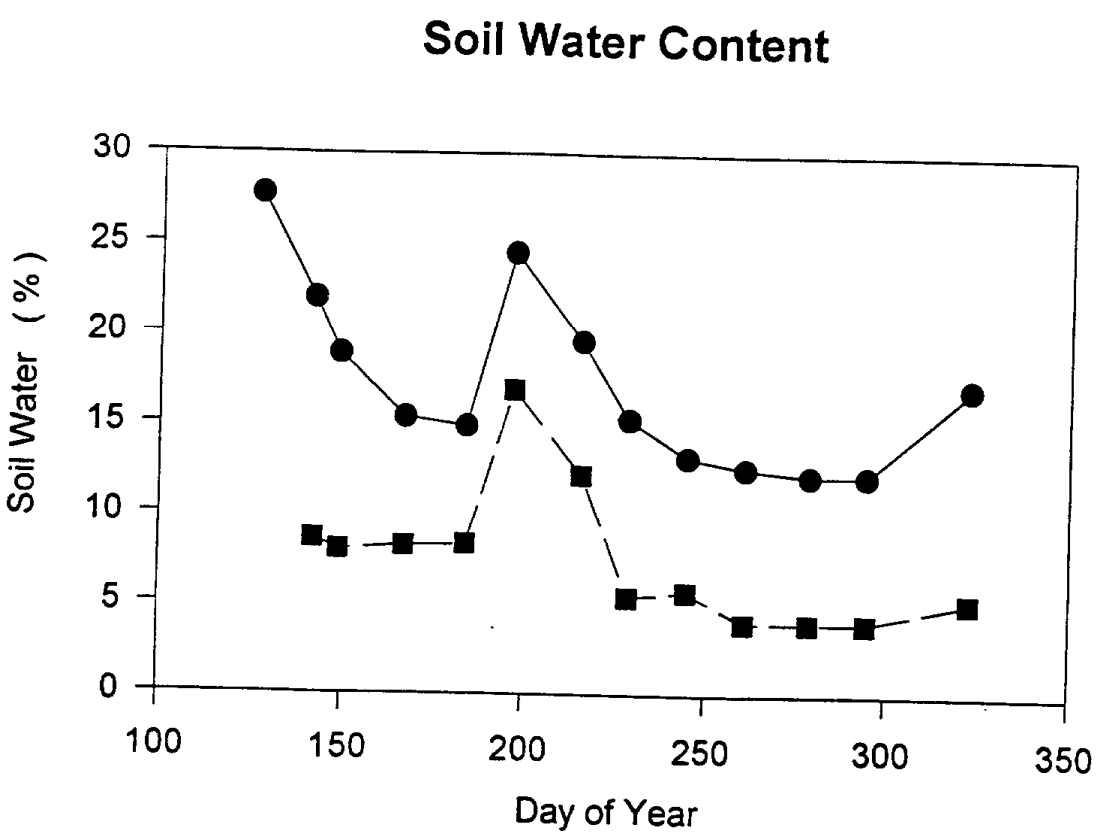

Soil Water
Soil Water (%)
35
30
25
20
15
10
5
120
140
160
180
200
220
240
260
280
Day of Year

Figure 3


Max Conductance 1992
Conductance (mol m-2 s-1)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
100
150
200
250
300
350
Day of Year


Soil Water Content
Soil Water (%)
30
25
20
15
10
5
0
100
150
200
250
300
350
Day of Year

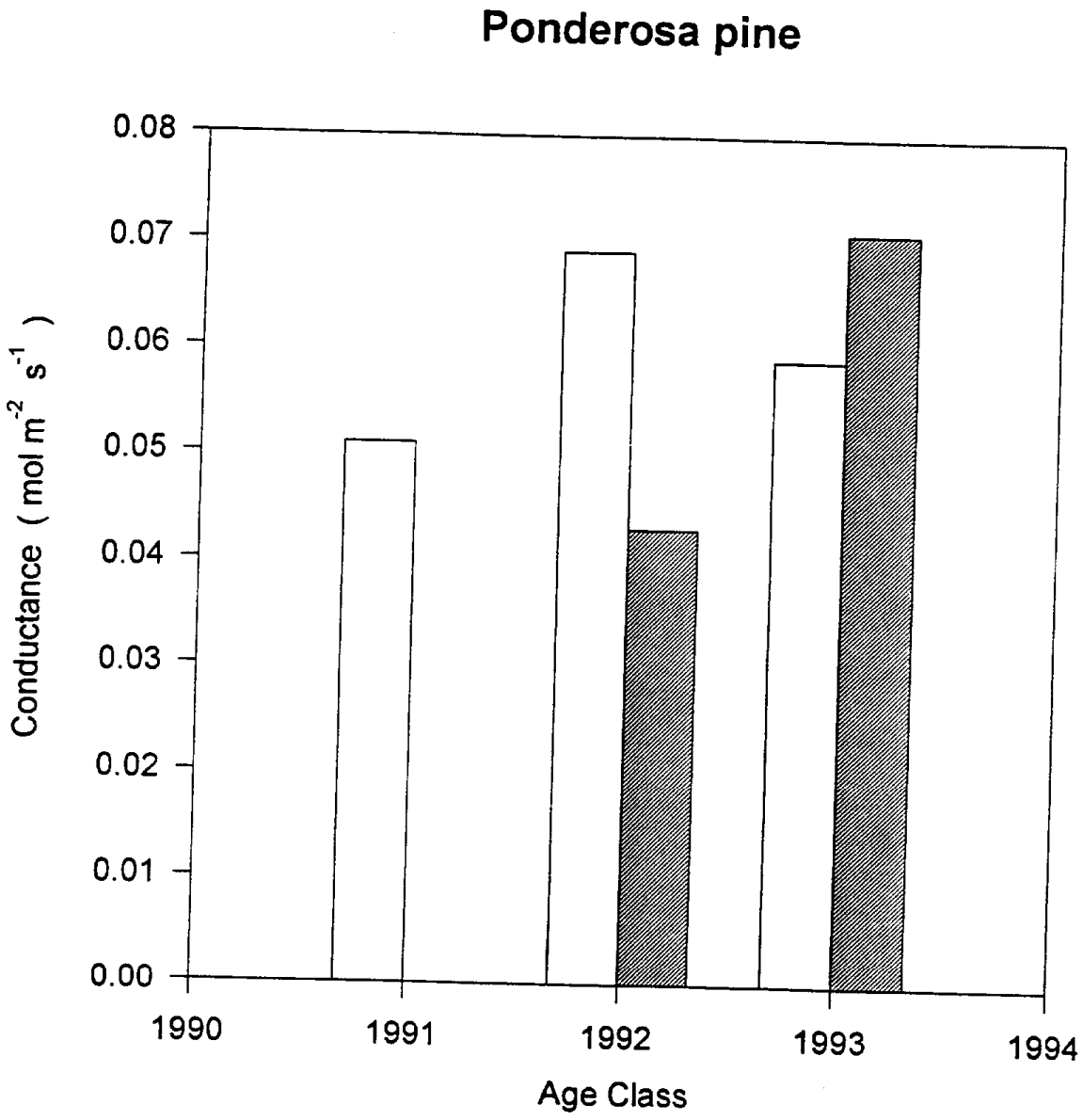

Ponderosa pine
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Conductance (mol m-2 s-1)
1990
1991
1992
1993
1994
Age Class

Figure 5

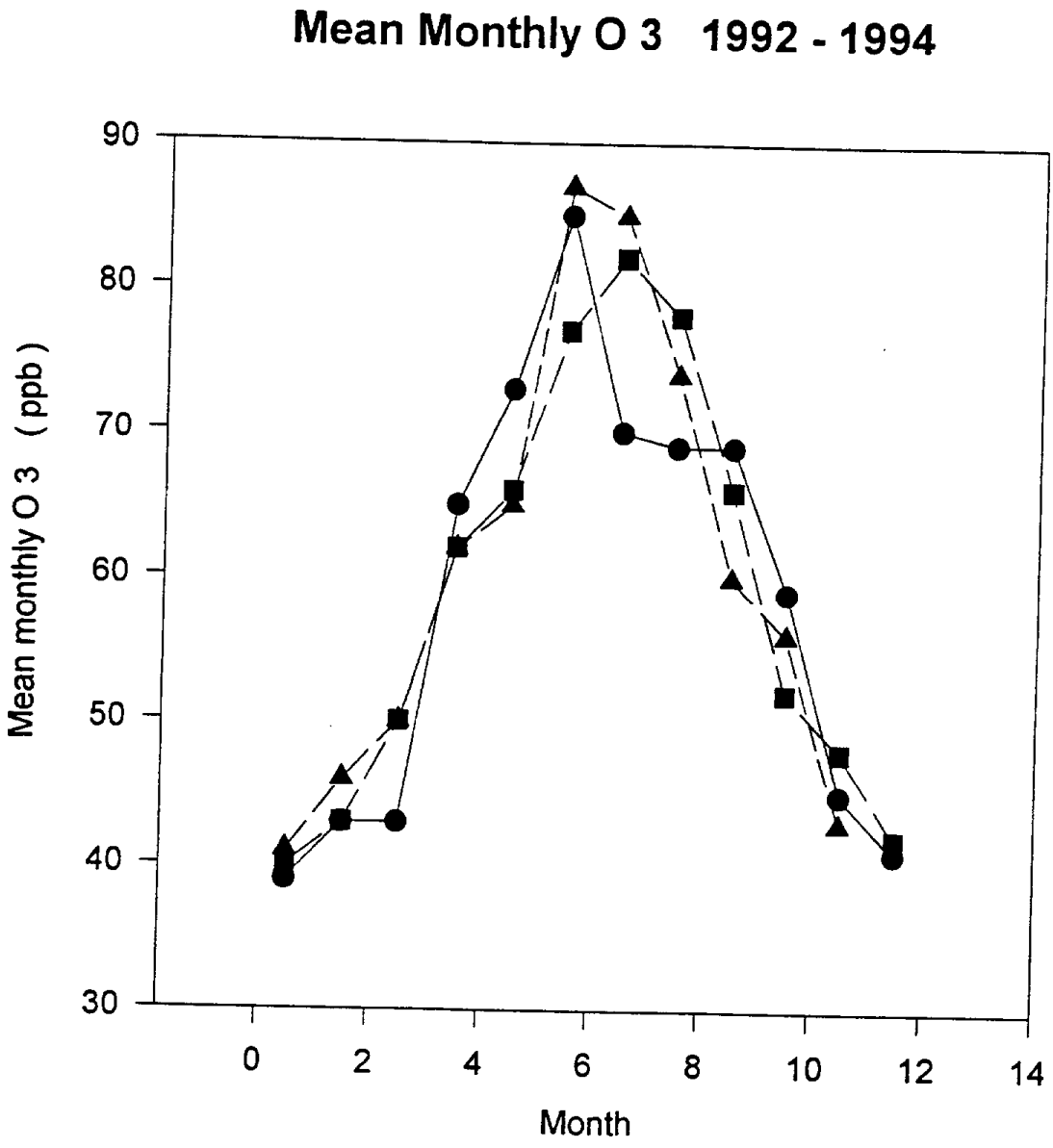

Mean Monthly O 3 1992 - 1994
Mean monthly O 3 (ppb)
90
80
70
60
50
40
30
0
2
4
6
8
10
12
14
Month

Figure 6

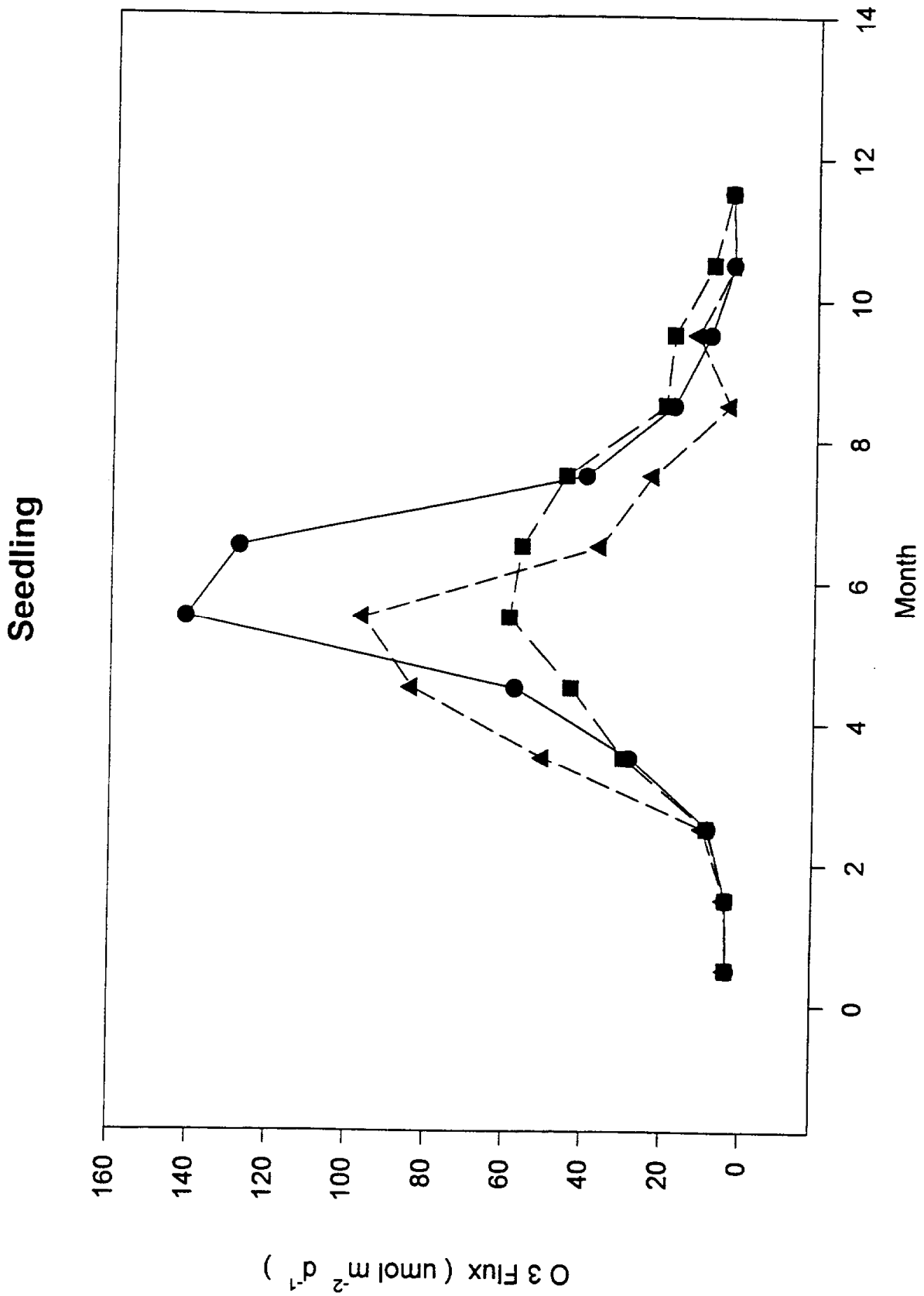

Seedling
O 3 Flux (umol m-2 d-1)
160
140
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
Month

Figure 7

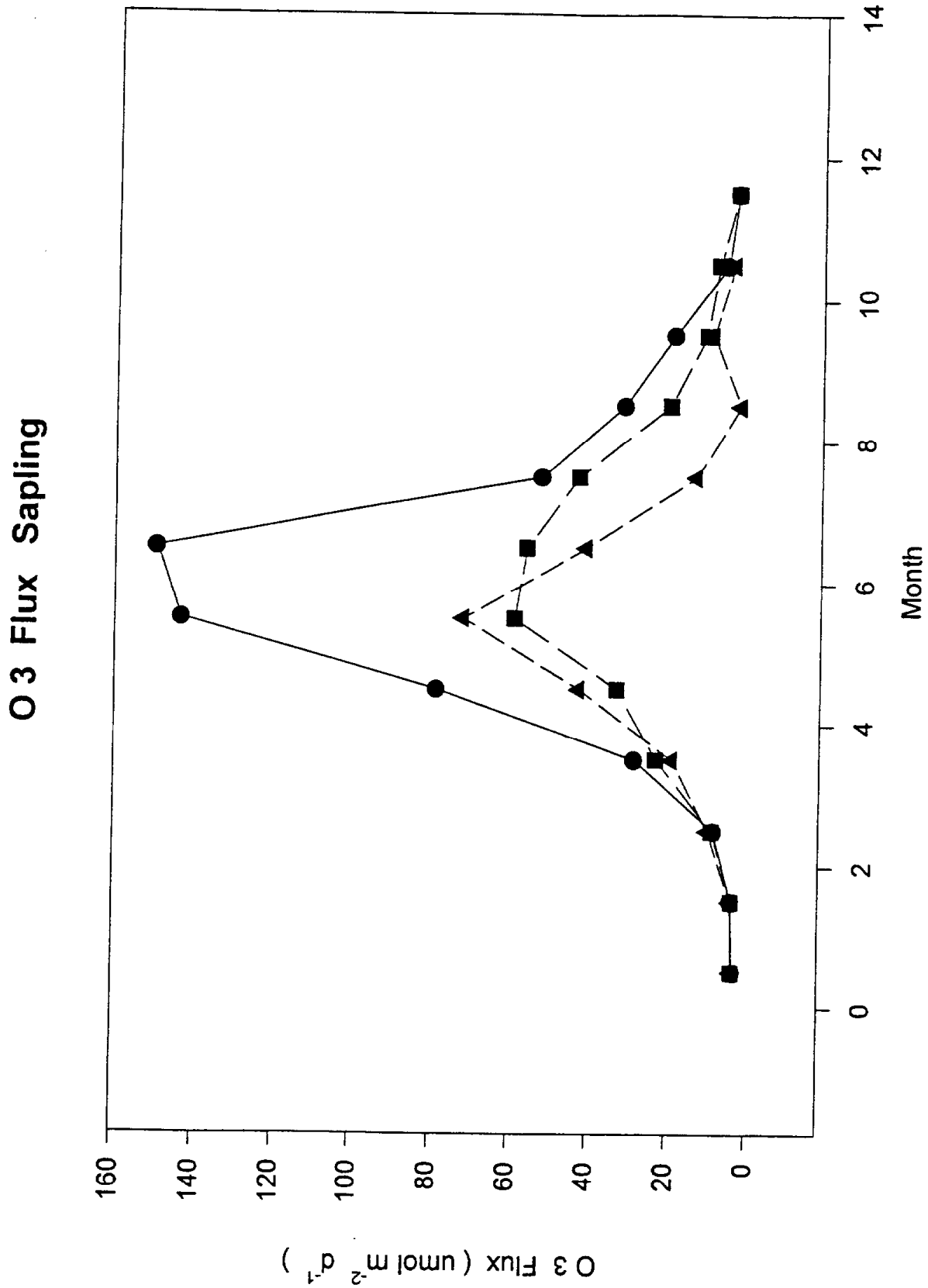

O 3 Flux Sapling
O 3 Flux (umol m-2 d-1)
160
140
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
Month

Figure 8

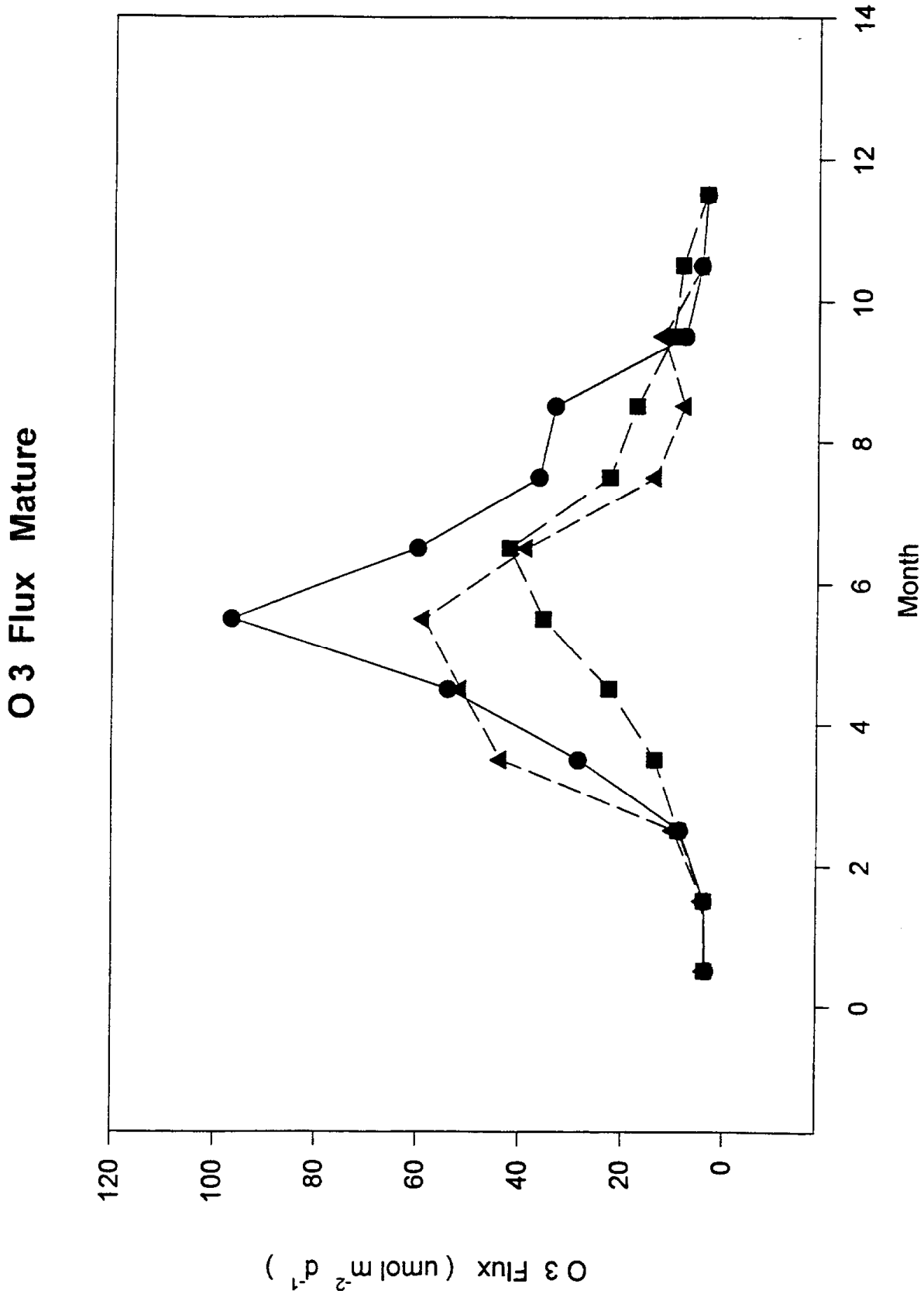
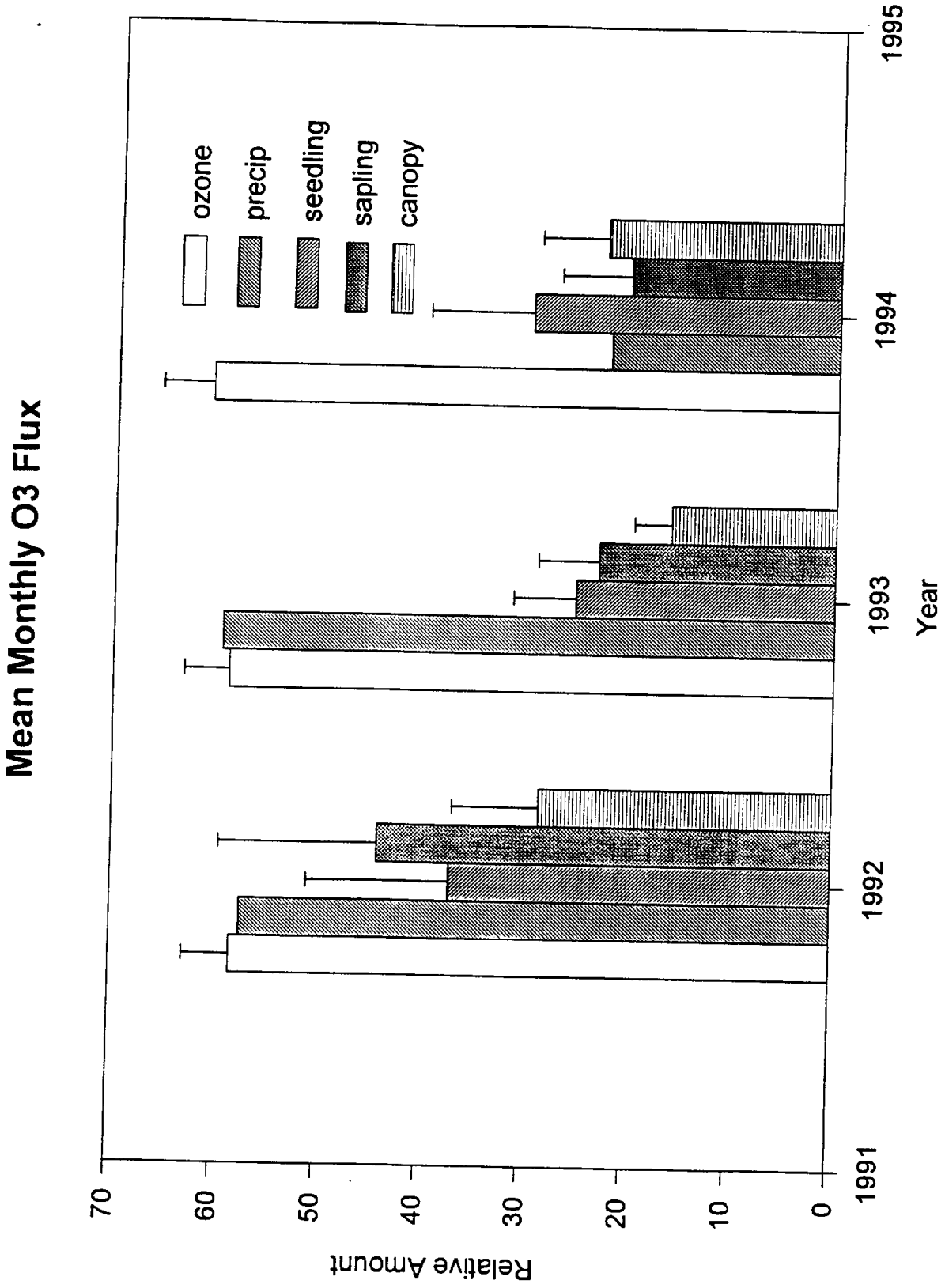

O 3 Flux Mature
O 3 Flux (umol m-2 d-1)
Month
0
20
40
60
80
100
120
0
2
4
6
8
10
12
14

Figure 9


Mean Monthly O3 Flux
ozone
precip
seedling
sapling
canopy
Relative Amount
0
10
20
30
40
50
60
70
1991
1992
1993
1994
1995
Year

CONCLUSIONS

* O3 flux variable across years

* O3 flux variable across tree age

* 60 - 70% of annual flux in May - July

* O3 flux is a function of annual ppt

* O3 flux also controlled by foliar dynamics

4. Air Pollution Impacts on Soil Biogeochemistry: Field Results and Modeling. Dr. Mark Poth, USDA Forest Service, and Dr. Dale Johnson, Desert Research Institute.

DR. MARK POTH: USDA Forest Service

I am going to present a summary of the ARB funded work by discussing the information we used to run the nutrient cycling model. Then I will evaluate some of our sites in the San Bernardino National Forest and the air pollution gradient there.

Figure 1 is an example of our data showing soil nitrogen content in relation to soil carbon at the Barton Flats site. Soil carbon is on the y axis, we have three soil horizons here, O_1, O_2, and the soil A horizon. The O_1 horizon is the litter that is deposited on the surface, the needle litter. The material at the O_2 horizon is starting to break down, and finally, the A horizon is the mineral horizon. We have the characteristic pattern of soil development here. There is a range of material input, and as you get mineralization and the breakdown, you approach some steady state that is defined by the overall slope. We needed a complete picture here, so we have also analyzed the trees. Figure 2 shows nutrient concentration relationships in fir needles. We found all combinations of plots for phosphorus, calcium, magnesium, potassium, nitrogen, carbon, and sulfur. Different sized circles were drawn for the age of the needles. For a fir tree that has several years of needles, the small dots would be the current year needles, and as they age, they would be represented by larger and larger dots. If we look at the relationship between calcium and magnesium in needles, we can see that calcium is very low in needles initially and as they age, they tend to build up calcium. You can also get a feel for some things that might make good index relationships. Many investigators like to look at nitrogen to phosphorus ratios, the idea is that we should always look at current year needles. However, if you look at nitrogen and phosphorus in Figure 2, it has a really good relationship if we throw out all the current year needles. We can use the needle data then to verify some of our assumptions about relationships. Figure 3 examines the relationship between percent of phosphorus and needle age. By comparing it to the litter data collected in a litter trap, we can verify some of our assumptions about use and allocation between years.

Figure 4 outlines characteristics of nitrogen saturated ecosystems compared to agricultural or other types of production oriented ecosystems wild land ecosystems evolved and developed under a climate where nitrogen inputs were very low. They developed to be nitrogen conservative; hence, with the change in the overall status of the atmosphere and the greater prevalence of nitrogen deposition, people are starting to worry about nitrogen saturation of ecosystems. What are the symptoms or characteristics of an N saturated ecosystem? What happens in a system that evolved under conditions in

which it received grams 2-3 kilos per hectare per year and now there is a input of 3, 4, 5, or 10 times that? Some of the hypothesized reactions would be that vegetation would no longer exhibit a positive growth response to fertilization. Available nitrogen is in excess of total demand within the system, and there would be sustained losses of nitrogen. The system, rather than conserving nitrogen as an evolved function, would become really leaky with lots of nitrogen leaving the system.

What are other kinds of things we can look for? Initially, we might see no discernible response or you might get a small fertilizer effect, you are enriching the system by removing some limitations (Fig. 5). You might get some altered phenology or physiology. There is a potential for soil acidification, decrease in mycorrhizal association with the fine roots. This is a complex symbiosis related to a partnership trading carbon for nutrient availability. If there are lots of nutrients available, we do not need that mycorrhizal partner. Nutrient ratios increase nitrate and cation leaching from soil and enhance nitrogen trace gas emissions. You end up with a situation (Fig. 6) in which there is excess nitrate in soil solution or stream water and a greater drought stress. You have added some nitrogen, you have lost those mycorrhizal partners, and you may be then set up for more drought stress. You will see an altered plant microbial community composition. The base factor has changed so you have changed the interrelationships within the ecosystem. You probably changed the susceptibility to pests and disease. One of the things that we know from crops and from fertilized forest systems is that insects really love plant tissue enriched with a lot of nitrogen. Finally, you may have problems with eutrophication of lakes.

We have looked at nitrate concentrations in the soil solution collected by the centrifuge method at two of the plots near Barton Flats, at the Camp Paivika site (which is on the more exposed west end of the San Bernardino mountains), and at Heart bar which is a relatively sheltered or low pollution site (Fig. 7). The grey is the deeper soil solution, and the black is the surface soil solution. Certainly, we have a difference between Barton Flats and our supposed high pollution site. During our intensive study in 1992, we looked at nitric oxide flux from the soil using a "closed box technique" (Fig. 8). This was all done during the summer when the soils are relatively dry. We were able to see at Camp Paivika, the high pollution site, substantial rates of nitric oxide flux. Flux from the soil at Barton Flats was slightly elevated. If we remove the water limitation from this biological process, we would see rates that are very respectable, rates typical in some cases of the situation for fertilized agriculture.

Finally, Figure 9 shows historical trends in soil pH in response to all this nitrogen input, and certainly at some of these sites we can see respectable drops in pH between the data that we have from 1975 and the current condition. To sum up our evidence for nitrogen saturation at these high pollution sites, we have a good collection of circumstantial evidence suggesting that at the high pollution sites, we may be reaching nitrogen saturation. In conclusion (Fig. 10 and 11), we have a data set that we can now use in a model to examine the variables that are going to be important as we approach nitrogen saturation.

These data indicate we may be achieving N saturation in some of these forests. We need to think about some of the long term consequences if this, such as problems with water quality. If we are already seeing this in the Los Angeles basin and the lower part of the state, what does this indicate about the situation in the Sierra Nevada? What does this mean for overall forest health? How do you determine overall forest health? A couple of the indications here can lead to diagnosis of adverse forest health. Perhaps lower rates of the tree death may occur if it were not for the nitrogen deposition inhibiting the mycorrhizae and hurting the tree nutrition, thus making it more susceptible to the drought year. There are a lot of "what if's" in that, but perhaps a little more effort on tree epidemiology would be useful.

Q (AUDIENCE) I take it that the next step is to study biologic consequences of N saturation. That is, what are the expected kinds of consequences that we would look as end point biological characters if this system becomes N saturated?

A (DR. POTH) Dale is going to address using the models to look at that. The nutrient cycling looks at a part of that process, but certainly there is the whole biological community with conditions changed to favor different species mixes. Are we going to have a lot of species changes and have a lot of trees dying? What about fire danger? We tend to blame it all on drought years, but we may be really compounding the problem with nitrogen saturation. How would we know that?

Q (AUDIENCE) You have shown some plots, specifically changes in nitric oxide flux, nitrogen, soil solution, and soil pH. The common complaint I have with any talk of this sort is changes mean nothing unless I have some feel of what the change means. Is it good, bad, or indifferent? Because something changes, it does not necessarily mean a thing in terms of the overall situation. Maybe I should not direct this question to you; maybe Dale will pick it up. I think when you show us a change, you ought to tell us if this is an important change. Other than a 20% change in soil saturation for example, that may or may not mean a thing. I do not know, and that is why I feel frustrated when I hear talks of this sort. I do not mean to criticize; I am just talking in general. I want to know what is the importance of what is being shown. The fact that we see numbers, and changes in numbers does not mean anything unless we get some feel of the importance of it. I am not so sure if that is a question or just a general comment or frustration.

A (DR. POTH) Your comment is one that I have commonly hear at presentations, and it means I have failed on the important question which is: so what! So what if the nitric oxide flux is higher? It is a very strong diagnostic symptom for excess nitrogen and probably means that we are in a saturated state.

Q (AUDIENCE) Is there a time interval over which we are proceeding toward nitrogen saturation. Do we have a long way to go?

A (DR. POTH) It probably means that we are there, but it is a lot of work to get all these

data. The way that you would show nitrogen saturation is through a large collection of circumstantial evidence, and it is a question of how much circumstantial evidence will it take before you commit to that conclusion. We can present a lot of different pieces, but where is the smoking gun?

Q (AUDIENCE) Is the smoking gun anthropological stressors? I am not totally clear what the percentage of change would be relative to the whole system, and what you would attribute to anthropological stresses in terms of soil nitrate.

A (DR. POTH) How much of this is just the natural variation in the system?

Q (AUDIENCE) Yes, how about a forest that is pristine? 50 years ago would it have done the same thing?

A (DR. POTH) Part of that is what Dale will address, and you can examine those kinds of things with a model. Things like soil acidification and pH changes are a natural part of weather variation. The question is whether we are accelerating it beyond what we need. That is what Dale will talk about.

Q (DR. TAYLOR) I have just one comment. If you scale up your NO measurements, they exactly account for the difference between Andrzej's estimate of nitrogen deposition and my estimate. As you know, I propose there was a loss of N. It is uncanny, but right on the button, although I realize that it is a point estimate.

(DR. POTH) My method measures direct flux from the soil, and we do not know how much is reabsorbed by the vegetation.

Figure 1

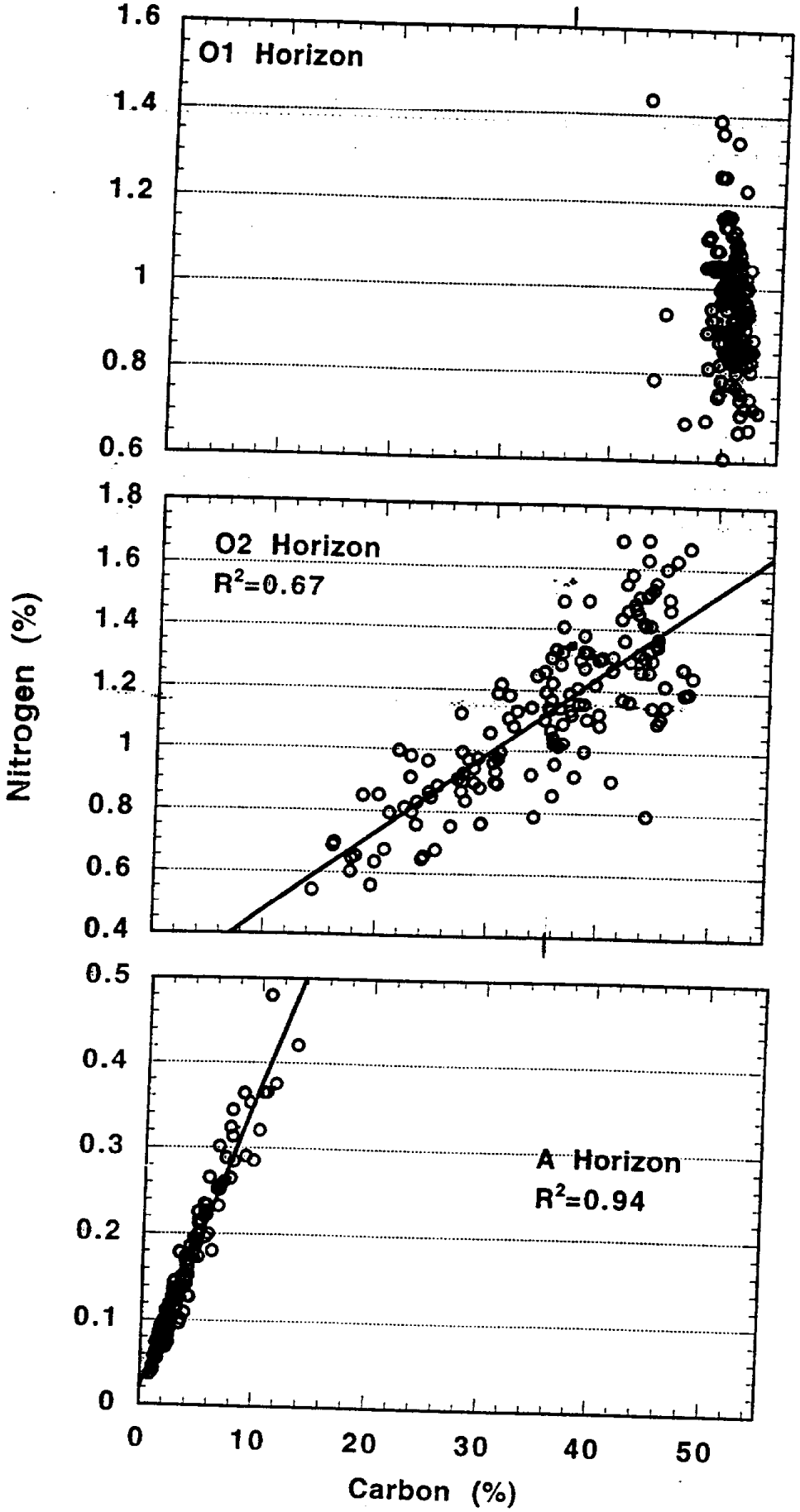
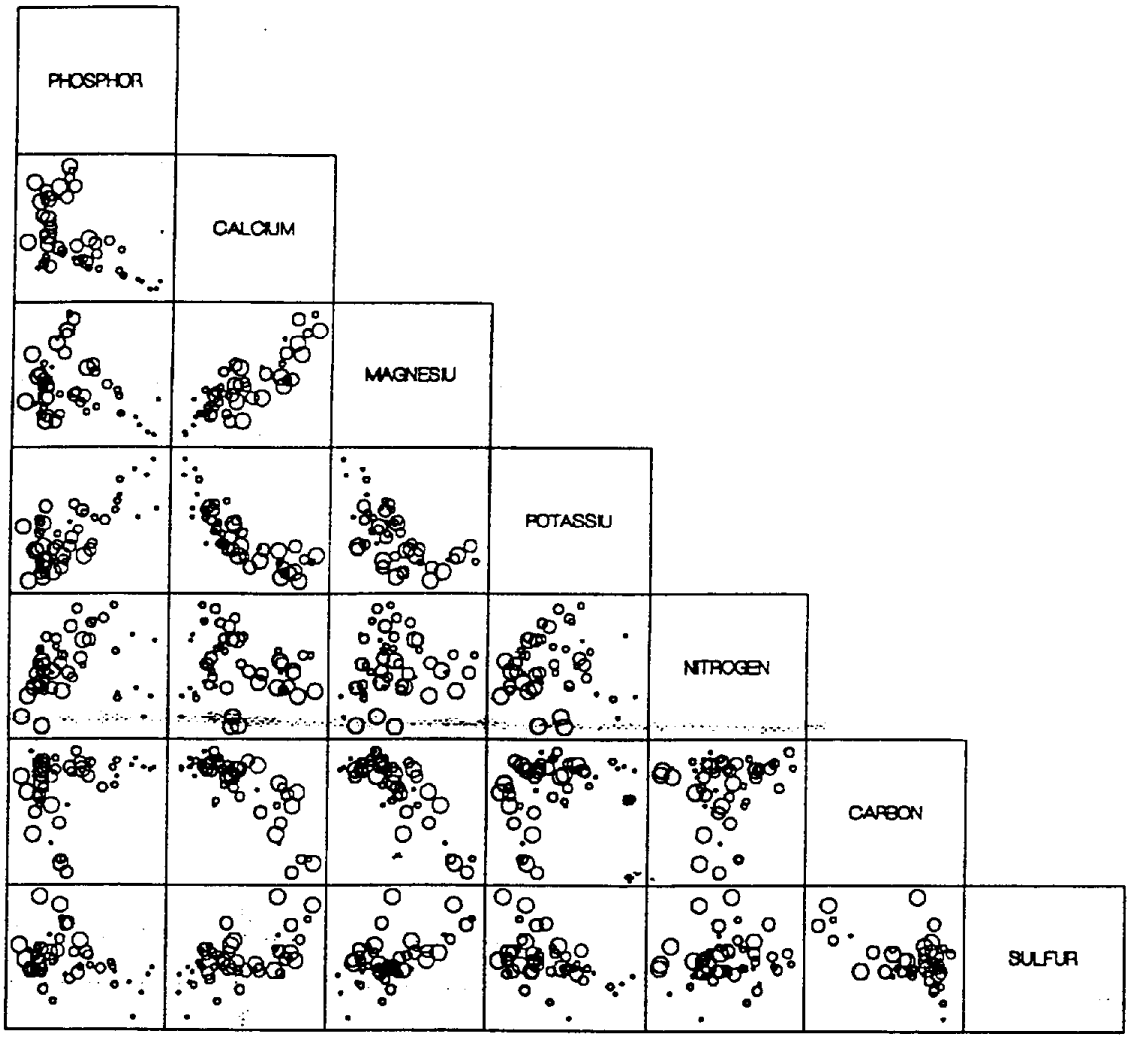

O1 Horizon
O2 Horizon
R^2=0.67
A Horizon
R^2=0.94
Nitrogen (%)
Carbon (%)
1.6
1.4
1.2
1
0.8
0.6
1.8
0.4
0.5
0.3
0.2
0.1
0
10
20
30
40
50

Figure 2



FOR NEEDLES BY AGE

Figure 3

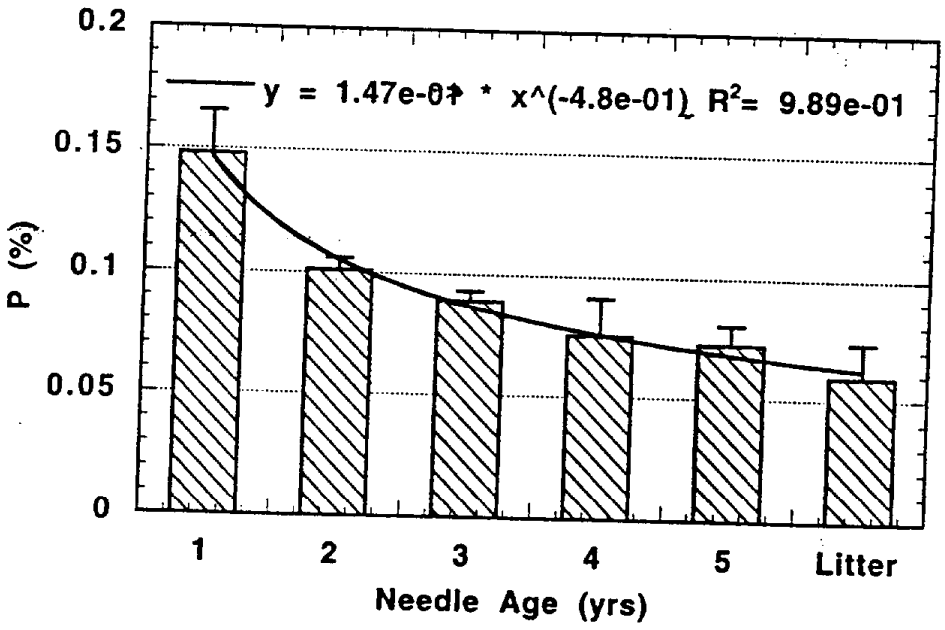

y = 1.47e-01 * x^(-4.8e-01) R²= 9.89e-01
0.2
0.15
0.1
0.05
0
P (%)
1
2
3
4
5
Litter
Needle Age (yrs)

Figure 4

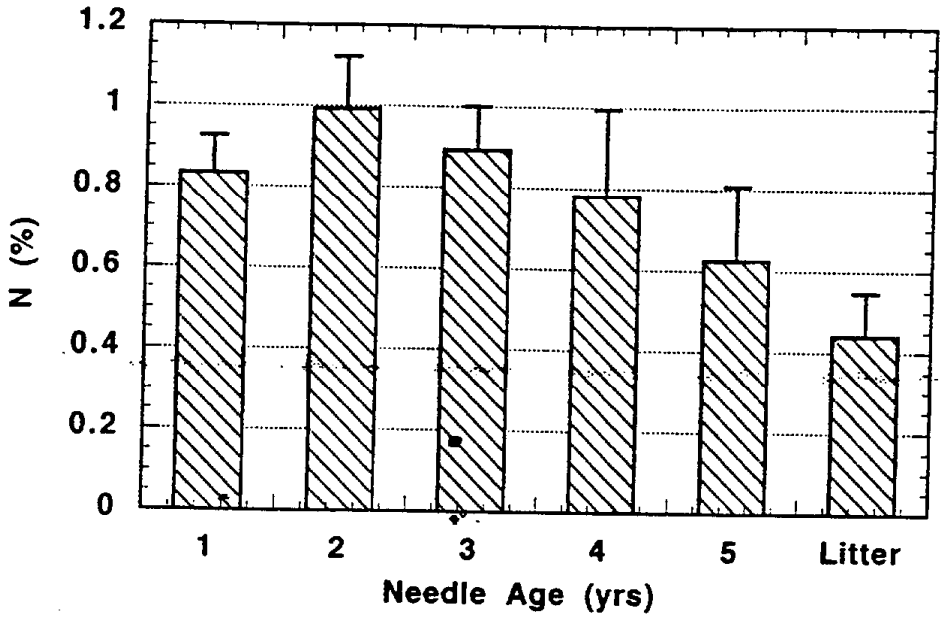


Figure 5

Nitrogen saturation of ecosystems
A readily available nitrogen supply in excess of total plant and microbial nutrient demand
Sustained nitrogen losses approximate or exceed nitrogen inputs--the nitrogen retention capacity of the system has been exceeded.

Figure 6

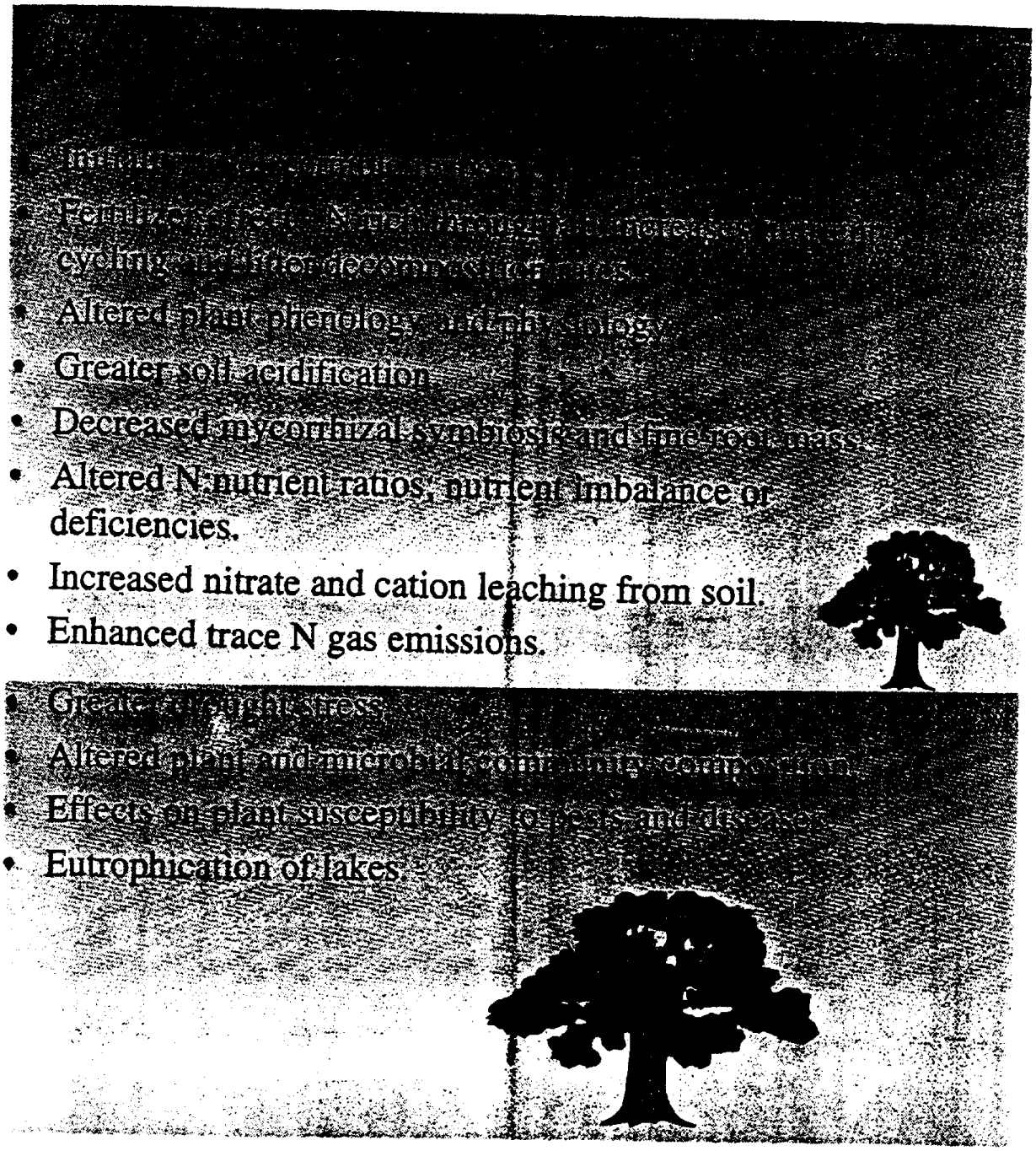

Fertilization effect. Stimulates plant growth, increases nutrient cycling, and litter decomposition rates.
Altered plant phenology and physiology.
Greater soil acidification.
Decreased mycorrhizal symbiosis and fine root mass.
Altered N nutrient ratios, nutrient imbalance or deficiencies.
Increased nitrate and cation leaching from soil.
Enhanced trace N gas emissions.
Greater drought stress.
Altered plant and microbial community composition.
Effects on plant susceptibility to pests and disease.
Eutrophication of lakes.

Figure 7

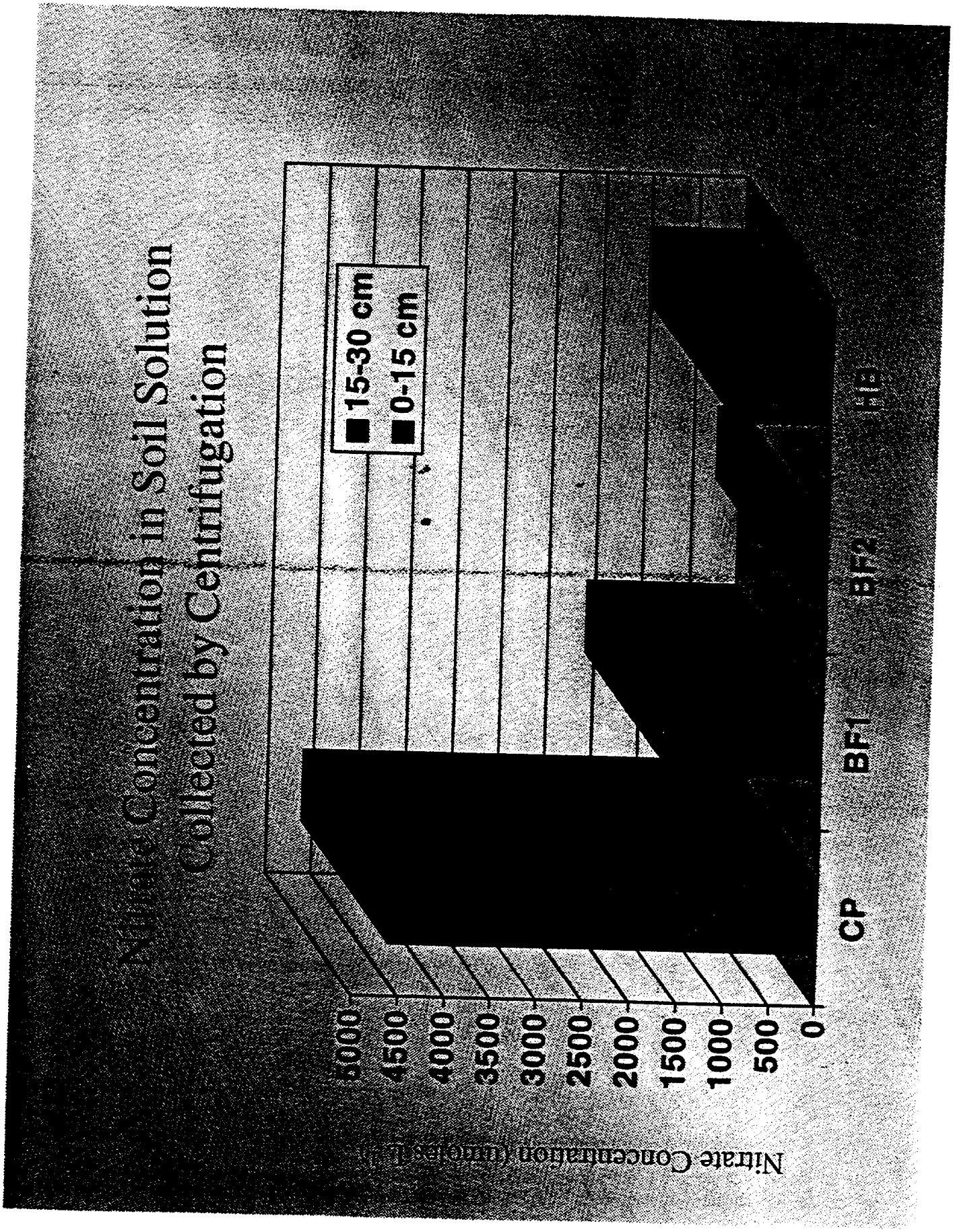

Nitrate Concentration in Soil Solution
Collected by Centrifugation
Nitrate Concentration (micromoles/L)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
15-30 cm
0-15 cm
CP
BF1
BF2
HB

Figure 8

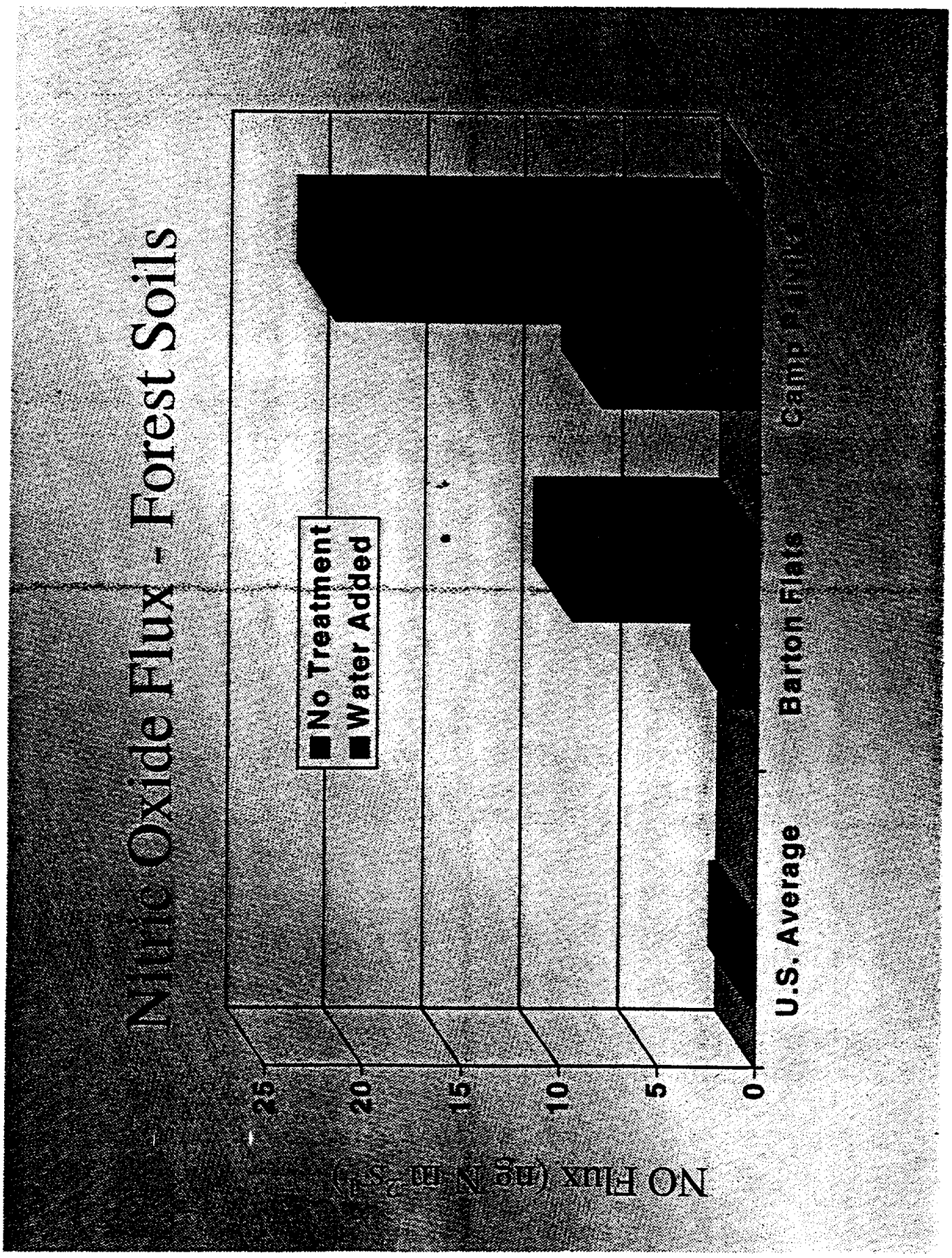

Nitric Oxide Flux - Forest Soils
No Treatment
Water Added
25
20
15
10
5
0
U.S. Average
Barton Flats
Camp 4

Figure 9

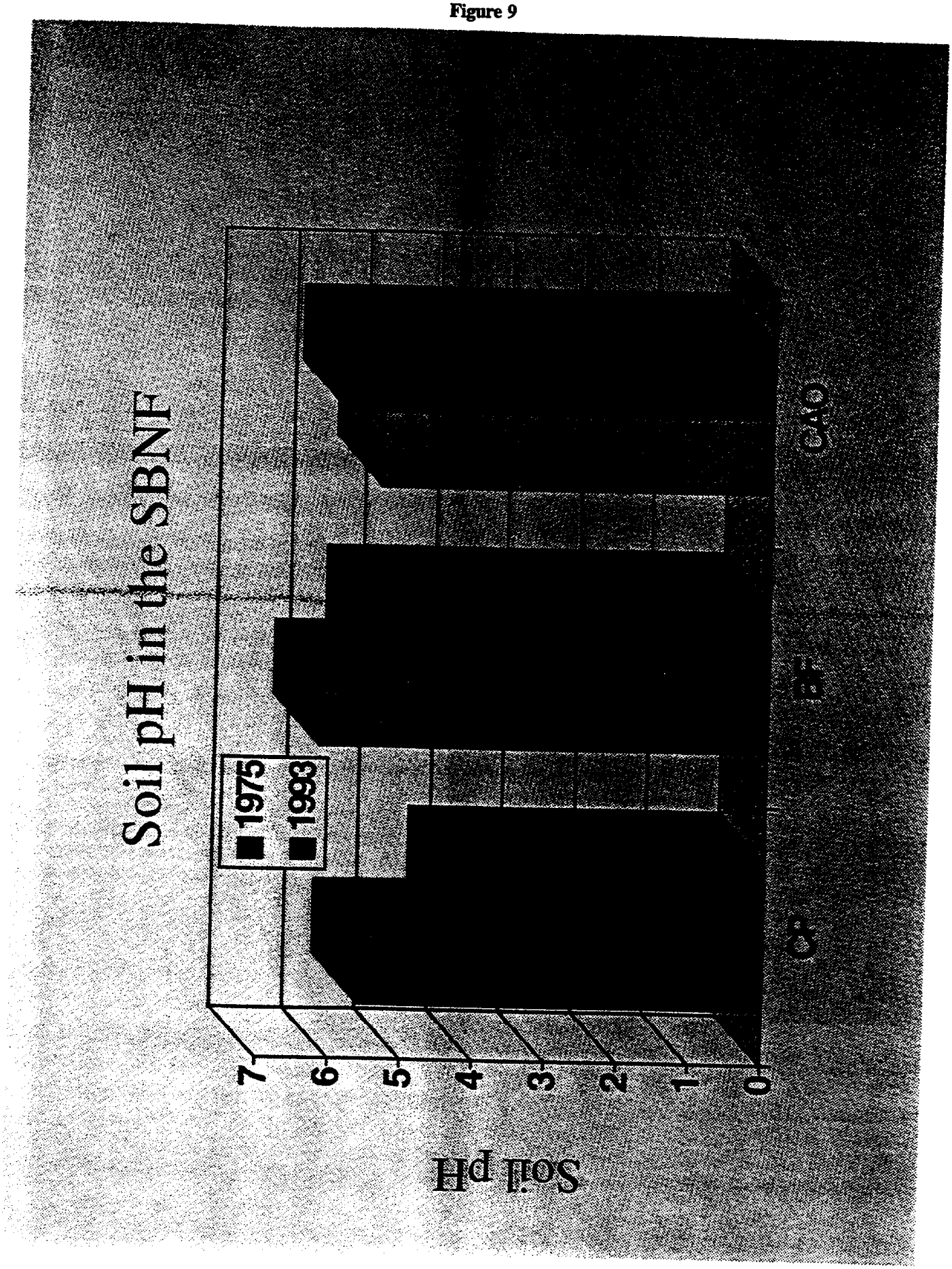


Figure 10

Summary of evidence on N limitation in the Pollution Mountains
Enhanced litter decomposition rates in high deposition sites.
Litter decomposition at CP is not N limited.
Greater soil acidity in high-pollution sites compared to low-pollution sites. Increasing soil acidity (from pH 5.6 to 4.3) during the last 20 years.
Lower soil C:N ratios and decreasing C:N ratios in the high-pollutions sites during the last 20 years.

Figure 11

Summary: Evidence for Nitrogen Limitation in the Pollution-Affected Coniferous Forests of Southern California
High foliar N concentrations in soil, foliage and litter, and high nitrate concentrations in soil solution
High foliar N:P ratios and low C:N ratios.
Nitrate concentrations in soil solution 10-40 times greater than in low-pollution sites.
Nitrogen fertilization significantly reduced foliar growth in ponderosa pine at a high-pollution site near Crestline, CA.
Elevated nitric oxide emissions from soil.

Air Pollution Impacts on Biogeochemistry: Field Results

- Baseline data defining the current forest status in the San Bernardino Mountains
- Evaluation of several sites in the San Bernardino Mountains along the air pollution gradient; testing for N saturation

Figure 12

Figure 13

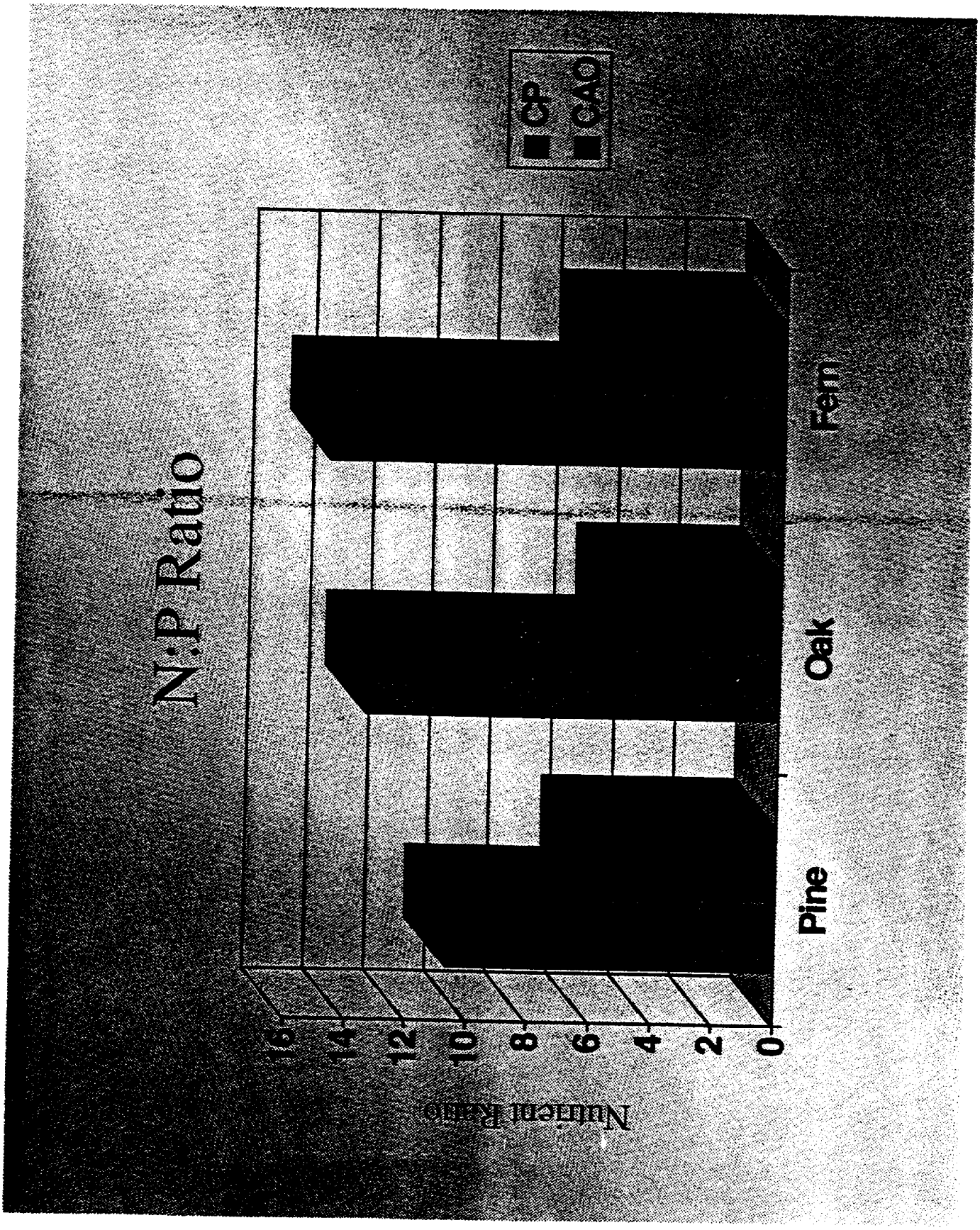
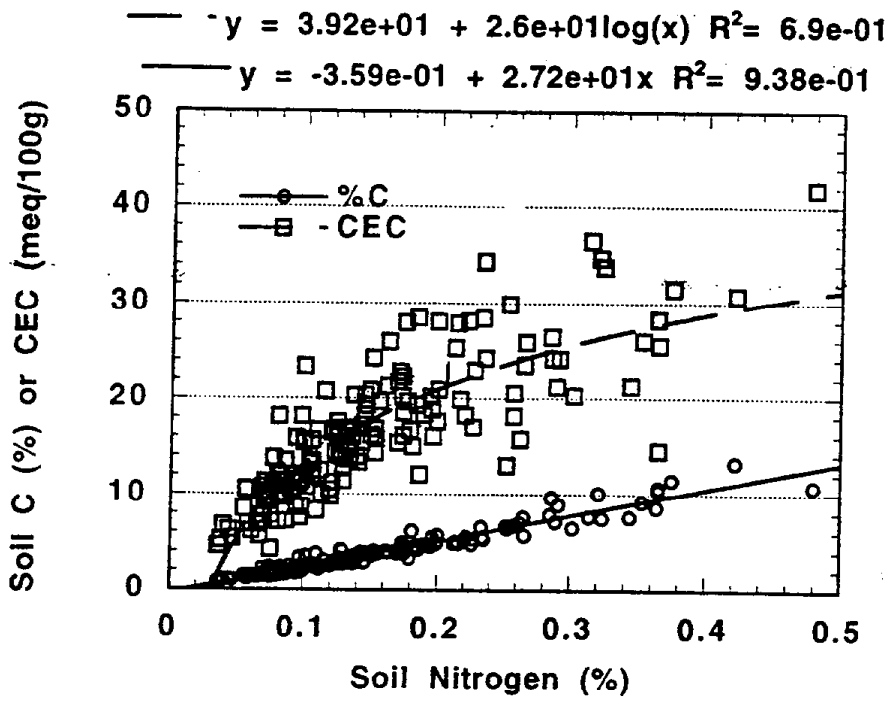


Figure 14


y = 3.92e+01 + 2.6e+01log(x) R²= 6.9e-01
y = -3.59e-01 + 2.72e+01x R²= 9.38e-01
%C
CEC
Soil C (%) or CEC (meq/100g)
Soil Nitrogen (%)
0
10
20
30
40
50
0
0.1
0.2
0.3
0.4
0.5

Summary of the Presentation: AAPP Workshop, 26 January 1995

Ecological Effects of Deposition: Case Studies -- Defining the Baseline (Forest Biogeochemistry)

Dr. Mark Poth

USDA, Forest Service, Pacific Southwest Research Station, Riverside, CA

Part of assessing forest condition is to carefully document current conditions. We have completed a detailed characterization of soils properties and plant nutrient status that can serve as a baseline for future reference. In addition we can also draw some conclusions about the susceptibility of these forests to acid (particularly N) deposition. We have analyzed stem, weed, litter, leaf and needle samples from ponderosa pine *(Pinus ponderosa Laws.)*, black oak *(Quercus kelloggii)* and white fir *(Abies concolor)*. We also collected and analyzed combined samples of roots. All tissues were tested for concentrations of N, P, S, Ca, Mg, K, Mn and Zn. No nutrient deficiencies are apparent. Nutrient concentrations were not normally distributed except for K.

Soils at the Barton Flats are relatively young. This is reflected in the relatively low clay content and the absence of significant clay movement (no argillic horizon) and the high base saturation of the exchange complex. Previous classification of the soils in this area included the finding of clay translocation and hence the presence of an argillic horizon. Based on our measured soil characteristics, these soils are insensitive to short-term pH influences associated with acid deposition. This is a result of the high base saturation and abundance of weatherable minerals in these soils. Hence, acute effects of acid deposition like aluminum toxicity should not be a problem.

Forests have evolved under conditions that are typically N-limited. This is evidenced by the response of most forests to N fertilizers. There is not an unlimited response to N additions. Hence, chronic deposition of N can produce N-saturation. Given the relatively young nature of these soils (relatively coarse texture, low clay content and low cation exchange capacity), the total capacity of the soil to immobilize continued N deposition will have limits. One good indicator of the change in N loading in these soils will be C:N ratio.

Chronic deposition of N has occurred in the Los Angeles Basin for at least the last 40 years. Elevated stream water NO_3^- concentrations have recently been reported for chaparral watersheds exposed to chronic N deposition in the San Gabriel mountains near Los Angeles. The high N losses from these chaparral ecosystems is an indication of N-saturation. A number of nutritional parameters across spatial and temporal gradients in the San Bernardino mountains support the hypothesis that the mixed conifer forest in the highly exposed western

end of the range is also N-saturated. Concentrations of NO_3^- in the soil solution and in soil extracts were 12 to 45 times higher at Camp Paivika (CP), a western high N deposition site, than at Camp Osceola (CAO, an eastern low-pollution site) during the summer months. Accumulation of NO_3^- in foliage of bracken fern and overstory species was also much greater at CP than at CAO. Nitric oxide (NO) fluxes during the summer from relatively dry soil at CP were approximately 20 times higher than for typical forests in North America. Nitrous oxide (N_2O) emissions, on the other hand, were low in the San Bernardino mountain sites. However, emissions of NO and N_2O were several-fold higher at CP than at Barton Flats, a relatively low-pollution site. Additional indicators of N enrichment at CP compared to the low N deposition sites include: low C:N ratios in soil and foliage, high foliar N:P ratios, and high soil acidity. From 1975 to 1994, soil pH decreased from ca. 5.8 to 4.0 near CP, and the soil C:N ratio at CP decreased from 22 to 18. At CAO soil pH (5.4 in 1975 and 5.3 in 1994) and C:N ratios (26.8 in 1975 and 25.9 in 1994) were relatively unchanged during the same time period. In summary, high NO emissions and elevated NO_3^- concentrations in the soil solution and in foliage at CP, indicate N in excess of biotic demand, with potential above-normal loss of N from the ecosystem -- and thus, a N-saturated condition.