DR. DALE JOHNSON: **Desert Research Institute**

Before I describe the modeling effort, I want to show a couple of figures on studies that are just under way near Reno that are an interesting comparison to Barton Flats. I would also like to acknowledge my colleagues Randy Dahlgren, Virginia Boucher, and Andrzej Bytnerowicz.

These sites are located near Reno. One of them is Little Valley just over from Lake Tahoe and one is near Truckee, California. In this case, the issue was of pollution of pristine waters by nitrate. Many researchers find nitrate increases during snow melt in stream waters. Goldman has been studying Lake Tahoe for 29 years now and he is finding that the lake is gradually becoming eutrophic. The secchi depth (a measure of water clarity) is decreasing, primarily because of nitrate deposition and that was the justification for this particular set of studies. I want to show you that we have high nitrate going through the system at Sagehen and we do not really know why. I have been trying to attract any collaborators and money to find out more about it.

Concentrations of nitrate in snow melt are shown in Appendix 3, Figure 4. We put collectors that collect snow melt as it naturally would melt into the soil. These levels were pretty high, 100 micromoles per liter, which is something like you see in the Great Smokey Mountains of North Carolina. It is one thing to see nitrate in snow melt, but to see it in soil solution (Appendix 3, Figure 5) where there should be some uptake of this available nitrogen is surprising. In fact, from March through May we saw 100 microequivalents in soil solution. I think there is a temporal uncoupling of nitrate release from the snowpack, probably due to the distillation effect, that concentrates the ions in the melt water. It may be due to sublimation of the snow too, in that particular year. That is just a teaser there and maybe Watson and someone else will get involved to try to help us sort out what is going on.

My main thrust here today though is to talk about the results of the Nutrient Cycling Model (NuCM) for the Barton Flats site for the last year and a half. I should give you a little background on NuCM. It is a stand level nutrient cycling model that was developed during the Integrated Forest Study. Rainfall pH in itself is an extremely poor indicator of any kind of effect because, for example, if nitrate comes in, and if it is taken up by the vegetation, hydroxide is released, and you have a neutralization. If ammonium ion comes in and is taken up you have acidification. If you have ammonium sulfate coming in, it is the same thing as acid rain if the ammonium is taken up, releasing hydrogen ions, and the sulfate goes through. It all depends on what happens in the system, and that is exactly what this model is designed to analyze.

One of the things that you need to know about the model before I show results is how it treats plant growth. It is not a plant growth model. You have to put in values that you expect for plant growth. If the nutrient model begins to run out of available supplies of nutrients, it will first reduce the concentration of nutrients in the tissue. Plants really do that before they stop growing. After it has reached a limit of reducing nutrient concentration, then it will reduce growth. Normally, we have a difference between projected and actual growth due to some nutrient limitation or other factor that develops within the model. The model has been calibrated for several sites including the Duke Forest, (an eastern hardwood forest in North Carolina), and the Great Smokey Mountains red fir sites. Now it has been calibrated for Barton Flats and Little Valley in the southwest. The Great Smokeys are definitely a nitrogen saturated site. Input is about 25-30 kilograms per hectare per year. The leaching rate is the same, and the uptake rate is only around 9 kilograms per hectare. Coweeta is about half of that. Duke is very poor in nitrogen. Little Valley Jeffrey pine is very poor in nitrogen. Sagehen is about twice its value, and Barton Flats is an intermediate situation. The other big factor is the base saturation which is the index of soil acidity. The Smoky soils are extremely acid, about as acid as they can get, and then Coweeta is more basic and Barton Flats is mixed.

We calibrated for Barton Flats, and ran scenarios where the deposition of nitrogen changed from less than 2 kilograms per hectare per year up to 95 (Fig. 2). If you multiply it out, the model actually gives you kilomoles per hectare as an output, multiply that over the 40-year interval that we ran the model, sum everything, and Figure 2 shows what happens. Notice that we have a rather low net retention down here at only 2 kilograms per hectare per year. This might seem unusual and you might think it is saturated, but it is really not because this is down to almost a baseline level of nitrate leaching here, and the deposition has very little to do with it. As we go up, therefore, there is greater retention until we get to 2 x N which is about 40 kilograms per hectare per year. Then we start dropping off and nitrogen comes through the system.

The simulated biomass (Fig. 3) shows this growth at the 0.1 x N, which is the two kilograms, and growth increases up to the factor 2. Between factor 2 and 5, there is no further change. The lines overlap, and that is the fully realized growth potential. We did not run across any other nutrient deficiency in these simulations except nitrogen. So the nitrogen deficiency in the system was satisfied at a rather high level of deposition, something in the excess of 20 kilograms per hectare per year. What are the side effects of that? Figure 4 is the nitrogen distribution in the year 40. There is very little on the soil exchanger until you get to the very high level, and that is a typical forest situation. There was also soil acidification at high N input. Mark mentioned that this occurred with high nitrogen inputs, and when you get up to 95 kilograms per hectare per year in the model, you have slow acidification. This is illustrated by exchangeable potassium. I suspect that if we run the model out another 40 years, it would have simulated a potassium deficiency. At first, however, from 0.1 to 0.5 x N, there is actually a net increase in system potassium, yet the soil is slightly acidified due to uptake. It is these kinds of interactions that can occur with increasing nitrogen, and they are not necessarily obvious unless you run a model like this.

Base saturation in the simulation went down continuously through time with all scenarios (Fig. 10). There was no deficiency realized during these 40 year simulations. If we carried it out further, maybe something else would have happened. I hasten to add that this is all a function of the weathering rate and the primary minerals that we allow into the model. I could get rid of most of this change pretty quickly by turning up the weathering rate. It is a user defined model. I insisted it be a user defined model, because no one really ever knows what the values of some important variables are, and that is one of the unknowns that you have deal with when you make simulations. In any event, Mark's field data are showing some pH decline indicating that base saturation is going down.

When I saw the model output, I initially did not believe the simulated peak levels of nitrate in soil solution and especially at the high end levels (Fig. 11). We saw levels that were 7000 micromoles per liter, and I thought that was just an error from the model and did not suppose it was really true. However, after collecting the centrifuge data, and we saw 5000 micromoles per liter. So, maybe that too has a little more validity than we first realized. Even with only 2 kilograms per hectare per year, peak summertime nitrate is right up there like in the Great Smokey Mountains. This is of little consequence, because it does not leach from the soil, and moisture levels are very low. It just sits there until uptake commences again, and is then taken down to 0. It is an interesting output.

To summarize (Fig. 13), the NuCM simulations for Barton Flats suggest the following hypotheses:

1. The reductions in nitrogen deposition would result in nitrogen deficiency.
2. Increased deposition would result in so-called saturation and possible reduction in base cations. That seems to be verified by the field data that were collected.
3. Summertime soil solution nitrate levels are very high due to low deposition, and this was also be seen out in the field.
4. Reduced nitrogen deposition a would result in increased base cation leaching because of an anion shift.

I want to end up with a couple of important points about models in general. What good are models? (Fig. 14) There are some predicted models, like yield tables, that are very good empirical models for what they are designed to do. Outside of their domain of reference, they are worthless, and that is certainly true of this model as well as any other model out there. I found the article about models by Orestes in Science to be extremely good (Fig. 14). It verifies my feeling on what we should be and should not be doing with models. Making policy predictions with models is shaky, in my opinion, although economists get away with it all the time. Maybe we should have higher standards than that. Figure 15 further quotes from that article. If one has a 10 year data set using five years to calibrate and then runs it for the next five years and asserts, "by God, it fits. It is wonderful that the model really works." This is not truly a test of the model. I think that models like this are so complicated that the best they can do is give you an idea of the collective implications of what you think you know. Sometimes you find out that implication is very far off, and sometimes you find out that it is good, for actually predicting what level of end-deposition in the forest will apply in the soil acidification. I will stop here and see if there are any questions.

Q (AUDIENCE #1) Since we are coming to the section on forest effects, I would like to propose a couple of statements, very general, and see how you people would modify this. First statement I think we all agree with is that pH and effects do not correlate in any really significant way.

Q (AUDIENCE #2) You mean pH in precipitation?

A (AUDIENCE #1) Yes.

Q (AUDIENCE #1) The second statement would be that maybe pH does not have effects, but buffering capacity or total available hydrogen ion may. The third is that there is nothing in this that suggests that you should do anything different from the control of nitrogen oxide emissions and keeping ozone levels low. In other words, if somebody asked us if we should have a special acidity standard would you say that there is evidence that we should?

A (DR. JOHNSON) I think acidity of incoming precipitation is really a rather minor consideration. So I agree with that completely as far as the effects that I study are concerned, pH is overemphasized. The one thing that it really does affect is the state of aluminum, and aluminum is sometimes toxic in roots.

There is the so-called "active acidity", which is pH, and that is a small pool. Then there is "reserve acidity" exchanges with the buffer pool. You can change the soil solution and therefore change the stream water pH drastically without changing the buffer capacity, and that is by simply adding mineral acid to soil. In doing so, you must balance those anions like sulfate and chloride with something. In acid soil, there is really only aluminum and hydrogen to speak of and, therefore, the concentrations of aluminum and pH can go up and down drastically over a short time with no change in the soil. So I would add that caveat to your first comment.

Q (AUDIENCE) The third question was, do you see anything in this that would suggest any kind of acidity standard other than just control of nitrogen oxides and the ozone.

A (DR. JOHNSON) Not me, no.

BRENT TAKEMOTO, MODERATOR

Thanks to all the speakers on the forest session. I think that these two projects brought together a lot of investigators with different backgrounds, and they were able to both collect field data and begin to study how models for either atmospheric deposition or effects on forest ecosystems should be investigated. I think we have made a big step there in starting these studies.

We will proceed next with Nehzat Motallebi who will handle the atmospheric process.

Figure 1

Simulated effects of N Deposition Rates on Growth and Nutrient Cycling in a Ponderosa Pine Forest

Dale Johnson
Desert Research Institute
and
University of Nevada, Reno NV

and

Mark Poth, Mark Fenn, Paul Miller,
and Andrzej Bytnerowicz
U.S. Forest Service Fire Lab
Riverside, CA

Figure 2

Simulated net ecosystem nitrogen balance under varying N deposition scenarios. (kmol ha^{-1} 40 yrs^{-1})

Scenario	0.1 x N	0.5 x N	1 x N	2 x N	5 x N
Deposition	5.5	27.3	54.6	109.3	273.1
Leaching	2.0	3.5	5.7	49.1	203.4
Balance	3.5	23.8	48.9	59.2	69.7
% Retention	63%	87%	89%	55%	25%

Figure 3

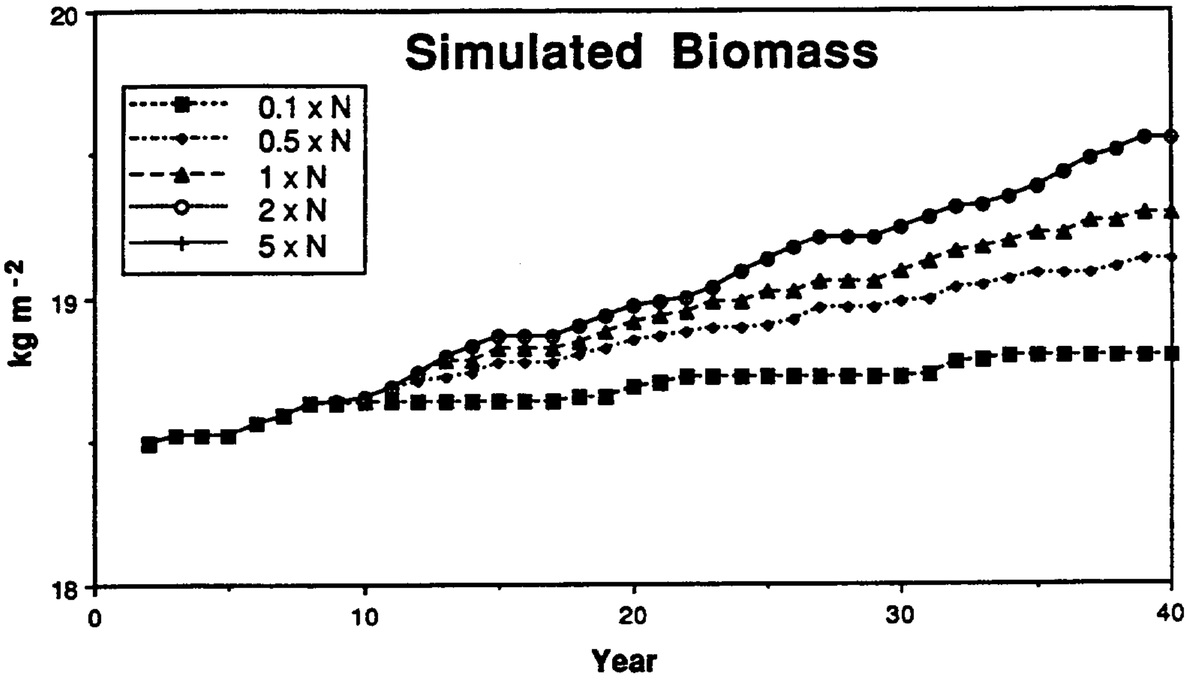
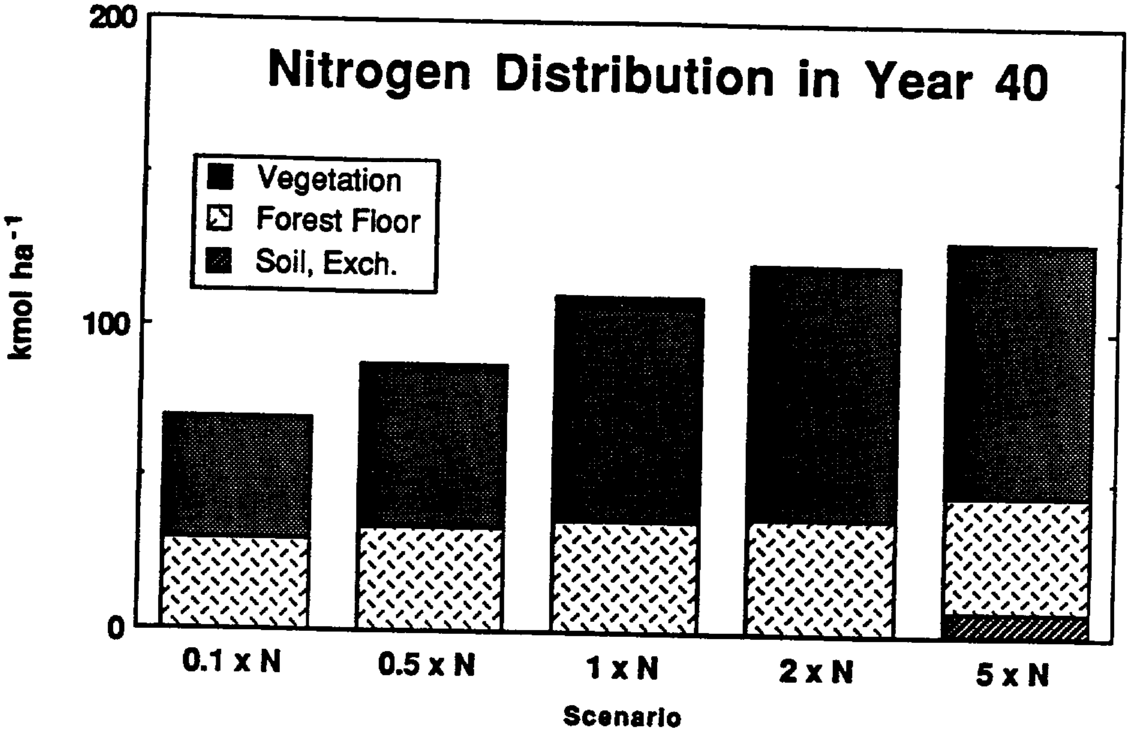

Simulated Biomass
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
kg m -2
20
19
18
0
10
20
30
40
Year

Figure 4


Nitrogen Distribution in Year 40
Vegetation
Forest Floor
Soil, Exch.
200
100
0
kmol ha^{-1}
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Scenario

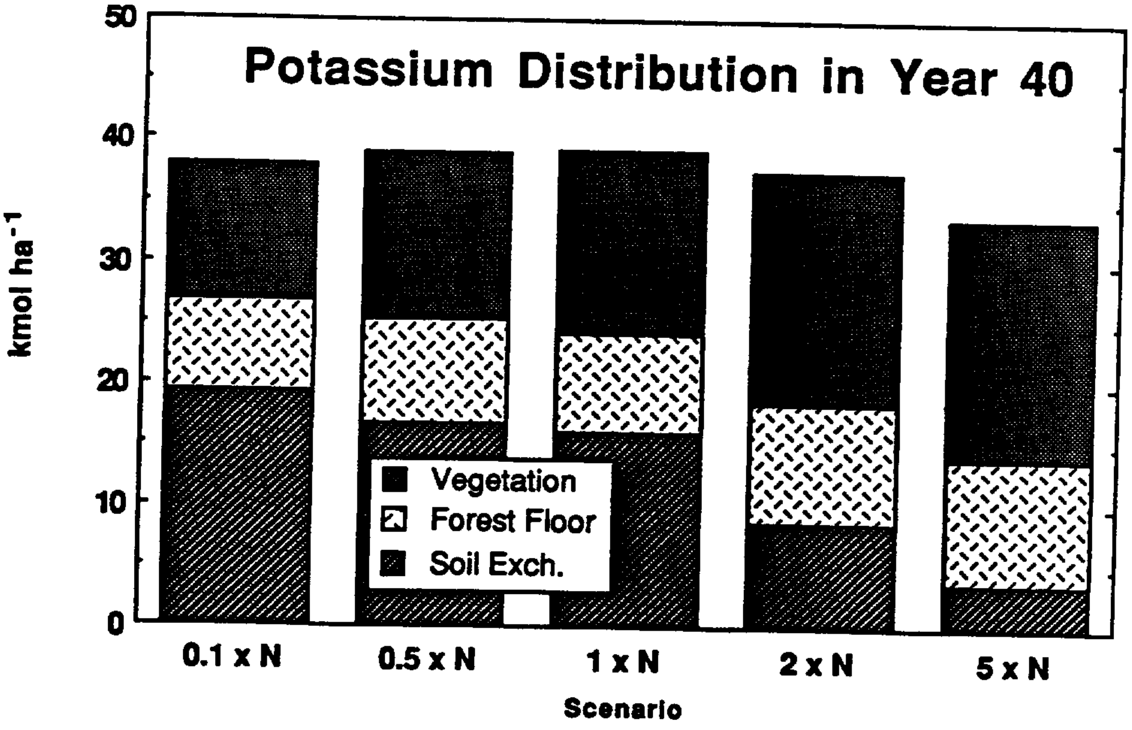
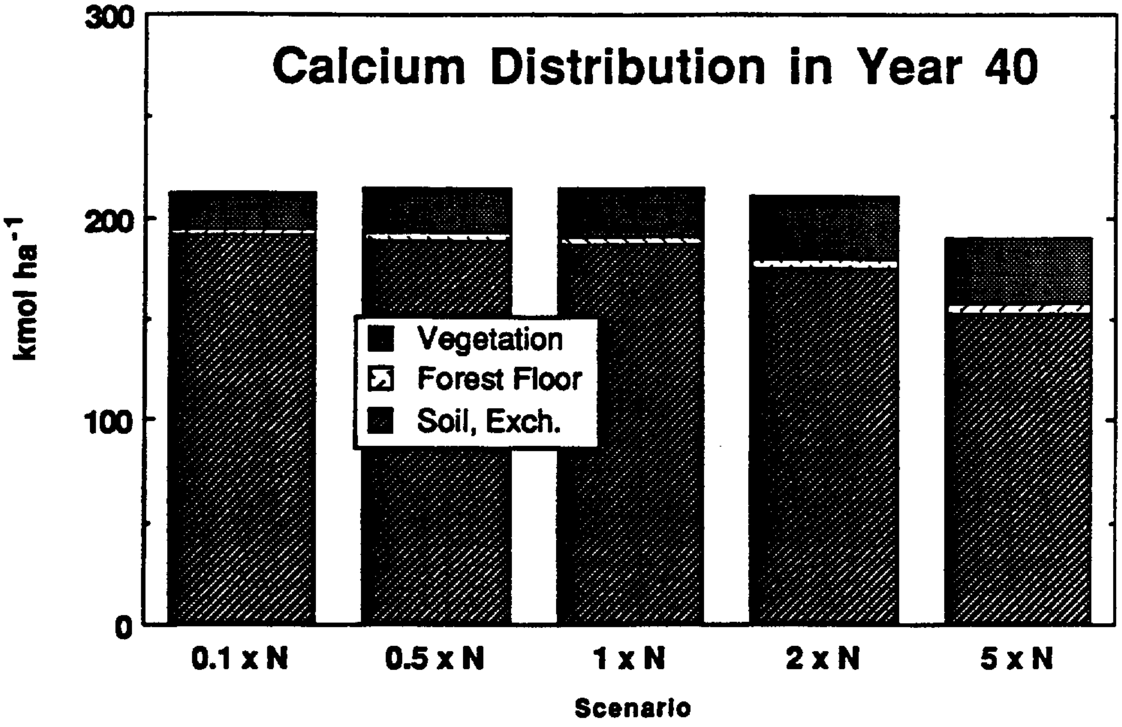

Potassium Distribution in Year 40
Vegetation
Forest Floor
Soil Exch.
50
40
30
20
10
0
kmol ha^{-1}
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Scenario

Figure 5


Calcium Distribution in Year 40
300
200
100
0
kmol ha^{-1}
Vegetation
Forest Floor
Soil, Exch.
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Scenario

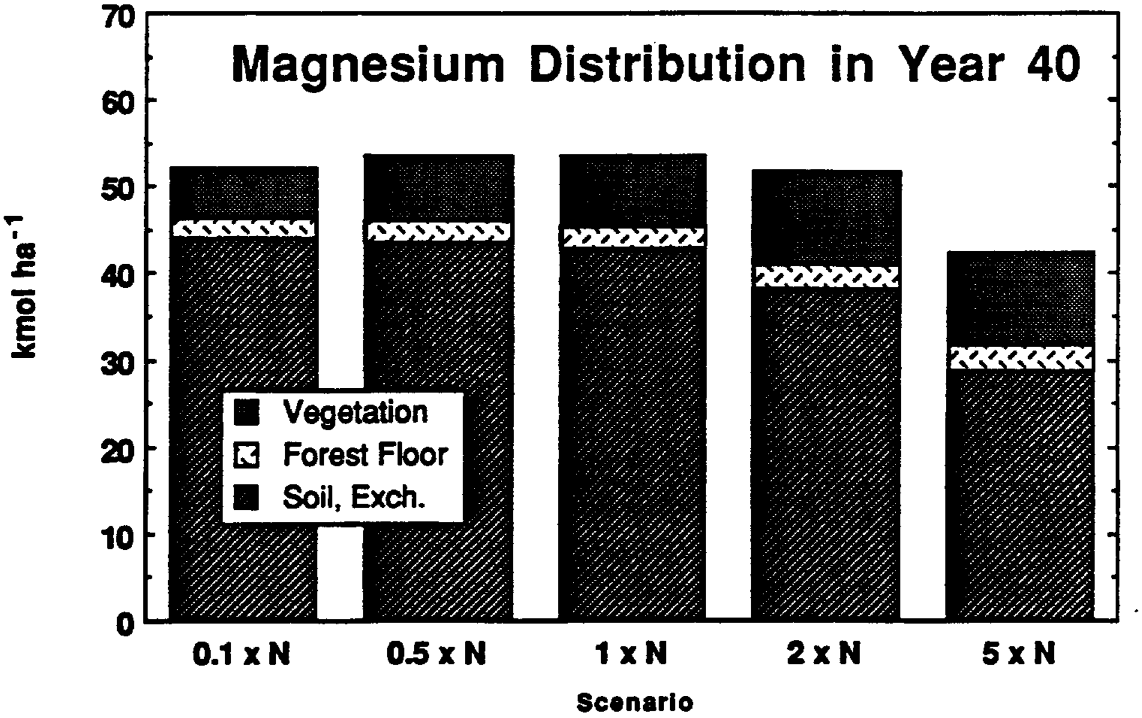
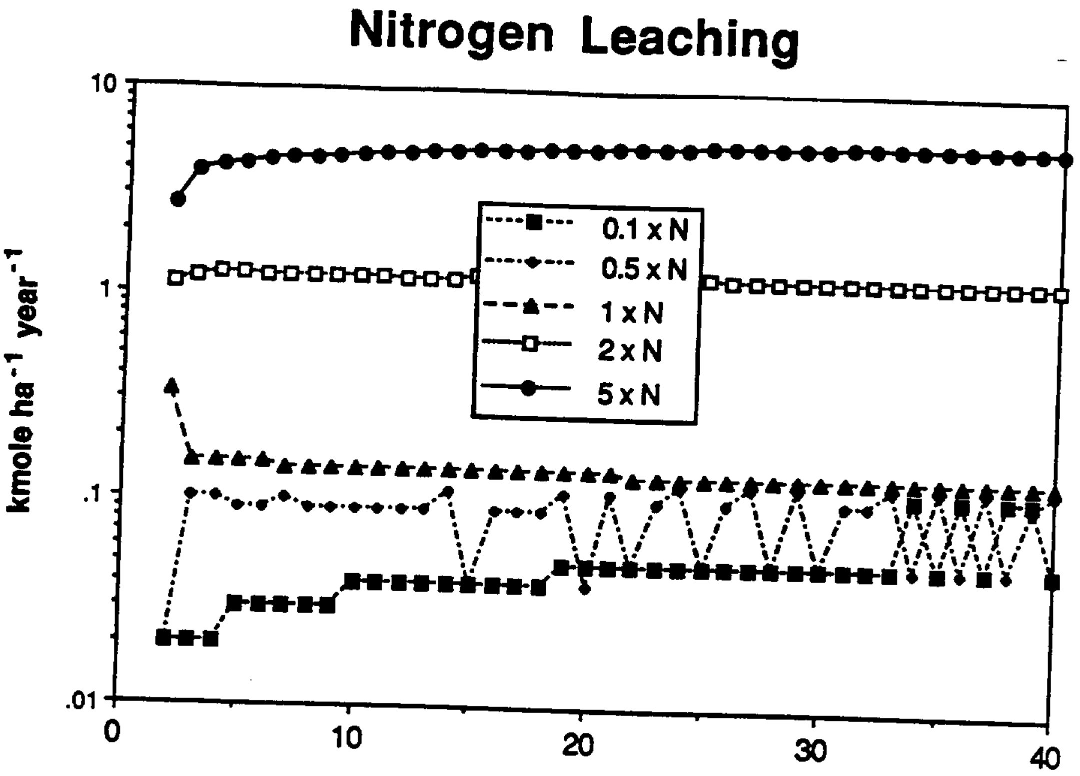

Magnesium Distribution in Year 40
70
60
50
40
30
20
10
0
kmol ha^{-1}
Vegetation
Forest Floor
Soil, Exch.
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Scenario

Figure 6


Nitrogen Leaching

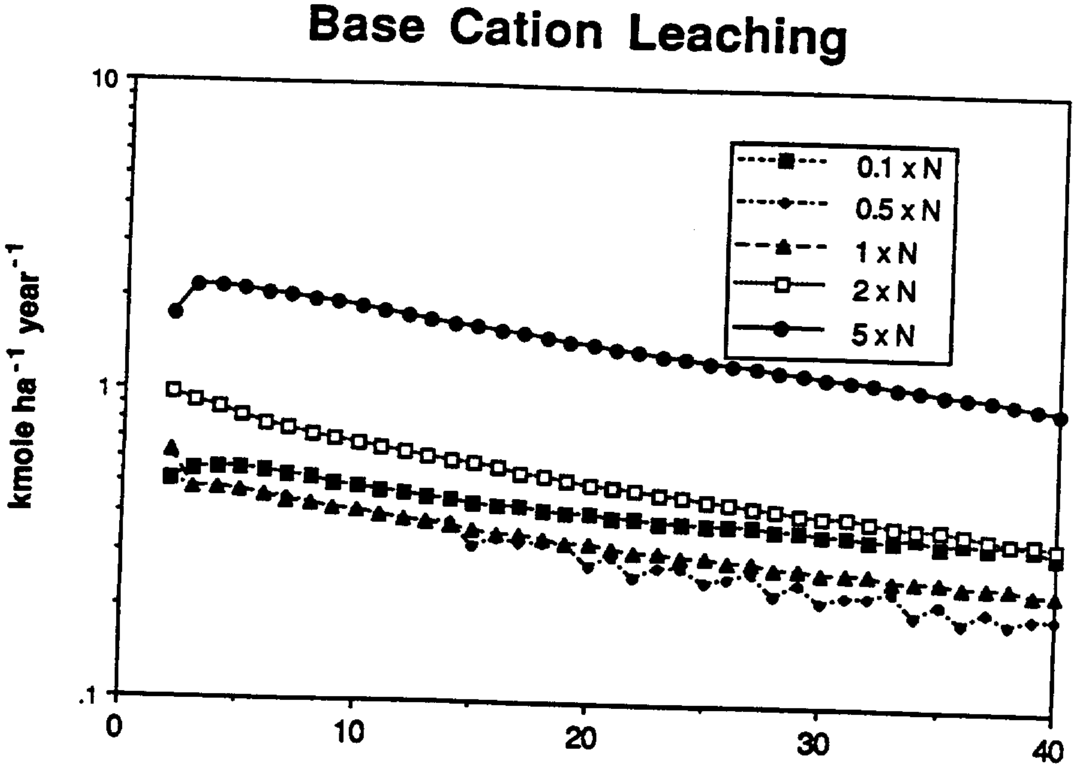
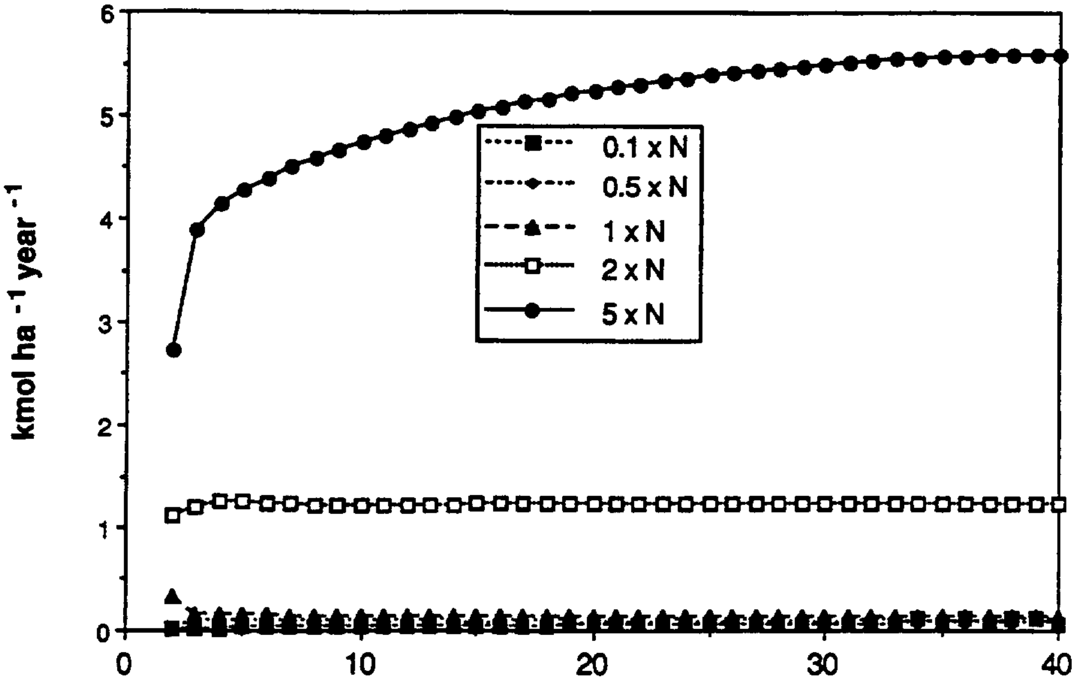
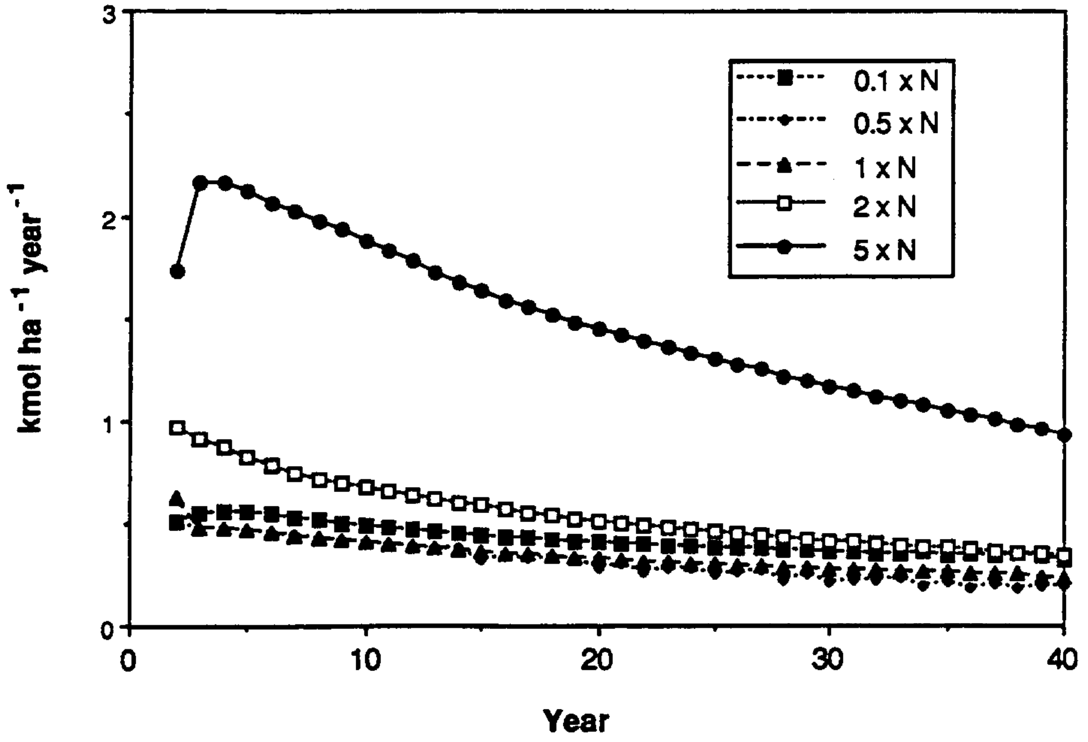

Base Cation Leaching

Figure 7



Nitrogen Leaching



Base Cation Leaching

Figure 8

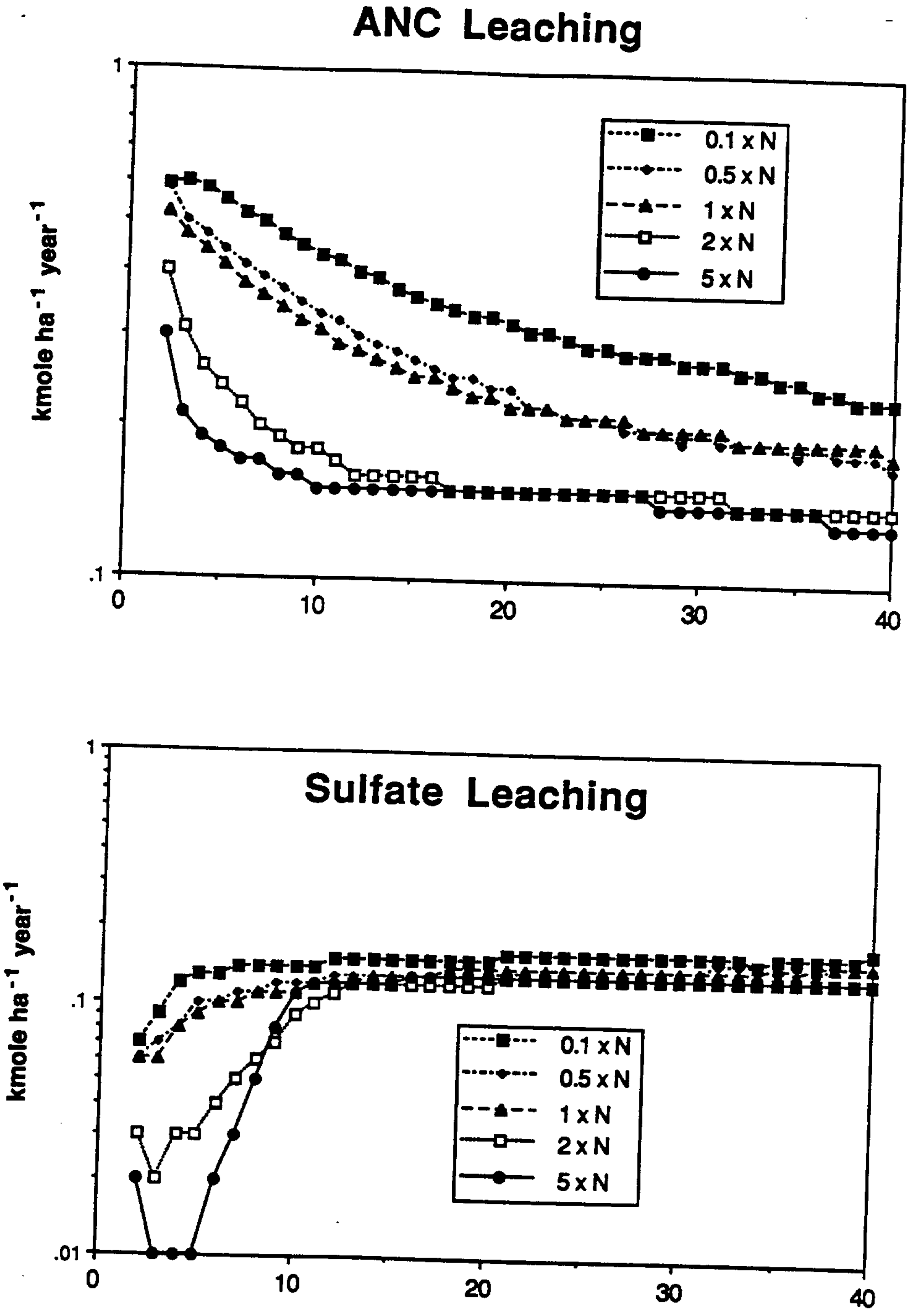

ANC Leaching
kmole ha^-1 year^-1
1
.1
0
10
20
30
40
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Sulfate Leaching
kmole ha^-1 year^-1
1
.1
.01
0
10
20
30
40
0.1 x N
0.5 x N
1 x N
2 x N
5 x N

Figure 9

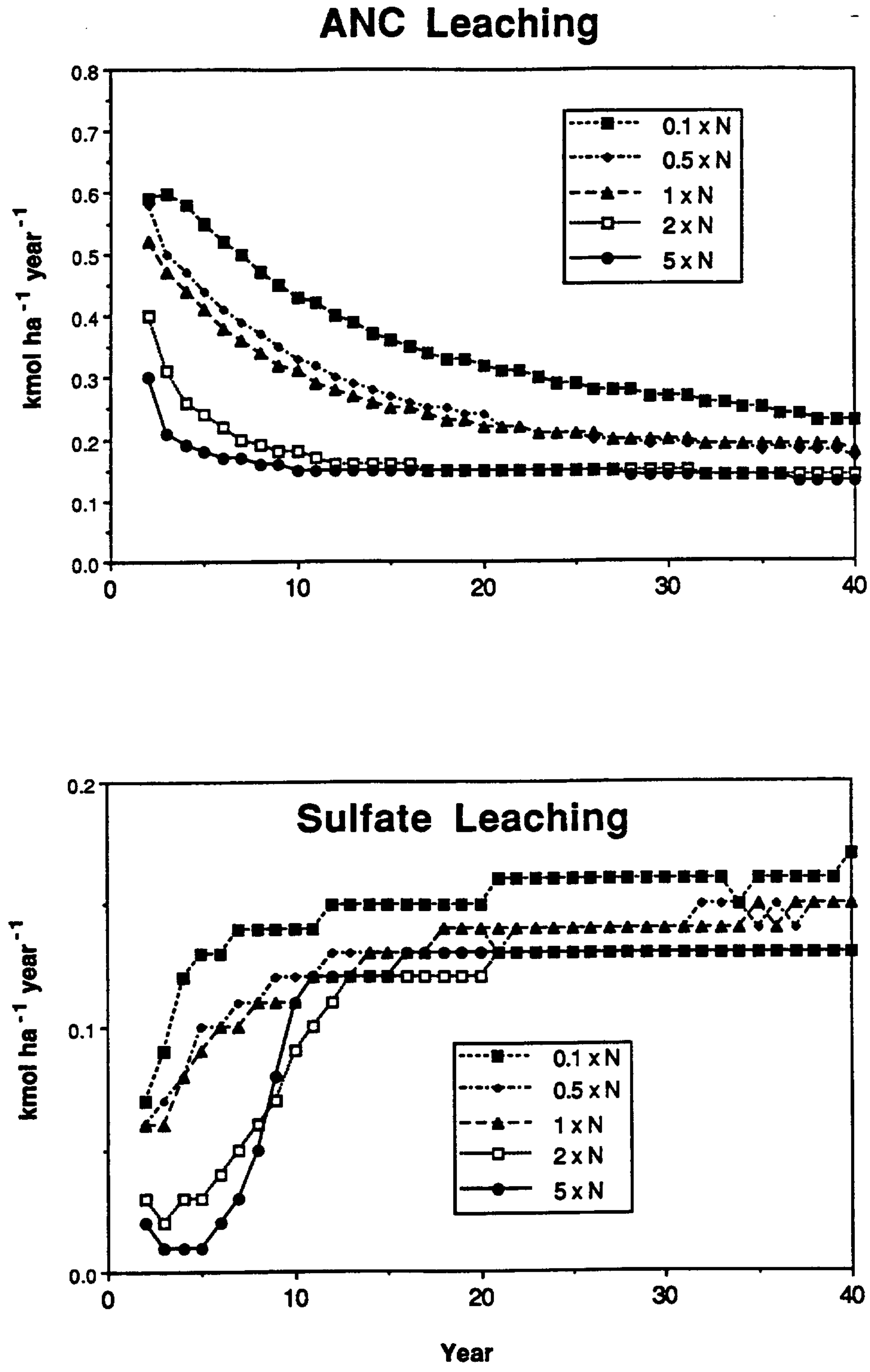

ANC Leaching
kmol ha -1 year -1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Sulfate Leaching
kmol ha -1 year -1
0.0
0.1
0.2
0
10
20
30
40
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
Year

Figure 10

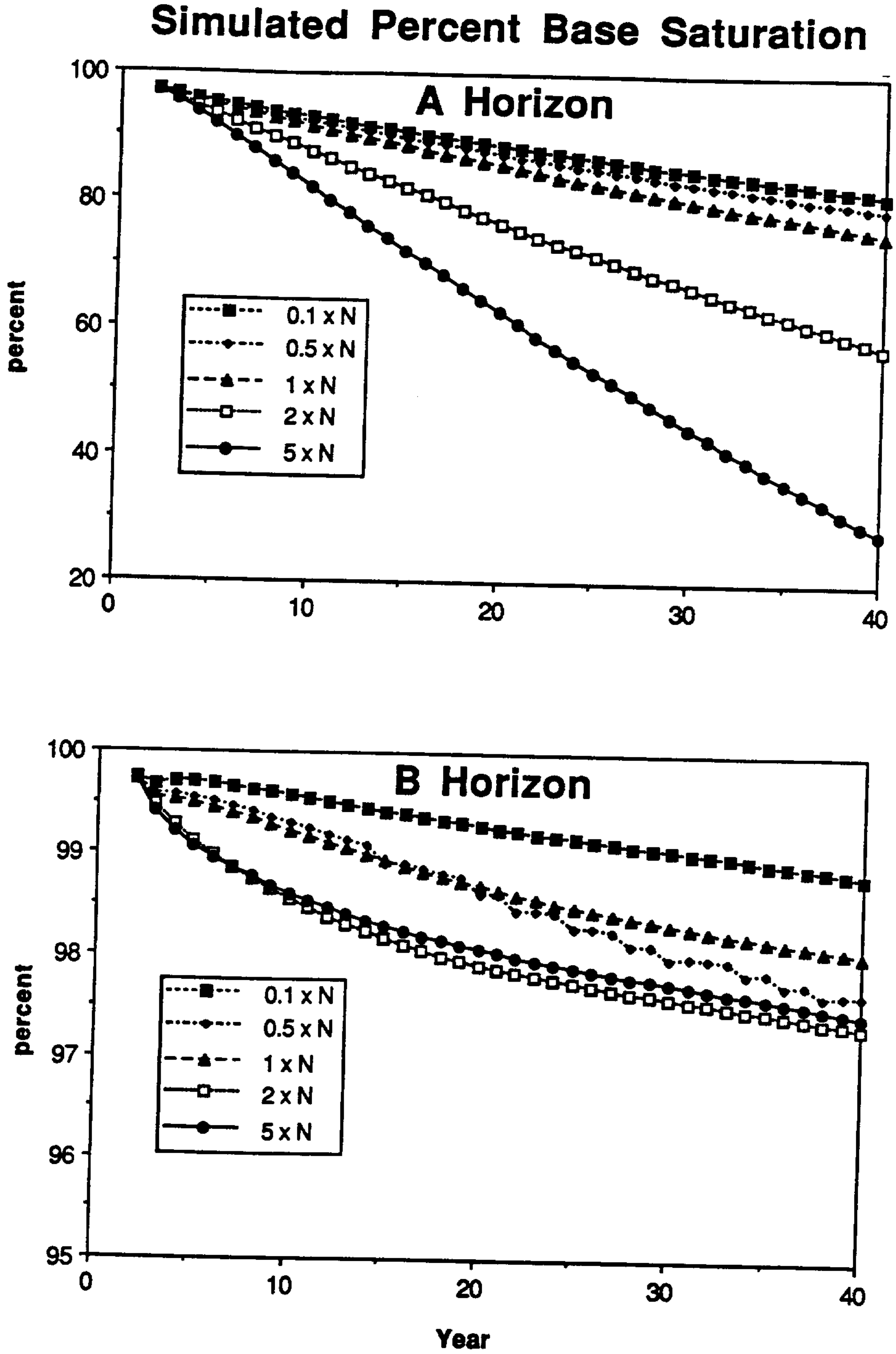
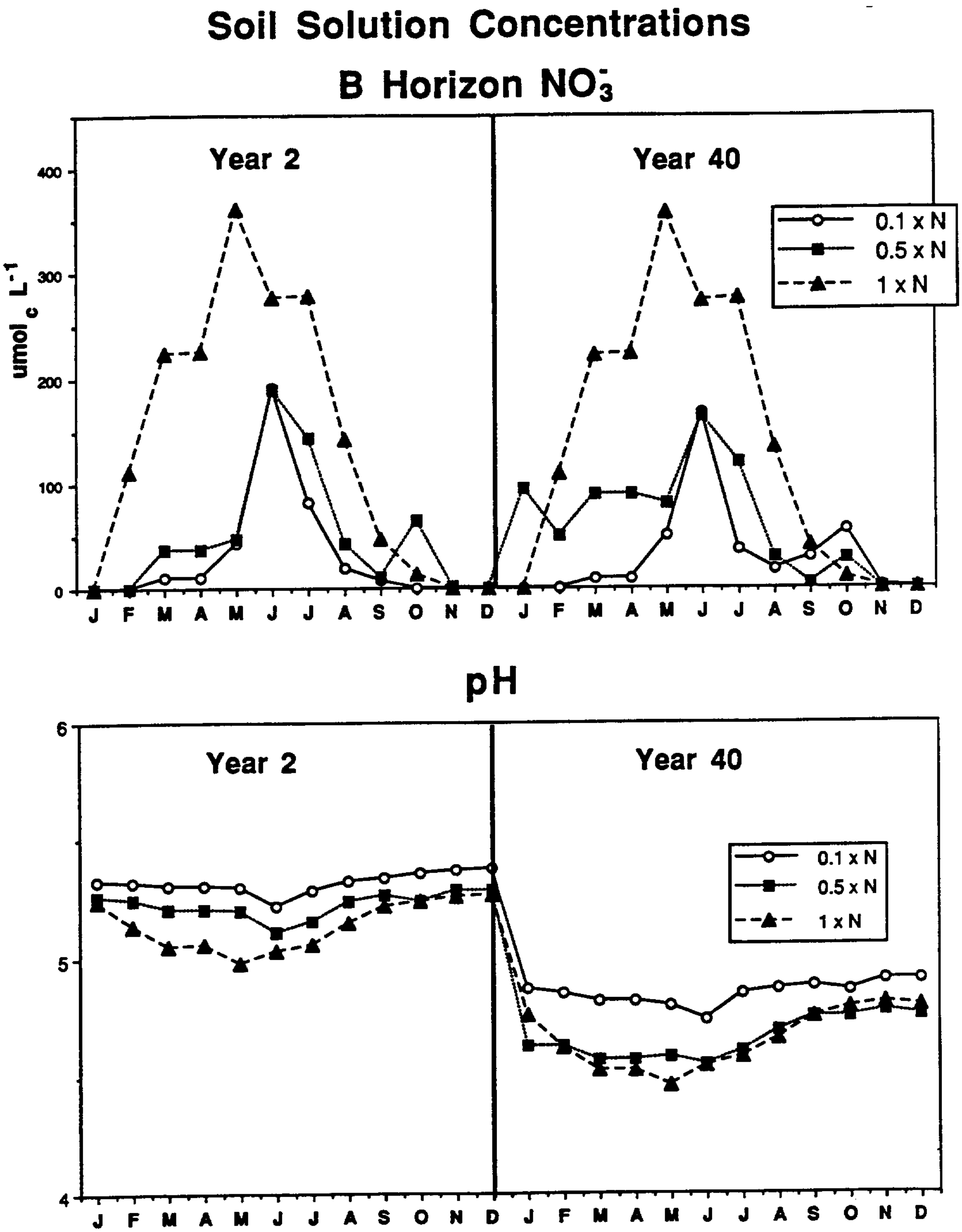

Simulated Percent Base Saturation
A Horizon
percent
100
80
60
40
20
0
10
20
30
40
0.1 x N
0.5 x N
1 x N
2 x N
5 x N
B Horizon
percent
100
99
98
97
96
95
0
10
20
30
40
Year
0.1 x N
0.5 x N
1 x N
2 x N
5 x N

Figure 11



Soil Solution Concentrations
B Horizon NO_3^-
Year 2
Year 40
umol$_c$ L^{-1}
400
300
200
100
0
0.1 x N
0.5 x N
1 x N
J F M A M J J A S O N D J F M A M J J A S O N D
pH
Year 2
Year 40
6
5
4
0.1 x N
0.5 x N
1 x N
J F M A M J J A S O N D J F M A M J J A S O N D

Figure 12

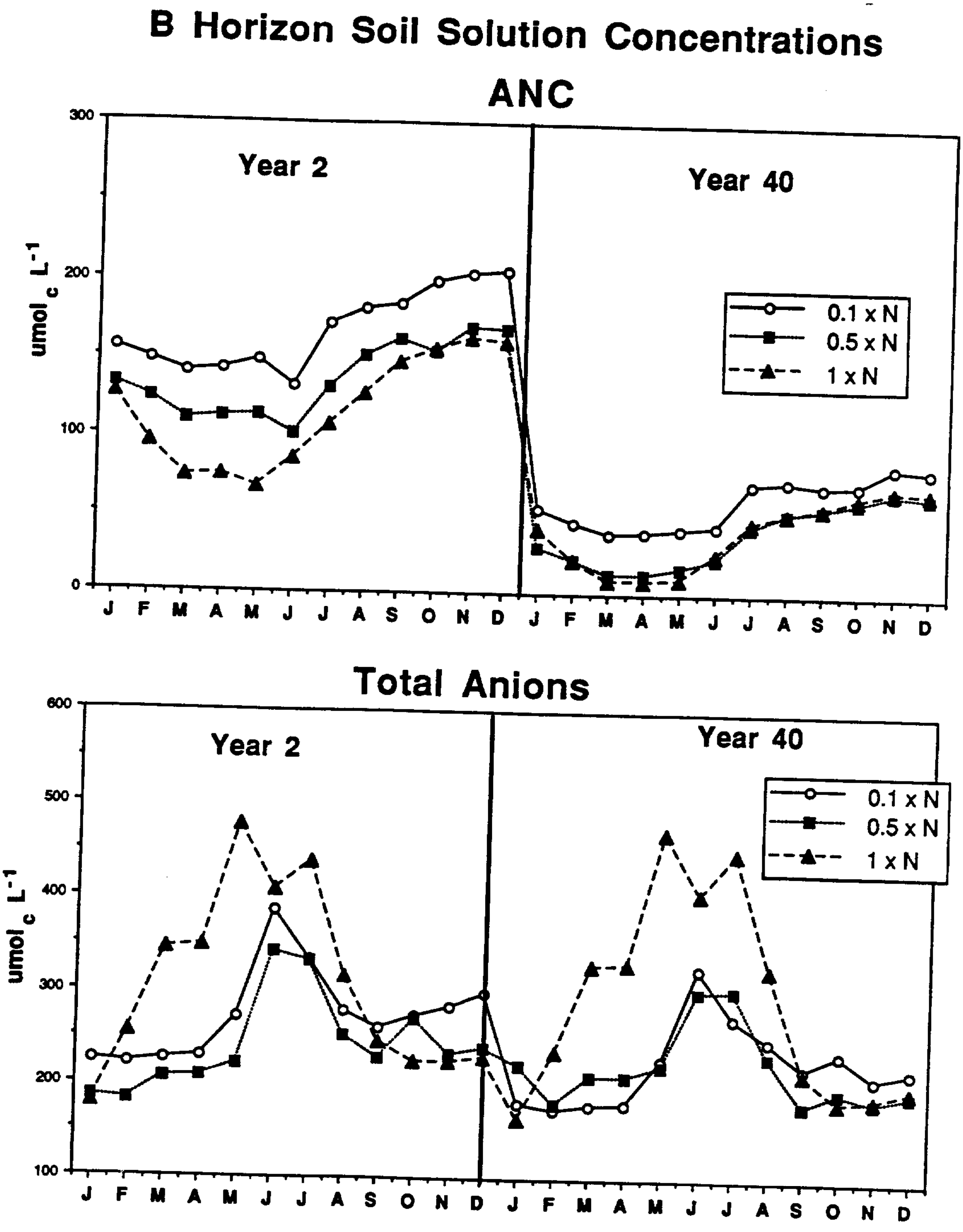

B Horizon Soil Solution Concentrations
ANC
Year 2
Year 40
umol c L-1
300
200
100
0
0.1 x N
0.5 x N
1 x N
J F M A M J J A S O N D J F M A M J J A S O N D
Total Anions
Year 2
Year 40
umol c L-1
600
500
400
300
200
100
0.1 x N
0.5 x N
1 x N
J F M A M J J A S O N D J F M A M J J A S O N D

Figure 13

Summary and Conclusions

NuCM simulations for Barton Flats suggest the following hypotheses:

- Reductions in N deposition would result in N deficiency
- Increases in N deposition will result in "N saturation" and possible reduction in soil base cations (e.g., K)
- Summertime soil solution NO_3^- concentrations are high even with low N deposition
- Reduced N deposition would result in increased base cation leaching because of anion shift

Figure 14

What Good Are Models?

Management:

Predictive models (especially simple ones, like yield tables) are used all the time to good effect when not extrapolated beyond their appropriate range of environmental conditions.

Scientific:

"Models are most useful when they are used to challenge existing formulations, rather than to validate or verify them. Any scientist who is asked to use a model to verify or validate a predetermined result should be suspicious" (Orestes et al 1994).

Testing Models

(Oreskes, Naomi, Kristin Shrader-Frechette, and Kenneth Blitz. 1994. Verification, validation, and confirmation of numerical models in the earth sciences. Science 263: 641-646).

Verification: Implies "truth", which is unattainable. All must be known to achieve this. A typical false "verification involves "calibrating" the model for one-half of a data set, and running it for the second half. But what happens if the environment changes (the rules change)?

"The goal of scientific theories (and, therefore, models) is not truth (because it is not attainable), but empirical adequacy (van Frassen 1980). Empirical adequacy may be judged by comparing model output with actual data in a blind test. (This is very seldom done, although often possible).

However, it will never be known with certainty whether or not the model obtains the right result for the wrong reasons (excessive "calibration").

C. Session 2. Atmospheric Processes.

DR. NEHZAT MOTALLEBI: Moderator

Good afternoon. My name is Nehzat Motallebi. I am with the research division of the Air Resources Board. Research on the atmospheric processes program is being conducted for three main purposes: 1) to understand the chemicals and physical processes that transform precursor initiators of acidic gases and aerosol particles in the atmosphere, 2) to estimate the fluxes of the wet and dry acidic deposition, and 3) and to characterize and quantify source receptor relationships between initiation of acidic pollutants and deposition of acidity.

We have six speakers for this section. These scientists have been principle investigators on several research projects, and they are leaders in their fields. The speakers have been asked to limit their presentation to 25 minutes, so that there will be five minutes available for brief questions at the end of the presentation. We will have an open discussion at the end of the sixth session, so I would appreciate it if you would hold your long comments and questions for this open discussion.

The topic of our first presentation is "A Summary and Evaluation of California Active Deposition Monitoring Program (CADMP) Data". This will presented by Dr. Charles Blanchard of Envair.

1. A Summary and Evaluation of CADMP Data. Dr. Charles Blanchard, Envair.

DR. CHARLES BLANCHARD: Envair

I would like to thank my colleague Harvey Michael, who has carried out most of the dry deposition calculations. The purpose of this presentation is not to discuss atmospheric processes, but rather the purpose is to present the data that have been gathered from the California Acid Deposition Monitoring Program, wet and dry deposition networks (Fig. 1).

The networks have produced several years of data, and it seems important to ask ourselves what we have learned from these data, to ask ourselves how well the networks have met their objectives, and simply just to make some of the numbers available. Nehzat mentioned the objectives of the monitoring networks. Let me just briefly run through them again (Fig. 2). The first is to quantify the range of concentrations and deposition occurring, both wet and dry, throughout the state of California, not just where we have our monitors. The second is to provide data that can be used by people who are studying acidic deposition; third, to provide data that could be useful for identifying emission source regions which are contributing to deposition in receptor areas, and fourth to identify possible trends over time. I would like to point out that the CADMP networks are not specifically oriented for carrying out research on atmospheric processes, nor are they compliance monitoring networks since there is no current acidity standard.

My strategy in this talk is largely going to be to tell you the results and omit details of how we got to them. Very briefly, I want to mention that the CADMP Wet Deposition Network uses the Aerochem Metric automated wet deposition sampler, which is no doubt familiar to many people here (Fig. 3). It is operated on a weekly basis. The samples are collected on the same schedule that the National Atmospheric Deposition Program uses, Tuesday to Tuesday. The period of records for which we currently have validated data runs from June of 1984 to July of 1990. There are more recent data; they are undergoing validation. There are a number of QA and QC protocols that are followed in collecting the samples and in analyzing the data. Just to mention a few: charge balance is checked, the specific conductance measured on the samples compared to conductance predicted from the chemical concentrations, ratios of different ions are checked, for example, the ratio of sodium to chloride, and suspect samples are reanalyzed. A certain percentage of the samples are also re-analyzed routinely. In terms of the statistical summaries that I will present in a few moments, I wanted to mention briefly that it is important to keep track of the completeness of sampling. We are after valid representations of annual averages or seasonal averages, both for concentration and for deposition amounts. Therefore, it was important to keep track of what fraction of the time the precipitation monitor was actually operational and what fraction of precipitation was actually collected and chemically analyzed (Fig. 4). We computed annual and seasonal averages. Concentrations are weighted by precipitation depth, and mass deposition was also calculated. In addition to computing the averages at sites, we carried out spatial interpolations of the data using a statistical method known has kriging. The purpose of this spatial interpolation was to generalize our data from the specific monitoring locations to larger geographical areas. The way that was done was to use the concentrations from both CADMP sites and the National Atmospheric Deposition Program sites. We combined those with information on precipitation from approximately 500 national weather service monitoring sites in or near California, and we carried out two different methods for investigating the uncertainties and the interpolation. The first was through the procedure itself. One of the attractive features of this method is that it generates estimates of your interpolation uncertainties, so you are not just presenting a bunch of numbers; you are presenting some uncertainty associated with that. In addition, we used a second procedure known as cross validation for generating some estimates of uncertainty. Figure 5 illustrates how the network looks. At its peak, CADMP had 35 sites in California. There are a number of sites that are inactive, and I believe the network is down to 25 sites now. There were also eight NADP sites located in California; four of the CADMP sites have been co-located with NADP sites for cross comparison. The CADMP data compared very well with the NADP data. When we carried out the interpolations, we made use of all monitors in California as well as some which were located just outside California. What you obtain when you start doing that is a series of maps such as Figure 6. We plotted nitrate deposition, that is wet nitrate deposition, from July 1988 through June 1989. This is for a one year period, and these have been interpolated to a grid which is 40 kilometers by 40 kilometers for each grid cell. Typically we did not see a lot of spatial variation in the precipitation chemistry, and in a large part of the state there was less than 2 kilograms per hectare per year of nitrate deposition. We also wanted to look at what our estimate of the uncertainties associated with those numbers were. The uncertainties for most of the deposition were less than 20%. Where we are trying to interpolate between sites, we look at larger uncertainties in the 20-40% range. As we get out to areas that have very little in the way of monitoring information, we are looking at uncertainties that are more on the order of 50%. The cross validation analyses that we carried out suggested that these uncertainties were probably too low in some areas, particularly areas such as along the coast or in areas where there are particularly steep gradients. Overall, we are typically looking at uncertainties that range between maybe 20% and perhaps up to a factor of 2 as we try to interpolate these results from the monitoring sites to the state as a whole.

If we turn back to the actual sites themselves, I would like discuss what we have seen in the six years of data. The maximum sulfate deposition during any of the six years at any of the sites has been less than 7 kilograms per hectare per year of some which can be attributed to sea salt (Fig. 7). If you make the calculation to correct for sea salt, the excess sulfate is less than 3 kilograms per hectare per year everywhere. Nitrate deposition was less than 8 kilograms per hectare per year. Ammonium was less than 3. To get some feeling for what this means, perhaps it is useful to compare these numbers to those from the eastern United States. In the area of highest deposition in the eastern United States, sulfate deposition exceeded 25 kilograms per hectare per year. Nitrate exceeded 15 kilograms per hectare per year, while ammonium is less than 4 kilograms per hectare per year. I have no expertise on effects; however, from what I have gleaned from the literature various target levels have been proposed for wet sulfate deposition. Typically, the numbers that I have seen have been in the range of 10-20 kilograms per hectare per year. Some investigators mean excess sulfate by those numbers, and sometimes they mean something different, perhaps even wet plus dry. The Canadian government, for example, is currently using a 20 kilograms per hectare per year target level for excess sulfate. As I mentioned earlier, in terms of interpolating the data from our limited number of monitoring sites to the state of the whole, we are typically looking at uncertainties in the range of 20% to a factor of 2. To clarify that, if one were to look at replicability at individual monitors, your uncertainty in terms of the precision of the monitoring at a particular monitor is probably on the order of 5-8%.

Figure 8 is my own personal evaluation of the capabilities of a CADMP wet deposition network in relation to the objectives that were stated for the network itself. First, it has successfully quantified the rates of wet deposition to within a factor of plus or minus 20% up to a factor of 2. In terms of providing data that may be useful for studies on effects, while I have no expertise in this, I presume that one would prefer data that had a factor of 20% uncertainty to data that had a factor of 2X uncertainty. Therefore, this suggests to me that data which are used in effect studies must be site specific data. We have not seen the data used extensively to evaluate linkages between source regions and receptor regions. That is not to say they cannot be so used; it just has not been extensively explored. Finally, there is a six year record of data available, and another four years are coming relatively soon. There is some utility in these data for identifying trends. My assessment of the six year record to date is that there is very little evidence of any trends.

Finally, I just put this last bullet up here, "Future Objectives" with a question mark to remind ourselves that we may now have objectives which differ from those that were originally stated, and there may be a need to think about the capabilities of this network in terms of potential future objectives.

I would like to turn to the dry deposition network (Fig. 9). I am going to try to largely gloss over methods and get to some numbers. Dry deposition sampling is carried out using a sampler designed by the Desert Research Institute. The sampler collects two, 12 hour samples. There are two size cuts: a 10 micron and a 2½ micron. The sampler also measures several gas phase species. There is a lot of redundancy in the sampler in the sense that you get both the PM 2.5 and the PM 10 measurement. There are some other redundancies as well. These are all very useful checks on the data themselves. A key species measured is nitric acid. There are two ways in which that measurement is done. One is by collection on a nylon filter, known as filter-pack nitrate. This particular measurement is subject to a bias from the disassociation of ammonium nitrate which can cause those numbers to be biased high. As John indicated earlier from some of his data, the amount of particulate nitrate which can volatilize can be quite high, and you will then see that appearing as an estimated nitric acid concentration. The second measurement is the so-called denuder difference measurement. This is actually a linear combination of three separate measurements. There is particulate nitrate as collected on a Teflon filter which is added to the filter pack nitrate to give total nitrate. From that total nitrate the concentration of nitrate on a nylon filter which is downstream of the denuder is subtracted. The purpose of the denuder is to remove nitric acid. When you remove nitric acid, what is left is particulate nitrate. Thus, true particulate nitrate is obtained from the filter downstream of the denuder. When you subtract that number from the total nitrate, the difference is the nitric acid concentration. I will come back to those measurements in just a couple of minutes.

I want to mention that these samplers do not run everyday. Samples are collected once every six days. We are trying to make some inferences of our annual deposition rates from once per six day sampling. A large number of QA QC protocols were followed both in the sampling and the handling of the data. Just to mention a few, there is a very useful capability of comparing the PM2.5 to PM10 concentrations to check for consistency. You can also compare mass to the sum of species concentrations. A charge balance provides another check. Finally, there is the ability to compare the data from the CADMP network to some other measurements. In particular, six of the CADMP samplers are co-located with ARB routine PM10 monitors.

What can we say about the quality of the data (Fig. 10)? First of all, the period of record was February 1988 through September of 1991 (the viewgraph should say 1991, not 1990). There were a number of systematic errors identified in the data base and corrected. Following those kind of corrections, the comparisons of mass as well as sulfate, nitrate, and ammonium concentration in the PM 10 side of the CADMP samplers to the data collected from the collocated routine PM10 monitors were very favorable.

The bad news is that the one species that we really care a lot about, nitric acid, appears to have substantial measurement problems associated with it. This was perhaps first evident when, in examining these data, we observed a decrease in the concentrations of nitric acid when calculated according to the denuder difference method over this 3½ year period at two of the sites, Los Angeles and Azusa. These happened to be the two sites where the highest nitric acid concentrations occurred. What was found in the data record was that the decrease was associated with a concomitant increase in the denuded particulate nitrate concentrations. That is, the particulate nitrate downstream of the denuders exhibited increases over time, and the seasonality that was apparent in the PM10 and the PM2.5 particulate nitrate concentrations disappeared for the denuded particulate nitrate. The PM10 and PM2.5 particulate nitrate were exhibiting winter maxima during the first year and at all other sites all year. However, the denuded particulate nitrate at those two sites started to show summer maxima. The suspicion was that the denuders performed well for perhaps a year and then began to allow nitric acid to pass. The effect of allowing the nitric acid to pass the denuders would be to cause the apparent particulate nitrate concentrations to increase, which would cause the nitric acid concentration to appear to decrease over time. That suspicion was particularly reinforced by the fact that there is no trend in the filter pack nitrate over that time, nor was there any trend in the ozone concentration over that time. So in the summer of 1993, a special inter-comparison study was established at Azusa, and a relatively new sampler was put in place next to the original sampler.

The denuded particulate nitrate was about 18 micrograms per cubic meter in the primary versus 11 in the co-located sample. That difference was enough to cause the apparent nitric acid concentration to drop close to 0 in the older data. Following those results, there was some cleaning and refurbishing of the original sampler, and during October the primary co-located samplers were run together. There was an additional check with a third channel on one of the samplers as well. Generally, good replication occurred in the samplers. However, when those data were compared to a co-located set of measurements obtained by the Tunable Diode Laser Absorption Spectroscopy (TDLAS) method, they were about 40% lower than the TDLAS measurements. At the same time, there was another sampler which is similar in some respects to the CADMP sampler. It was used in the SCAQS study. There are some key differences in terms of the flow rates. Its ratio compared with the TDLAS was about 0.7. We have got three different sets of measurements here. CADMP is about 40% lower than the TDLAS. The SCAQS is about 30% lower than the TDLAS. Finally, there is a fourth sampler, a two week sampler, the one that was used in the epidemiological study. It was run for two weeks and compared to the two weeks of data from the other samplers, and as I recall, it was about, 25-30% higher than TDLAS measurements. The bottom line on all of this is that there is a lot of uncertainty with these measurements. We could be off by 35%, and more effort is needed to try to untangle some of that. Let us try to keep some of those measurements in perspective; there are significant measurement uncertainties.

Everything that George Taylor said earlier is applicable to how we carried out the calculations of deposition. The CADMP network provided us with measurements of ambient concentration as well as certain meteorological measurements. In order to estimate deposition, the inferential method was applied and fluxes were inferred from the product of concentration and deposition velocity (Fig. 11). The deposition velocity was calculated on an hourly basis using the meteorological measurements as well as characteristics of the surface at the sites. In essence, we used the same model described earlier, the big leaf model. However, we also made some modifications to it to account for its use in a western setting.

Remembering now what we have in the way of fluxes, they are not measurements but, rather, the product of a model. This model is thought to produce uncertainties along the order of 30-50% in the best of circumstances, that is, in homogeneous uncomplicated terrain. As we all know, the terrain here in California is not very homogeneous and uncomplicated; therefore, we need to remember that for any numbers that are generated here, the uncertainties of the model itself are compounded by our application to a California setting where we have incomplete input data, and they are complicated by questions of the accuracy of the measurements. I am going to suggest that we are probably looking at uncertainties that are more like a factor of 2 when we look at these numbers.

There are 10 sites in the dry deposition network (Fig. 12). Three of the sites are rural, Gasquet, Yosemite, and Sequoia. The other seven are urban sites, Sacramento, Fremont, Santa Barbara, Long Beach, downtown Los Angeles, and Azusa. The coverage of the state is very limited. There are three sites in the South Coast Air Basin; otherwise, the sites are rather scattered. So putting all that together, here at last are some numbers (Fig. 13). This is an estimate of the mean annual dry deposition of particulate nitrate, NO_2, and nitric acid at each of the 10 sites. This is for the period of 1988 through 1991, expressed in terms of kilograms of nitrogen per hectare per year. If we just step back, look at the data and ask ourselves "Now what does this tell you?", we will probably see a couple of things. If we just look at the difference among the sites and contrast them to the wet deposition data where there is a fairly uniform pattern across the state, what you have here is a tremendous range geographically in the levels that you see, two orders of magnitude. In terms of these particular species, particulate nitrate in all cases is a relatively small component. NO_2 and nitric acid are the larger components at all the sites. Which dominates depends on the site; I think it is important to remember that these are urban sites, these are in-source regions. NO_2 concentrations are certainly higher than would be indicated at someplace like Barton Flats. At several of the sites, nitric acid is clearly the dominant contributor, even keeping in mind our factor of 2 errors or uncertainty. This highlights the importance of accurate nitric acid measurements. Figure 14 is a closer look at the three rural sites, Gasquet, Sequoia, and Yosemite. I tried here to provide a comparison of the wet to the dry deposition fluxes for sulfur and nitrogen. What I referred to as oxidized sulfur species in the wet deposition is of course sulfate; in the dry, it is the sum of deposition due to SO_2 and particulate sulfate. In the case of wet, oxidized nitrogen is nitrate; dry is the sum of the three species you saw in the preceding graph, namely particulate nitrate, NO_2, and nitric acid.

The lesson that I want to draw here is that it is not true that dry deposition exceeds wet deposition throughout California at these rural sites. While Gasquet looks like it is higher than the other two, about half of the sulfur in wet deposition is contributed by sea salt. Even with factor of 2 errors on these dry estimates, we still see that they are probably about the same magnitude as the wet.

Now the picture changes when we look at the urban sites (Fig. 15). Here we have six sites, and I am trying to not only provide a comparison of the wet and the dry, but also of these numbers in relation to emission densities in the air basin where the sites are located. First consider the emission numbers. Fremont is in the Bay area, and this is the emission density for NOx in the San Francisco Bay area. Long Beach, Los Angeles, and Azusa are all in the South Coast Air Basin, so that represents the emission density for NOx in the South Coast Air Basin, followed by the emission density for NOx for the San Joaquin Valley and for the Sacramento Valley. In contrast to our rural sites, the wet deposition numbers are much smaller than the dry deposition numbers, certainly much smaller than the emission density. Dry deposition numbers in relation to the emission densities, are probably sensible numbers even though I am calling them factor of 2 uncertain. If we look at the sites in the south coast air basin, Azusa's dry deposition rate for oxidized nitrogen species is roughly 60% of the emission rate, which is pretty consistent with the notion that we could be exporting a certain amount of NOx reaction products out of and beyond Azusa. Bakersfield and Sacramento are interesting because the calculated dry deposition numbers exceed the emission densities. It is probably not true that these are the emission densities for the whole San Joaquin Valley and the whole Sacramento Valley, since these sites are in the urban areas. Perhaps it would be instructive to compare these deposition rates to the emission densities of the counties in which those sites were located.

My personal evaluation of the dry deposition network is shown in Figure 16. First, it has provided so far numbers which are indicative of the magnitude of wet deposition. These are subject to the idea that we probably have a factor of 2 uncertainty. The data base itself certainly has some potential utilities for identifying trends if the focus is on the ambient concentrations. One would not want to confuse the trend analyses with the modeling in the dry deposition by looking at trends in the dry deposition rate. We would want to look at the ambient concentration itself; there are 3½ years of data validated and another 3 years or so available soon. There is a real need to resolve nitric acid measuring difficulties because it is such a large component of the nitrogen deposition. It is important to have those measurements more carefully characterized in terms of inaccuracies. Why is more not said about this? My opinion is that there is a need to evaluate the accuracy of the inferential method. It has been evaluated by comparison to micrometeorological measurements, by means of which fluxes are computed at various locations, almost all of which are in the eastern United States. It is that particular set of comparisons that has led to the general assessment that the inferential method is accurate to about 30-50%. However, we have not seen any of those of comparisons. It was particularly interesting this morning to see the consistency in the comparison between Andrzej's experiments and the product of this particular model. However, in my opinion, there is still a need to really evaluate the accuracy of the method.

Finally, my last point is that one needs to consider the network in relation to the future objectives for the network. There are only 10 sites there, covering an enormous geographical range. How is one to try to extrapolate from those sites to the state as a whole? It is a particularly difficult problem.

Q (DR. PITTS) I have one question or just a statement. Is there any place in the literature that this information will be applied to existing CADMP data that people are using? Will people have access to the information that you generate here?

A (DR. BLANCHARD) It is a great idea.

Q (DR. PITTS) I think that it is an idea whose time has come, because I am kind of tired of people using data from the data set of those end models and coming out with something before this thing fits. It seems to me that we should consider several things that we used to apply years ago . There is an uncertainty in the model, and then there are these data. How is the information coming out of that model? Maybe that is something to consider in the future efforts.

Figure 1

SUMMARY AND EVALUATION OF CALIFORNIA ACID DEPOSITION MONITORING PROGRAM (CADMP) DATA

CHARLES L. BLANCHARD
ENVAIR

AAPP WORKSHOP
JANUARY 26-27, 1995

Figure 2

OBJECTIVES OF CADMP MONITORING

- QUANTIFY RANGE OF CONCENTRATIONS AND DEPOSITION
- PROVIDE DATA FOR EFFECTS STUDIES
- PROVIDE DATA USEFUL FOR IDENTIFYING CONTRIBUTING EMISSION SOURCE REGIONS
- IDENTIFY POSSIBLE TRENDS OVER TIME

NOT OBJECTIVES:

> RESEARCH ON ATMOSPHERIC PROCESSES

> COMPLIANCE MONITORING

Figure 3

CADMP WET DEPOSITION SAMPLING

- SAMPLER: AEROCHEM METRIC AUTOMATED WET-DEPOSITION
- SAMPLING PERIOD: WEEKLY
- PERIOD OF RECORD: JUNE 1984 - JULY 1990
- QA/QC PROTOCOLS

  > CHARGE BALANCE
  > CONDUCTANCE
  > ION RATIOS
  > RE-ANALYSIS

Figure 4

WET DEPOSITION DATA ANALYSES: METHODS

- SAMPLING COMPLETENESS
    - > TIME
    - > PRECIPITATION AMOUNT
- ANNUAL AND SEASONAL AVERAGES
    - > CONCENTRATION (DEPTH-WEIGHTED)
    - > DEPOSITION
- SPATIAL INTERPOLATION: KRIGING
    - > CADMP AND NADP/NTN CONCENTRATIONS
    - > PRECIPITATION AMOUNT ~500 NWS SITES
    - > CROSS-VALIDATION

Figure 5

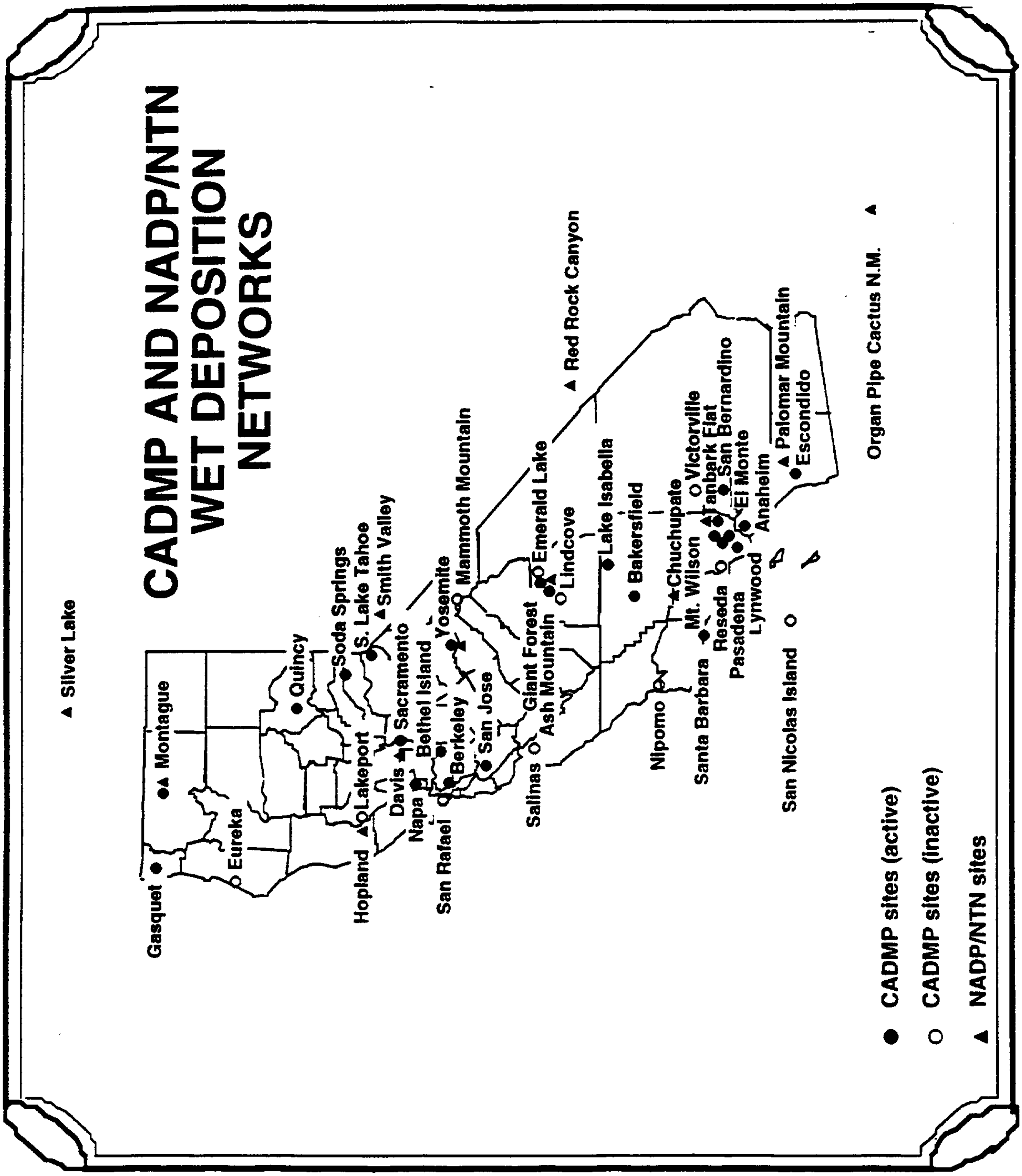

CADMP AND NADP/NTN WET DEPOSITION NETWORKS
Silver Lake
Gasquet
Montague
Eureka
Quincy
Soda Springs
S. Lake Tahoe
Smith Valley
Hopland
Lakeport
Davis
Sacramento
Napa
Bethel Island
San Rafael
Berkeley
San Jose
Yosemite
Mammoth Mountain
Salinas
Giant Forest
Ash Mountain
Emerald Lake
Lindcove
Red Rock Canyon
Lake Isabella
Bakersfield
Nipomo
Santa Barbara
Mt. Wilson
Chuchupate
Reseda
Pasadena
Lynwood
Victorville
Tanbark Flat
San Bernardino
El Monte
Anaheim
Palomar Mountain
Escondido
San Nicolas Island
Organ Pipe Cactus N.M.
● CADMP sites (active)
○ CADMP sites (inactive)
▲ NADP/NTN sites

Figure 6

Figure 7

SUMMARY OF WET DEPOSITION AMOUNTS

- MAXIMA:
  - SULFATE < 7 kg / ha - yr
  - xs SULFATE < 3 kg / ha - yr
  - NITRATE < 8 kg / ha - yr
  - AMMONIUM < 3 kg / ha - yr
- EASTERN U.S.:
  - SULFATE > 25 kg / ha - yr
  - NITRATE > 15 kg / ha - yr
  - AMMONIUM < 4 kg / ha - yr
- TARGET LEVELS IN OTHER LOCATIONS:
  TOTAL OR xs SULFATE 10 - 20 kg / ha - yr
- UNCERTAINTIES: 20% - 2X

Figure 8

EVALUATION OF
CADMP WET DEPOSITION NETWORK

- QUANTIFICATION OF WET DEPOSITION AMOUNTS (+/- 20% TO 2X)
- NEED FOR SITE-SPECIFIC INFORMATION FOR EFFECTS STUDIES
- UTILITY FOR LINKING SOURCE TO RECEPTOR REGIONS INCOMPLETELY EXPLORED
- POTENTIAL UTILITY FOR IDENTIFYING TRENDS, BUT NONE EVIDENT TO DATE
- FUTURE OBJECTIVES?

Figure 9

CADMP DRY DEPOSITION SAMPLING

- DRI SAMPLER

  > TWO 12-HOUR SAMPLES
  > PM10, PM2.5, GAS-PHASE
  > HNO3: FILTER-PACK
  DENUDER DIFFERENCE

- SAMPLING PERIOD: ONCE PER SIX DAYS

- QA/QC PROTOCOLS

  > PM10 VS. PM2.5 CONCENTRATIONS
  > MASS VS. SUM OF SPECIES
  > CHARGE BALANCE
  > COMPARISONS TO OTHER MEASUREMENTS

Figure 10

CADMP DRY-DEPOSITION DATA QUALITY

- PERIOD OF RECORD: FEB 1988 - SEP 1990
- SYSTEMATIC ERRORS CORRECTED
- PM10 MASS AND CONCENTRATIONS SIMILAR TO COLLOCATED PM10 MONITORS
- DECREASE IN DENUDER DIFFERENCE HNO_3 AT LOS ANGELES AND AZUSA
- HNO_3 INTERCOMPARISON (AZUSA, 1993)
    - > PRIMARY/COLLOCATED DENUDED PARTICULATE NITRATE ~ 1.6
    - > CADMP/TDLAS ~ 0.6
    - > SCAQS/TDLAS ~ 0.7

Figure 11

CALCULATION OF DRY-DEPOSITION FLUXES

- MEASUREMENTS

  > AMBIENT CONCENTRATIONS
  > METEOROLOGICAL PARAMETERS

- INFERENTIAL METHOD

  $F = C * V_d$

- LIMITATIONS

  UNCERTAINTIES ~ 50%

Figure 12

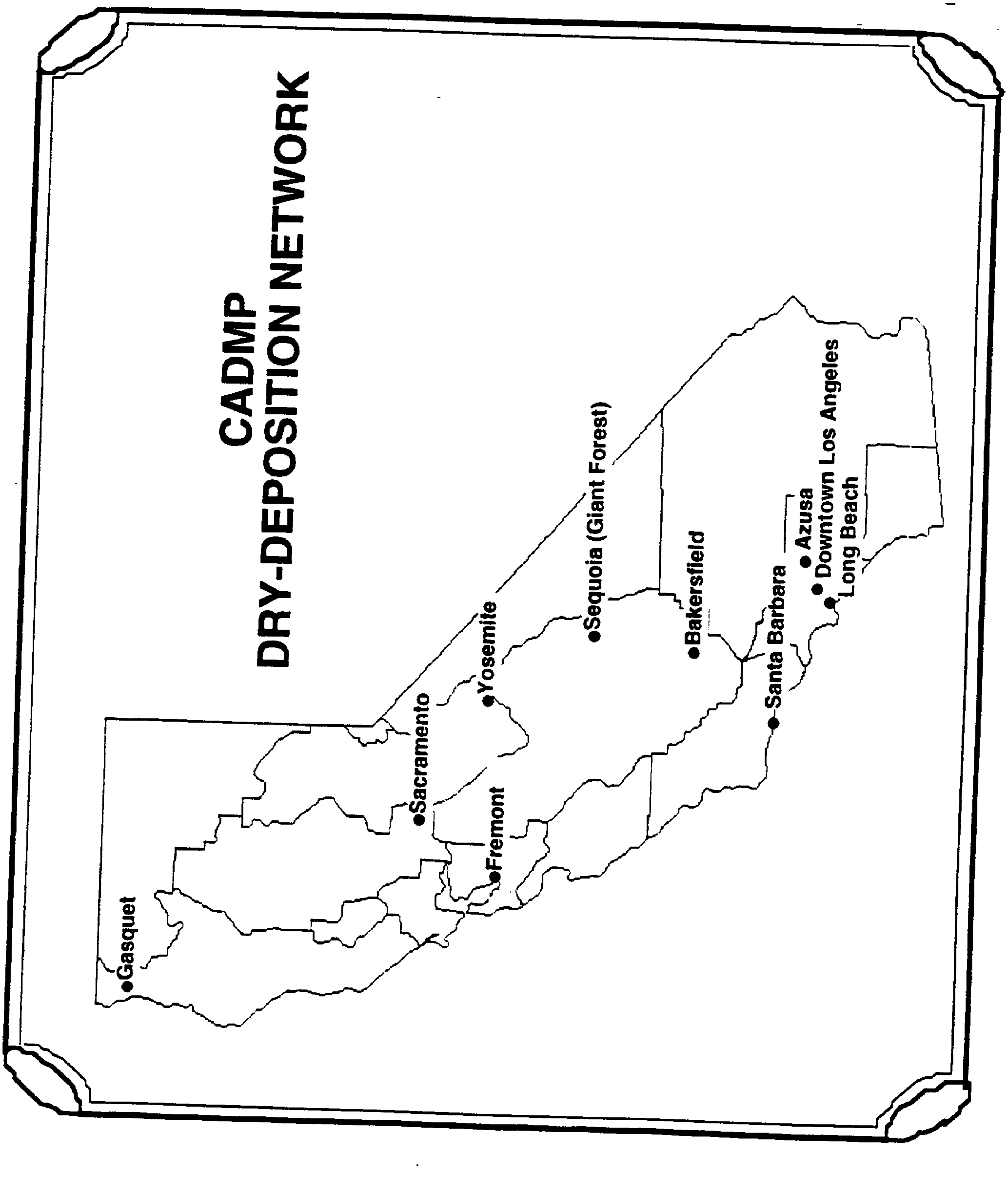
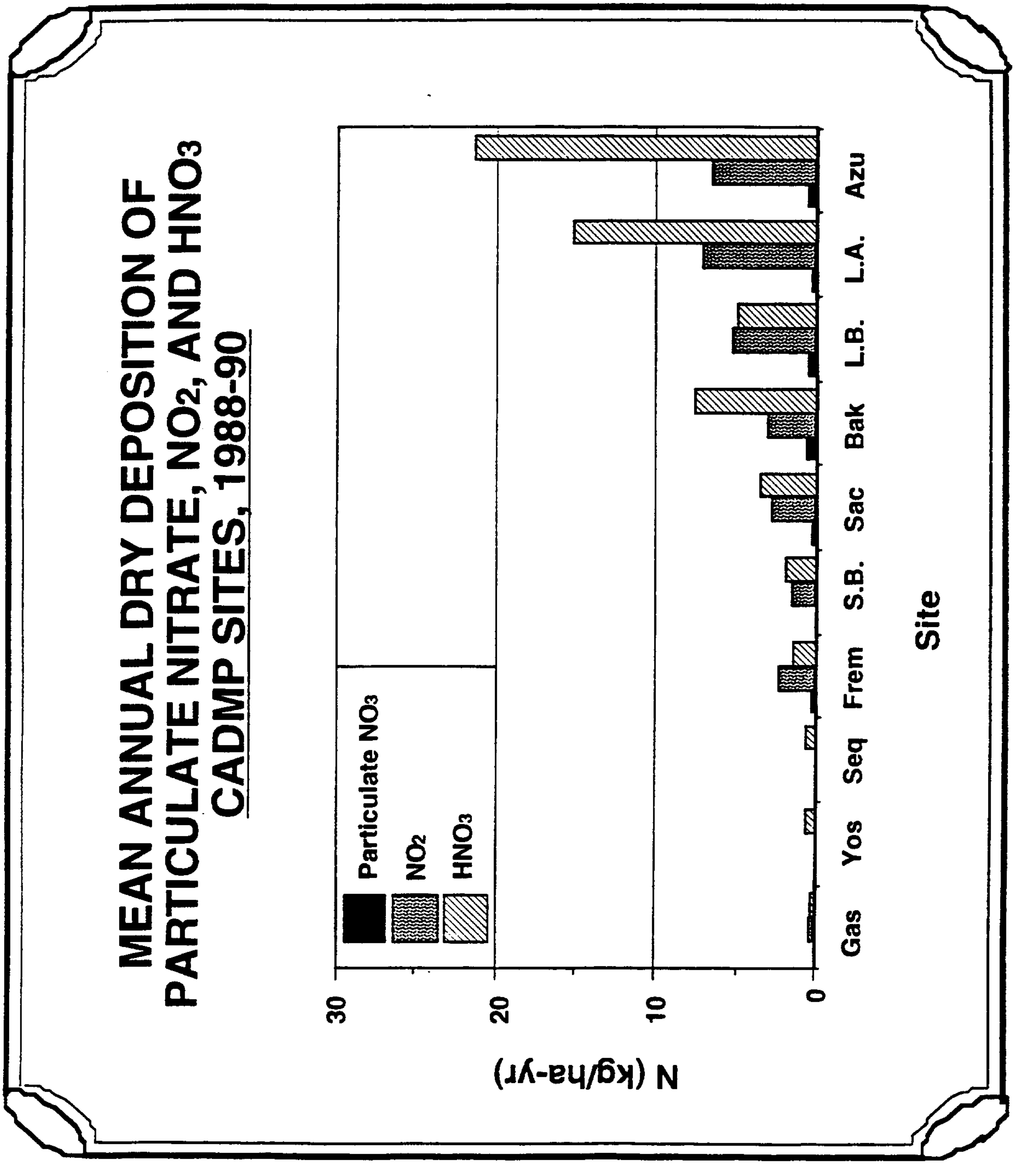
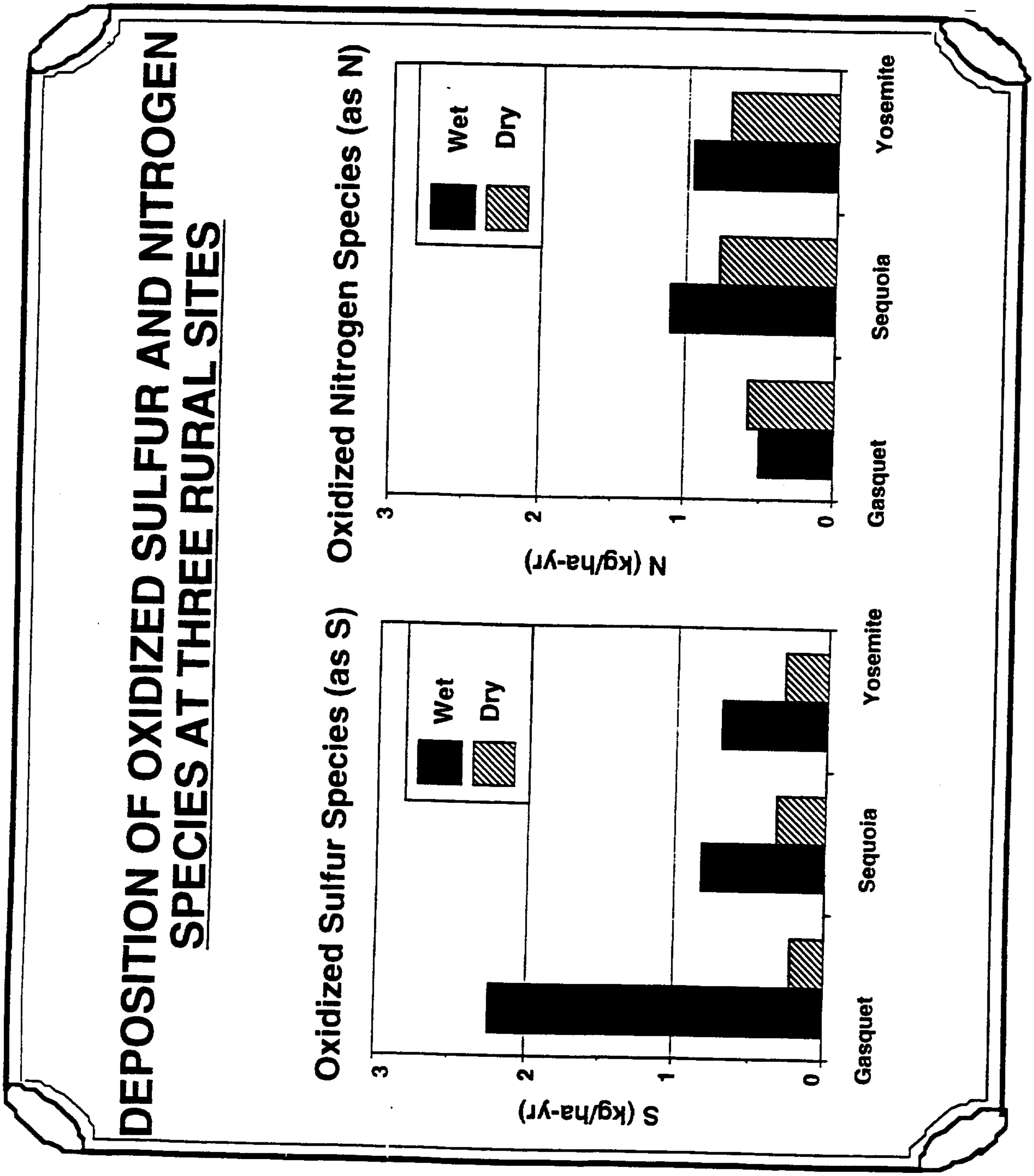

CADMP
DRY-DEPOSITION NETWORK
Gasquet
Sacramento
Fremont
Yosemite
Sequoia (Giant Forest)
Bakersfield
Santa Barbara
Azusa
Downtown Los Angeles
Long Beach

Figure 13



MEAN ANNUAL DRY DEPOSITION OF PARTICULATE NITRATE, NO_2, AND HNO_3 CADMP SITES, 1988-90

Figure 14



DEPOSITION OF OXIDIZED SULFUR AND NITROGEN SPECIES AT THREE RURAL SITES

Figure 15

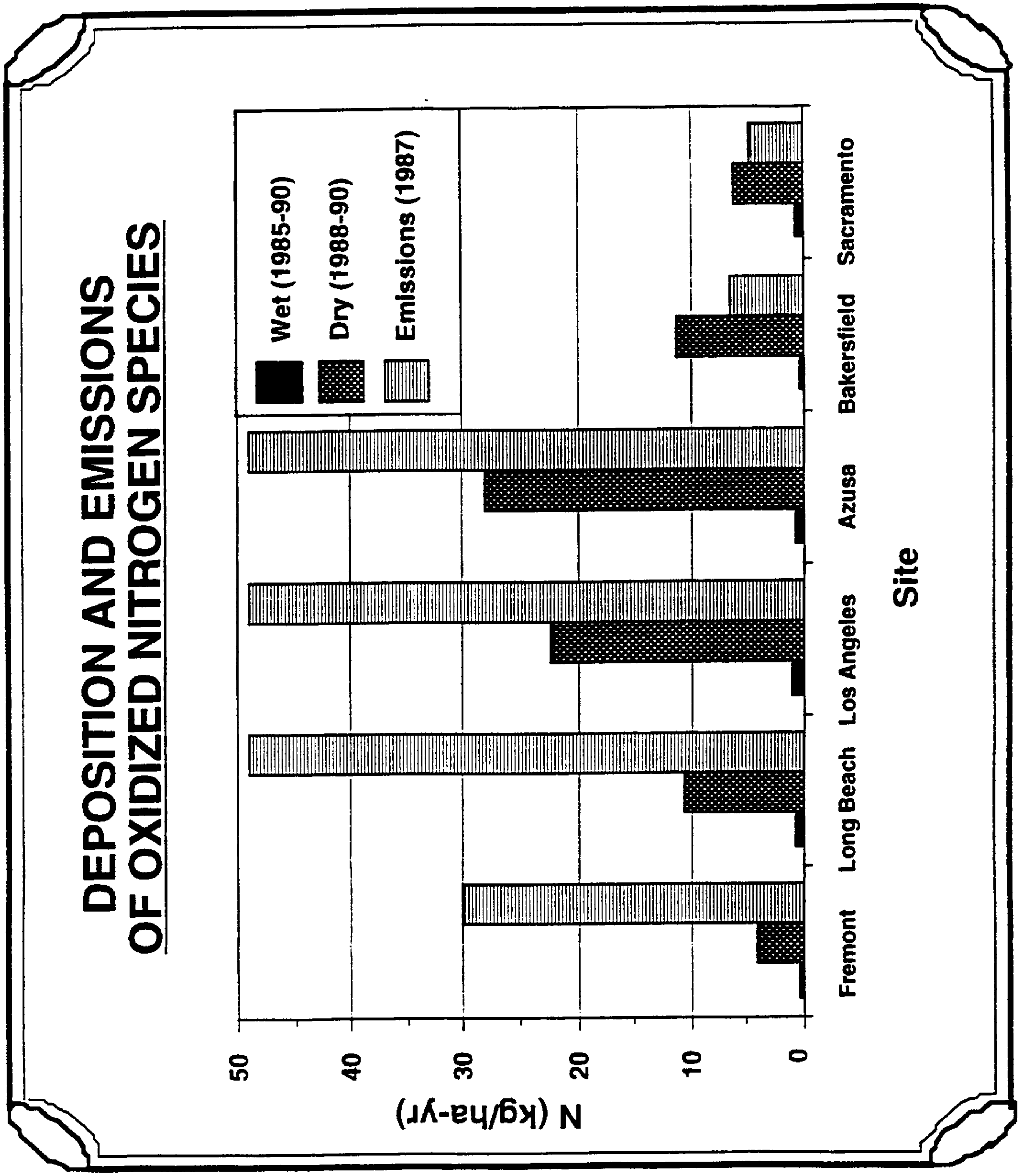

DEPOSITION AND EMISSIONS
OF OXIDIZED NITROGEN SPECIES
Wet (1985-90)
Dry (1988-90)
Emissions (1987)
N (kg/ha-yr)
50
40
30
20
10
0
Fremont
Long Beach
Los Angeles
Azusa
Bakersfield
Sacramento
Site

Figure 16

EVALUATION OF CADMP DRY-DEPOSITION NETWORK

- INDICATIVE OF MAGNITUDES (FACTOR OF TWO UNCERTAINTIES)
- POTENTIAL UTILITY FOR IDENTIFYING TRENDS FROM AMBIENT CONCENTRATIONS
- NEED TO RESOLVE HNO_3 MEASUREMENT DIFFICULTIES
- NEED TO EVALUATE ACCURACY OF THE INFERENTIAL METHOD
- NEED TO CONSIDER THE NETWORK IN RELATION TO FUTURE OBJECTIVES

DR. NEHZAT MOTALLEBI: Moderator

The topic of our next presentation is "Evaluation of Sampling Methodology for Acidic Species" presented by Mr. Dennis Fitz of CE-CERT, UC Riverside.

2. Evaluation of Sampling Methodology for Acidic Species, Dr. Dennis Fitz, CE-CERT, UC Riverside.

MR. DENNIS FITZ: CE-CERT, UC Riverside

We are trying to develop a new generation of samplers for acidic species, one that will give us more accurate results and hopefully one that will be easy to use out in the field, and may be even cheaper to operate (Fig. 1). The basic outline of my presentation is shown in Figure 2. I am going to define the species that we are interested in measuring and summarize some of the methods that are currently used. I am going to review some of the new filter artifact data that we collected in Riverside last October which is going to help us design the new type of sampler. I am going to present the new measurement approach and some of the work that we have been doing to evaluate it. We have a new type of denuder near completion, and I am going to show you some of the results that we are getting from that. Then since this is a mid-term report, I am going to conclude with mention some of the remaining work that we need to do.

The basic species of interest are shown in Figure 3. We are talking about acidic species here, but we have to include ammonia because it is going to affect what happens with all these acids. Basically, we are looking at particulate nitrate, its gas phase analog, nitric acid, nitrite (which we find is fairly important), its analog nitrous acid, ammonium, ammonia, acetate, and formate, with the associated acetic acid and formic acid which are in very high concentrations too. Sulfate does not really have a gaseous analog because the sulfuric acid would be a particulate.

Figure 4 outlines the current routine sampling technologies. Now there are some very specialized methods. If you go out in the field with a tunable diode laser, and if you have enough money, you can get data on some gas species for one site for maybe a few months. We want to look at the routine technologies. We really do need to collect a lot of data. With nitrate, the basic method is to remove the nitric acid vapor first because of the equilibrium of ammonium nitrate between nitric acid and ammonia. You have to remove the nitric acid first, then you use a specialized filter to sample the particulate nitrate. With ammonium, usually just the filter is used; this is done because there is typically a lot more non-volatile ammonium sulfate around. However, in a place like the Los Angeles area, we are finding that there is not that much sulfate, so we really do need to use the denuder approach for ammonium just as we do for nitrate. Acetate and formate, if there is any, is usually picked up on a filter. Nitrite is really tough to measure because it is usually oxidized to nitrate before we get it to the laboratory. We do not see a lot of this being reported, and many do not even analyze for nitrite. They just do a typical nitrate analysis. They are probably using a wet chemical method and do not even see the nitrite and sulfate.

The denuder is usually used to measure nitric acid. We have heard about the filter pack which I do not even really consider. I do not think that it is a good measuring method at all, especially in this area. The denuder method can be used in a direct mode where you actually extract the denuder coating material and analyze it for nitrate, or you can use the denuder difference method, and that is used on the CADMP sampler. By taking difference of two measurements, you can calculate the nitric acid. The data are subject to much more error because there are two measurements and a subtraction of large numbers. If you are getting a small difference, you can very easily have a 50% error.

Ammonia analysis usually requires a specialized back filter which quantitatively adsorbs the ammonia. Some people use the denuder, but typically that is not done. It was done during SCAQS, and it was found to be necessary.

Acetic acid and formic acid are usually at the back filter. It is coated with potassium carbonate or potassium hydroxide, a strong base to adsorb the acids. Nitrous acid is generally measured using a direct denuder method. Figure 5 shows that basic sampler types that we use now, and some of their attributes. The direct denuder has good specificity and sensitivity. The maintenance is complicated, and it is fairly costly. It is very difficult to maintain a system out in the field because of the cost of the equipment.

The denuder difference method has pretty good specificity but so-so sensitivity, because you are taking a difference. The cost of maintaining it and building it is moderate. The filter pack of course has poor specificity but good sensitivity, and it is cheap, but I do not even want to use that one at all.

This is the basic CADMP sampler (Fig. 6). As you can see it is fairly complicated. Do not look at all of the little pieces of it, what is important here is that it is a complicated sampler. It has a lot of sample lines, a lot of filter packs, and a lot of things that can go wrong. The lines have to be maintained so that it will pass nitric acid. Usually these are washed with dilute nitric acid, so you can get a good efficiency of nitric acid going through the sampler. This does not even sample ammonia by a denuder method or any other method.

When I first started working with the Air Resources Board in devising a new sampler, I proposed what is shown in Figure 7 and it would do just about everything. However, this design is going to be another complicated sampler with many filter packs and inlet systems. We really did not want to do that. We had a better idea. Our goal was to design and evaluate an inexpensive and easily serviced direct denuder type sampler for these acidic species (Fig. 8). This is what we really need to do, and in this way we can get rid of the complicated design.

Before I get into that, I want to show some of the results that we got from sampling in October in Riverside (Fig. 9). Some of it is a little bit surprising. We know that carbonate filters have an artifact. They collect nitrous acid and it probably oxidizes, so you get a lot of nitrate. These are just open faced filters, with Teflon front filters, so you are just sampling gases. When we put three of these carbonate impregnated quartz filters in a row, we got quite a bit of nitrate on the top one, we got a lot on the second, and we got a lot on the third. This is because nitrous acid is not quantitatively picked up by the filter. It is ending up on the second, fourth, and successive filters. Then we used sodium chloride which is really the most accepted way to do it. We got a huge difference. Remember this is in Riverside. We probably have fairly high concentrations of nitrous acid. This was October so this is probably a little bit out of the ordinary, but it serves to show what kind of artifacts you might be observing when you choose the wrong coating material. There was still a little bit on the second and third (NaCl coated and nylon) ones, and we are not really sure to what that is due. We can show in the laboratory that these quantitatively remove all the nitric acid. With nitric acid removed, something else was still picked up, and that is one the things that we are going to look into.

Now here is a real surprise (Fig. 10). As the control, we just used nylon filters. Nylon filters are supposed to be very specific and quantitative for nitric acid. We got a lot on the back filter. We think that during these 24-hour collections, nitrous acid was picked up. Nylon has some affinity for collecting nitrous acid. Its variable and depends on temperature, humidity, and a lot of other factors. But these results were really a surprise, nylon filters are not necessarily that specific for nitric acid. We were sampling particle-free air, so we were just looking at nitric acid and other vaporous nitrogen containing species. It appears to be a shot gun pattern. There does not seem to be any relationship, and if we collected more data, we would probably find out it was just a pure shotgun pattern. There is really no relationship.

We also looked into collecting formic acid and acetic acid, again using a Teflon front filter to remove particles (Fig. 11). We had a pair of hydroxide impregnated filters, and with formate, we had absolutely nothing on the back filter. We had 13 collections there and not one of them was above the detection limit for this study. We always found a fair amount of acetate on the second filter. Something is getting through even though it is not acetic acid, which is quantitatively removed by that filter. It could be the decomposition of PAN. If we plot the acetate in a little more detail (Fig. 12), there definitely is a relationship here. The bottom one is a lot lower of course, but there is definitely a relationship. It seems like there is an intercept, so the two are probably related somehow.

Now, I would like to get into what the new sampler is going to look like (Fig. 13). The top part of the figure is just the plumbing. Let us get into the sampler is itself. This is basically a 47 millimeter open face filter holder with the inlet at the bottom of the figure. The air comes in, and across the denuders. These are very small denuders. This is a new type of denuder that we are developing. It is essentially like a filter. You can put it right in a filter pack, and you can stack a number of them together. The first one is a sodium chloride coated denuder. That will remove the nitric acid. The next, which are actually two, are sodium carbonate coated denuders. These remove nitrous acid and organic acids, but remember those are not removed quantitatively. We need a backup filter to measure how much of this is really due to some of these other artifacts. The next denuder is the ammonia denuder, which is coated with a citric acid. Now the third one is one that you do not see very often. We are trying to see if we can actually capture the particle nitrite as nitrite. This is a denuder that will remove the ozone. A potassium coated denuder, which is what we are going to try first, should work. That means if you have nitrite that makes it through, it is going to stay as nitrite since it will not tend to be oxidized by the ozone. This is something new and we do not know if it is going to work, but we are giving it a try. On the Teflon filter, you collect all your usual particulate sulfate, nitrate, ammonium, and measure mass. The back filters are pretty standard among denuders. You have a sodium chloride coated filter which will trap any nitric acid which is vaporized off of this filter. A citric acid coated filter will trap any ammonia which is vaporized from the Teflon filter. Whether we can put all of these in one filter holder or not, we are not sure, but at least it is a start. We may need two filter holders like this, but the key is, instead of having a complicated big system, we have contained in one filter holder everything we need to do the complete analysis. It is a direct denuder approach. You do not have the take the difference of anything.

The first question is, will this work? I am calling this the CE-CERT denuder for lack of a better word for right now (Fig. 14). It is very compact, and you can treat it like a filter. You do not need a special housing. You do not need to laminarize the flow. It is very simple so you do not have to have a big inlet system in the front. It has good theoretical particle penetration. We are testing penetration right now, and we do not yet know what the answer is. It is very inexpensive; they are throw away. They will cost you a dollar or so. You can coat it with any kind of material you want, and it holds a fair amount of coating so you should not be limited by the amounts that you sample. You should be able to sample for more than 2-3 days if you want it to.

We had to test this denuder, and we used a standard type of system. We tried nitric acid first, and we actually tried it under the worst conditions possible (Fig. 15). We were using about 35 ppb nitric acid under fairly dry conditions of 10-15% relative humidity. This is a basic test set up. We had zero air coming through, and a bubbler to humidify it. We sent some zero air through a permeation tube that had nitric acid in it, and then we had the major flow which was just the dry air. Everything then mixed, and we took off the excess. We put the test denuder in and we had a pump to control the flow. This can control anywhere from a ½ liter a minute to 20 liters a minute. Then, we sampled with a NOx analyzer. We put the converter right up front; it is actually outside of the instrument, so we could avoid any losses in the line and through the instrument. Once it goes through that, it is just NO, and easy to deal with. This was actually the first time we tried a sodium carbonate coated denuder. Figure 16 shows the removal efficiency, and at 600 ml a minute, it is virtually 100%. Now it is real hard to tell if it is exactly 100%, because you are looking at a very small amount going into the NO_x analyzer. You are right around the detection limit and it might be about 0.5 ppb going into the NOx analyzer for detection. However, it is essentially 100%. It does drop down with increasing flow rate. This is not what I predicted. At 10 liters a minute, we are still at 92%. Now if you take two of these filters, and put them together, you get the expected result. We put two in series, and it is 100% right across the board, up to 19 liters a minute where it dropped down to about 98%. So, two of these denuders take out nitric acid.

The results from the sodium chloride coated denuder are shown in Figure 17. We really want to use the sodium chloride denuder, but we had problems with it and we are still trying to resolve them. I am calling this the Type I denuder. We have several different types of substrates. With 9% coating, I tried to maximize the amount of sodium chloride on it. When we put this in dry nitric acid at low flow rates, it worked well. We got 90% efficiency. It took awhile to stabilize, and we still have not figured out why. We raised the flow rate, and the efficiency was only about 70-80%. It stayed there for awhile and then started to drop, which is a problem. Then we tried putting two in a row, figuring, we should get some better results with that, and it did help. It brought up the efficiency to 97% right away, but at 19 liters a minute, it went up to 86% and then dropped off. We tried to use other substrate types, and we got good efficiency at first, but these substrates, while they had a better physical design, did not adsorb as much of the coating solution, so it would drop off in a few minutes. Clearly, we are close on sodium chloride. We may actually be able to use sodium chloride under normal ambient conditions, because we are really hitting it with about the highest nitric acid you will see under the driest conditions, which is really the worst case.

Right now, we are doing some testing to see what we do next (Fig. 18). This is to test the particle penetration. We are doing this in ambient conditions using standard 47 millimeter filter holders. We are going to look at the sulfate on each one of the Teflon filters, and this will give us a measure of particle penetration under actual ambient conditions. Part of the problem is that we tried to sample during the last month, and we have had nothing but rain for the last three or four weeks. As soon as the weather clears up, maybe we can actually run a few samples. We have run three of these so far, but we really do need to see what the particle penetration is. We also want to see how well this denuder works under actual ambient conditions. Wintertime is not the best time to be doing it, but it is all we have. We will get a measure of how well the denuder works by using a reference. It is a Teflon filter followed by two nylon filters. I want to collect more data to see if what we call the nitrous acid problem is showing up on the second nylon filter.

Figure 19 shows the conclusions. We passed the first big hurdle. The basic denuder concept really works. We know that sodium chloride is the choice for doing nitric acid. It seems to work the best, but we do have some collection difficulties with it right now.

But what are we going to be doing with it in the future (Fig. 20)? We are going to test particle penetration and then figure out how to solve the sodium chloride collection problem. We might be able to throw in a few more denuders if particle penetration is not a problem. We can test some more denuder substrates, and we can look at other coatings. There are some other chlorides, for example, that have been used. Maybe it will work in ambient air because the concentration typically would not be as high, and you have more humidity, especially in the Los Angeles area. Once we pass this hurdle, we have to look at the penetration of all the other species through the filter denuder set-up that I showed you at first. We are going to look at HONO, PAN, acetic and formic acids, ammonia, and ozone penetration through the sampler. Finally, we will hopefully get all of the remaining problems solved in the next six or seven months. We want to do a field test that has actual spectroscopic methods of determining nitric acid, formic acid, and ammonia. We will use an FTIR and tunable diode laser. That is where we are right now.

Q (AUDIENCE) Dennis, I know you are also evaluating the CADMP sampler. I think it would interesting if you describe some of the results you found from that.

A (MR. FITZ) That was actually done, but when we went over the subject of the penetration, it kind of fell by the way side. I have done some of the work. We fabricated a Teflon plenum to put around the inlet of the CADMP in the field, and then attached Teflon filters to this plenum so we could use the CADMP sampler to pull ambient air and remove the particles. We were looking for nitric acid or any other vaporous acid. This was done with the co-located sampler that was used in Azusa for about a year without being cleaned during that period. We found small losses of nitric acid of about 15% through the inlet assembly. We also found that the denuders seemed to work well, with over 90% efficiency. When we ran it in the day, we got those results. When we ran it at night, we got some very strange results, and again I think it was nitrous acid. We did not get the 90% efficiency in the denuder. It was variable. It was anywhere from 20% to maybe 70% or 80%. We are not looking at collecting more nighttime data right now. Basically, for collecting nitric acid in the daytime, it is still working after a year and still looking fine.

Q (DR. PHALEN) On the part of the penetration data, I would expect that would be very strongly particle size dependent, so how will you search the limits of upper and lower bounds of particles size for penetration?

A (MR. FITZ) Well you could do it in the laboratory and go through all kinds of particle sizes, or you can do what we are going to do, ambient air containing something like sulfate is going to have particles in the 0.4 to down to maybe 0.2 or smaller in that normal ambient size range. That is where the nitrate particles are going to be too. We are going to do a comparison on the real world rather than go to the laboratory where it would probably take us a couple of months to generate all the particle sizes, and analyze various filters.

Q (AUDIENCE) Is there hydrochloric acid, coming off the sodium chloride in the denuder?

A (MR. FITZ) There should not be.

Q (AUDIENCE) Why not?

A (MR. FITZ) What you are going to get is sodium nitrate. Oh, I guess there would be. It was the nitrate that is not coming off. That is why you cannot use this to measure chloride with and that is one of the reasons that in some samplers in which you do try to measure chloride, you cannot use sodium chloride. It is bad enough having the chloride there, but it is going to come off as HCL.

Q (DR. KLEINMAN) I have got two questions. One, is there another way you can stop the acidity? Do you have spacers between these filters?

A (MR. FITZ) We will find out if it is necessary. Now basically we are using established filter holder with the standard Teflon spacers, but we are stacking them up in a bigger Teflon nut.

Q (DR. KLEINMAN) I found with particle penetration studies that if you layered the filters one on tope of the other you ended up with a thick filter and the particles could diffuse through from the top into the bottom. I assume gases could do the same thing. I think a spacer tends to change the dynamics of the situation. You might find that you do get some differences.

A (MR. FITZ) We would rather not use spacers because they are difficult to fit in there.

Q (DR. KLEINMAN) The other comment is, that we find some of commercially available nylon filters that were carbonate impregnated to improve nitric acid adsorption were different from batch to batch. You may want to check your supply differences.

A (MR. FITZ) You might want to have it analyzed. That would explain what we saw.

Figure 1

EVALUATION OF A SAMPLING METHODOLOGY FOR ACIDIC SPECIES

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(CE-CERT)

UNIVERSITY OF CALIFORNIA
RIVERSIDE

PRESENTED AT THE AAPP ASSESSMENT WORKSHOP
JANUARY 26, 1995
COSTA MESA, CALIFORNIA

Figure 2

OUTLINE

- DEFINE SPECIES, SUMMARIZE METHODS
- REVIEW NEW FILTER ARTIFACT DATA (RIVERSIDE)
- PRESENT NEW MEASUREMENT APPROACH
- DESCRIBE NEW DENUDER AND EVALUATION
- CONCLUSIONS AND REMAINING WORK

Figure 3

SPECIES OF INTEREST

PARTICLE	GAS
NITRATE	NITRIC ACID
NITRITE	NITROUS ACID
AMMONIUM	AMMONIA
ACETATE	ACIDIC ACID
FORMATE	FORMIC ACID
SULFATE	

Figure 4

CURRENT ROUTINE SAMPLING TECHNOLOGIES

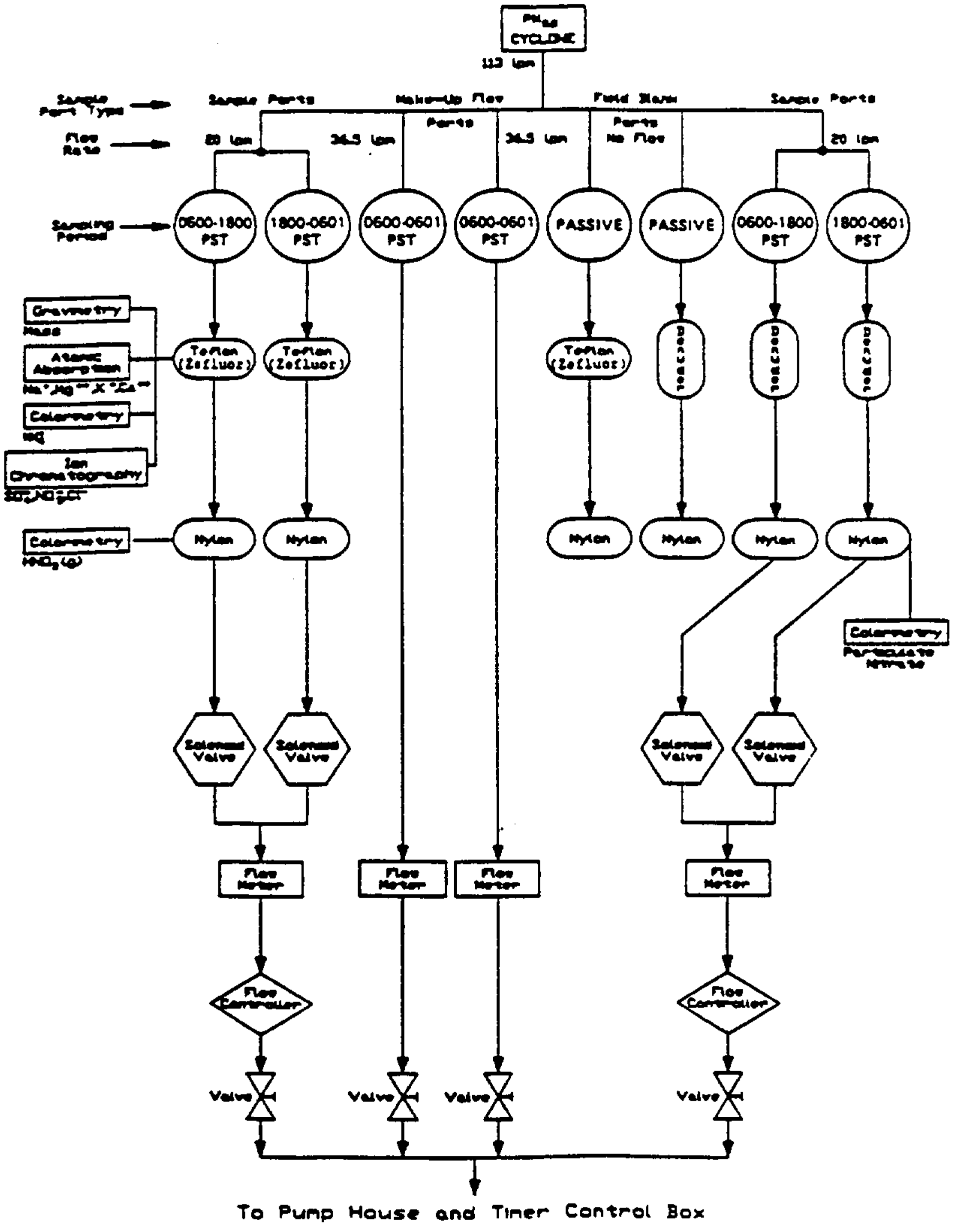
SPECIES	METHOD
NITRATE	REMOVE NITRIC ACID VAPOR, SPECIAL FILTER
AMMONIUM	FILTER (SOMETIMES DENUDER)
ACETATE	FILTER
FORMATE	FILTER
NITRITE	FILTER
SULFATE	FILTER
NITRIC ACID	DENUDER(DIRECT OR DIFFERENCE)
AMMONIA	SPECIAL BACK FILTER (SOMETIMES DENUDER)
ACETIC ACID	SPECIAL BACK FILTER
FORMIC ACID	SPECIAL BACK FILTER
NITROUS ACID	DENUDER (DIRECT)

Figure 5

EXISTING SAMPLER TYPES

ATTRIBUTE	DIRECT DENUDER	DENUDER DIFFERENCE	FILTER PACK
SPECIFICITY	GOOD	GOOD	POOR
SENSITIVITY	GOOD	MODERATE	GOOD
MAINTENANCE	POOR	MODERATE	GOOD
COST	POOR	MODERATE	GOOD

Figure 6



Sampling and measurement flow diagram for the CADMP $PM_{2.5}$ unit.

Figure 7

Schematic Drawing of the Proposed Acidic Species Sampler-PM2.5

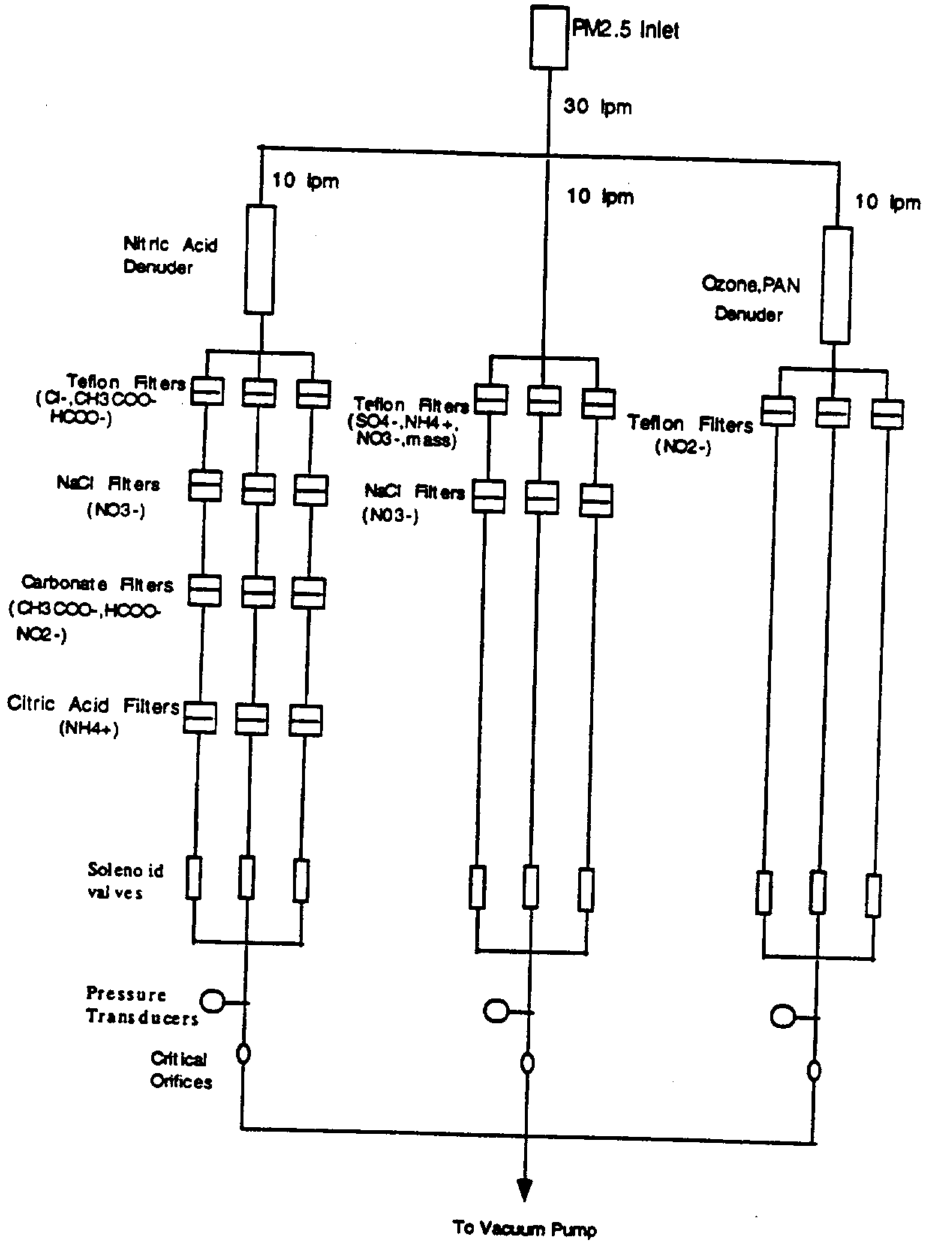


Figure 8

PROJECT GOAL:

DESIGN AND EVALUATE AN INEXPENSE AND EASILY SERVICED DIRECT DENUDER TYPE SAMPLER FOR ACIDIC SPECIES

Figure 9

NITRATE SAMPLING-RIVERSIDE

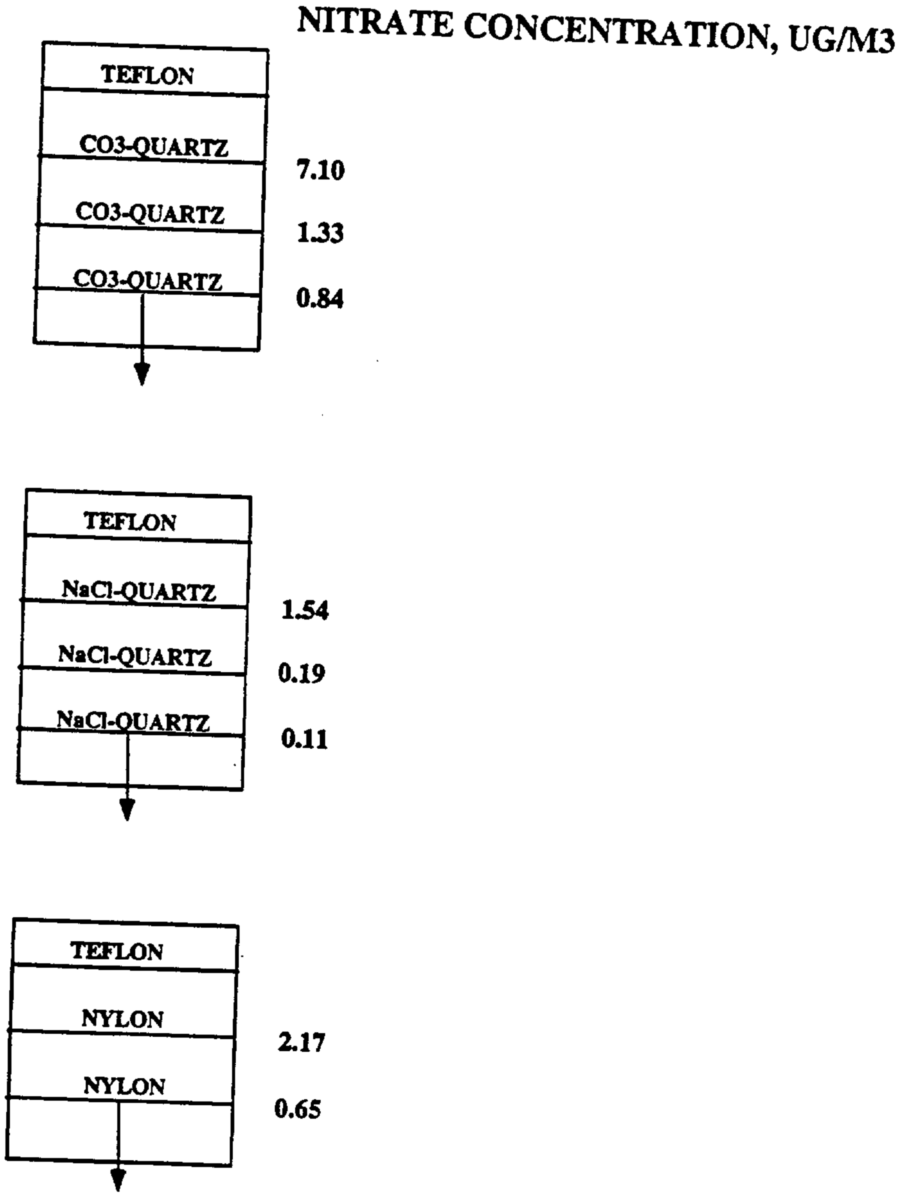


Figure 10

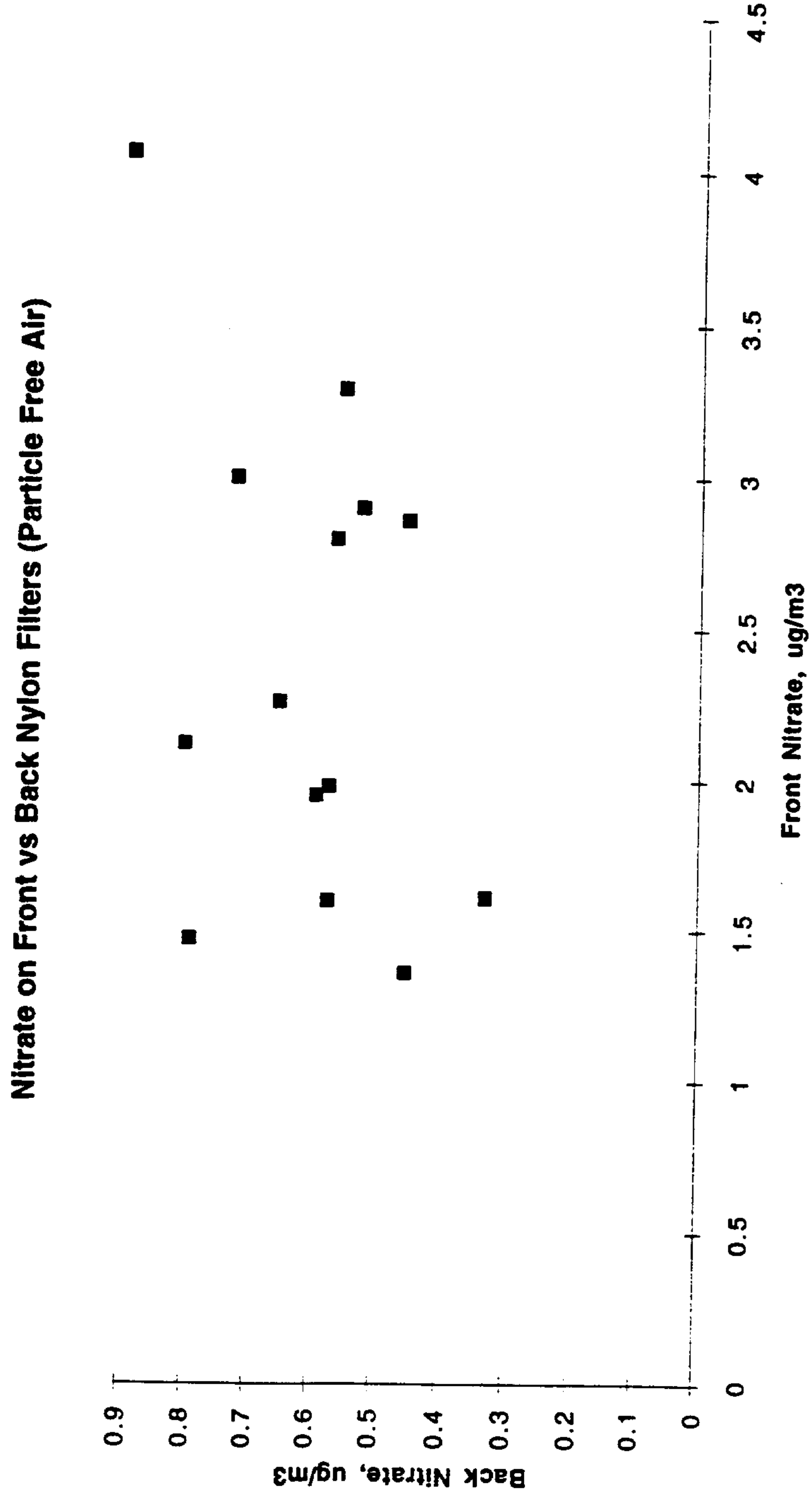
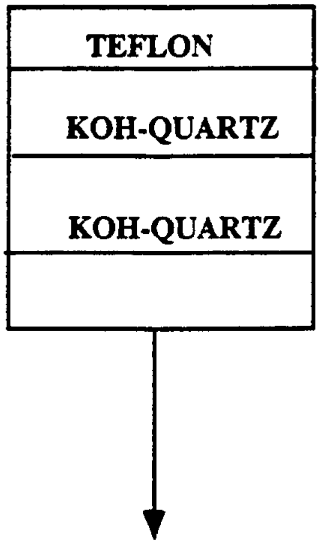

Nitrate on Front vs Back Nylon Filters (Particle Free Air)
Back Nitrate, ug/m3
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Front Nitrate, ug/m3
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5

Figure 11

FORMATE AND ACETATE SAMPLING
RIVERSIDE



MEAN CONC (13 SAMPLES), UG/M3

FORMATE	ACETATE
5.3	10.6
<0.3	1.8

Figure 12

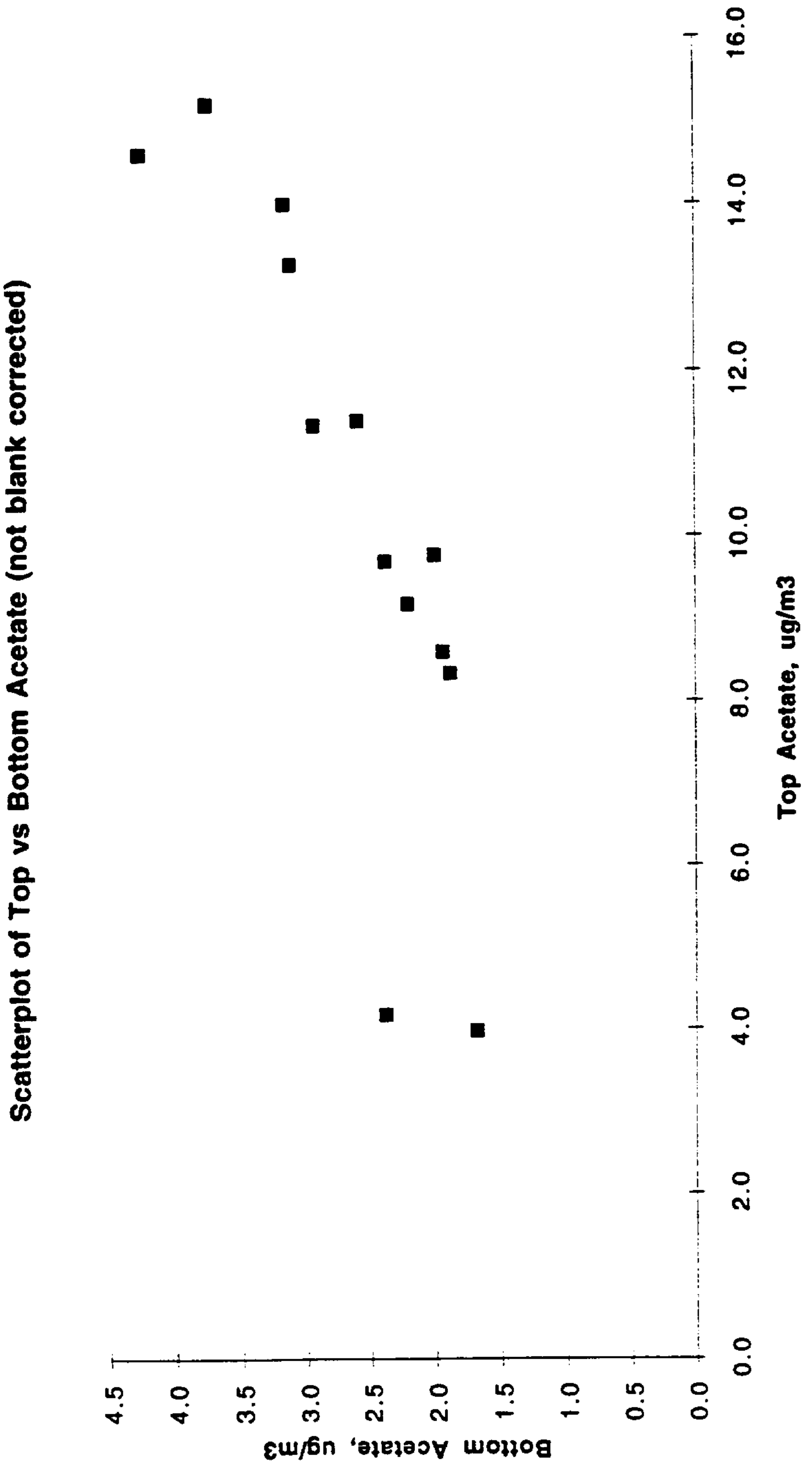

Scatterplot of Top vs Bottom Acetate (not blank corrected)

Figure 13

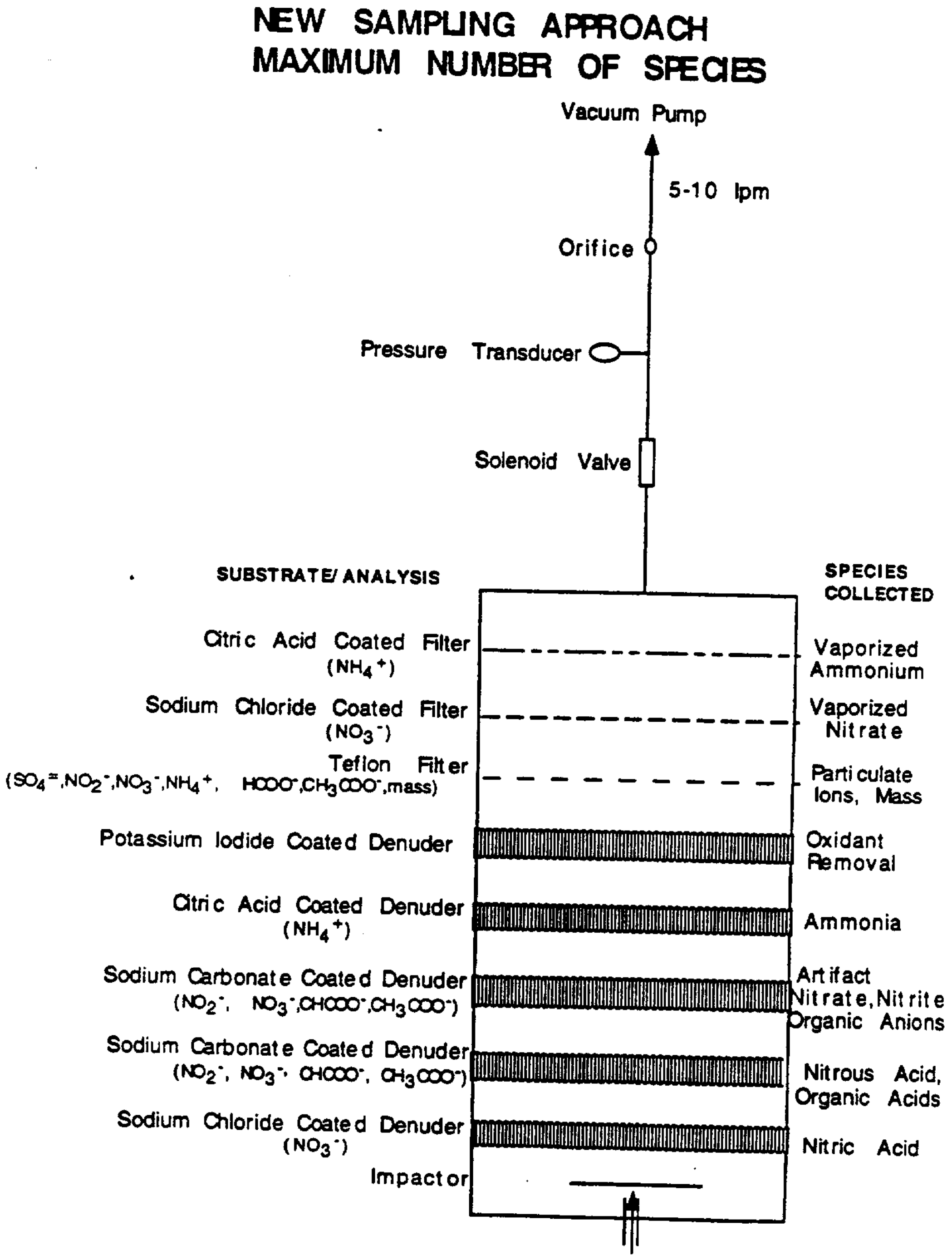

NEW SAMPLING APPROACH
MAXIMUM NUMBER OF SPECIES
Vacuum Pump
5-10 lpm
Orifice
Pressure Transducer
Solenoid Valve
SUBSTRATE/ ANALYSIS
SPECIES COLLECTED
Citric Acid Coated Filter (NH4+)
Vaporized Ammonium
Sodium Chloride Coated Filter (NO3-)
Vaporized Nitrate
Teflon Filter (SO4=,NO2-,NO3-,NH4+, HCOO-,CH3COO-,mass)
Particulate Ions, Mass
Potassium Iodide Coated Denuder
Oxidant Removal
Citric Acid Coated Denuder (NH4+)
Ammonia
Sodium Carbonate Coated Denuder (NO2-, NO3-,CHCOO-,CH3COO-)
Artifact Nitrate,Nitrite Organic Anions
Sodium Carbonate Coated Denuder (NO2-, NO3-, CHCOO-, CH3COO-)
Nitrous Acid, Organic Acids
Sodium Chloride Coated Denuder (NO3-)
Nitric Acid
Impactor

Figure 14

CE-CERT DENUDER CHARACTERISTICS

- COMPACT-TREAT LIKE A FILTER
- NO SPECIAL HOUSING NEEDED
- GOOD THEORETICAL PARTICLE PENETRATION
- INEXPENSIVE
- EASILY COATED

Figure 15

DENUDER TEST SCHEMATIC-NITRIC ACID

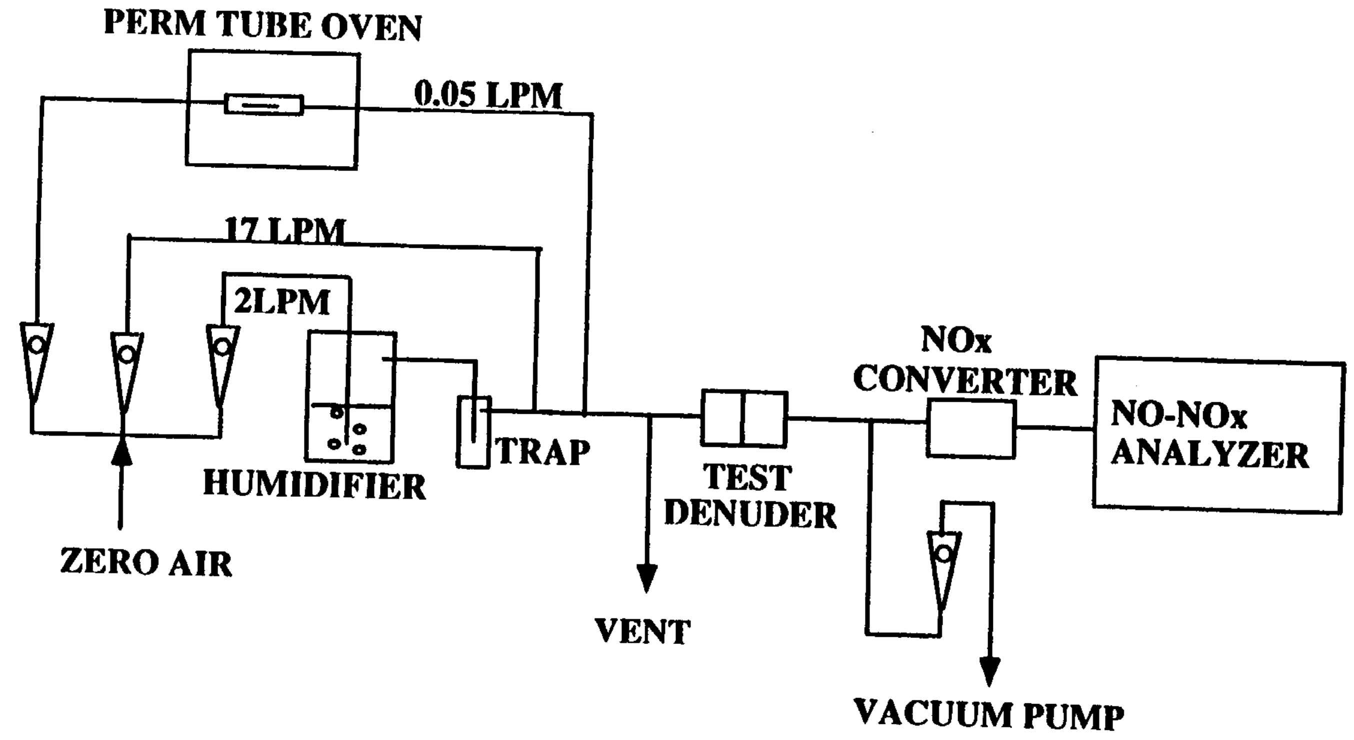


Figure 16

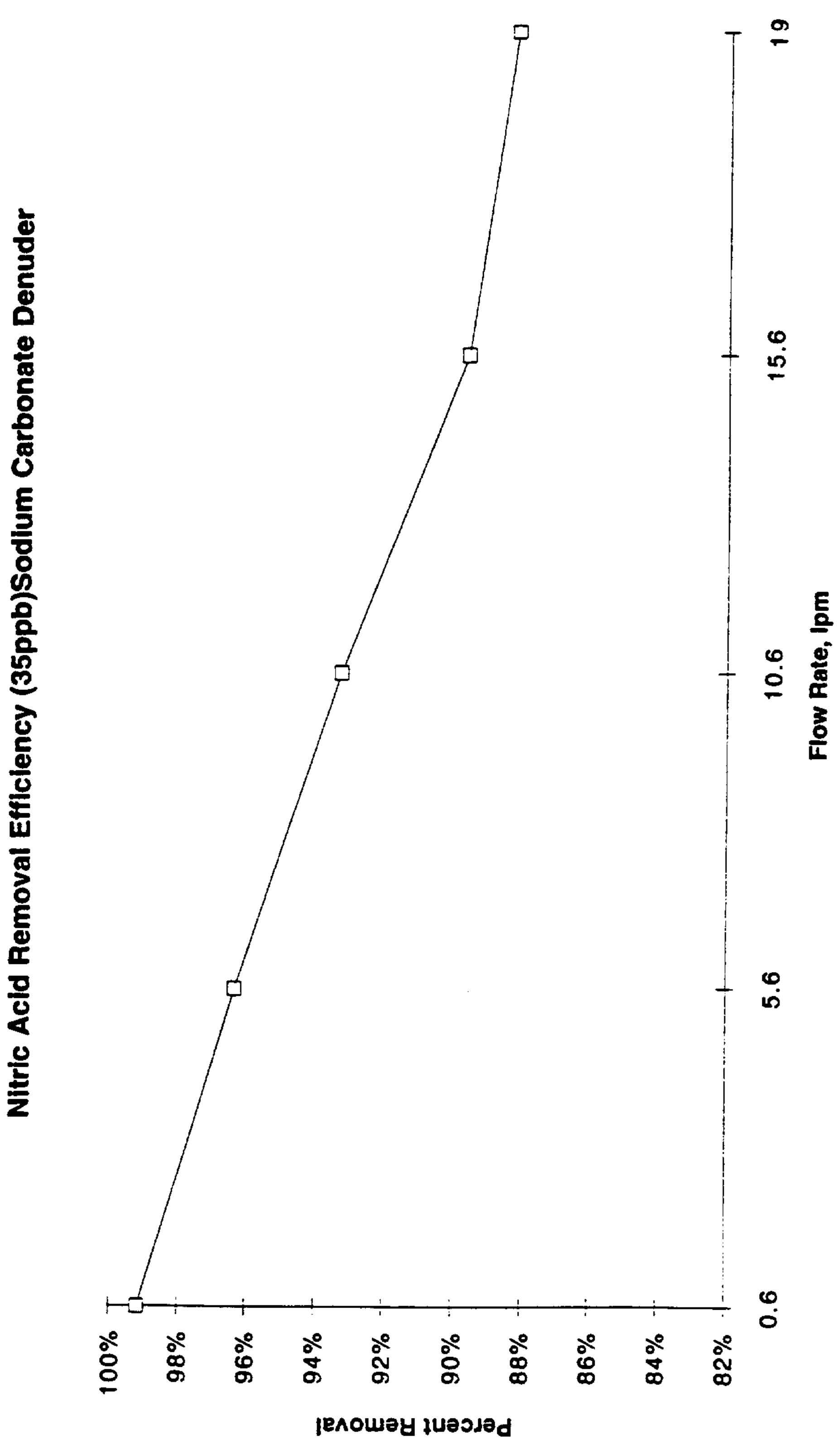

Nitric Acid Removal Efficiency (35ppb)Sodium Carbonate Denuder
Percent Removal
100%
98%
96%
94%
92%
90%
88%
86%
84%
82%
0.6
5.6
10.6
15.6
19
Flow Rate, lpm

Figure 17

NaCl DENUDER EFFICIENCY TESTS (34PPB)

DENUDER	FLOW LPM	HNO3 REMOVAL EFFICIENCY	COMMENTS
9% TYPE 1	0.6	96%	> 1HR TO STABALIZE
9% TYPE 1	15.6	73%	30MIN TO STABALIZE THEN SLOW DROP
2-9% TYPE 1	0.6	97% IN MINUTES	TWO IN SERIES
2-9% TYPE 1	19.6	86% IN MINUTES	TWO BETTER THAN ONE SLOW DROP OVER NIGHT
9% TYPE 3	5.6	97%	RAPID DROP IN MINUTES
9% TYPE 4	5.6	97%	RAPID DROP IN MINUTES

Figure 18

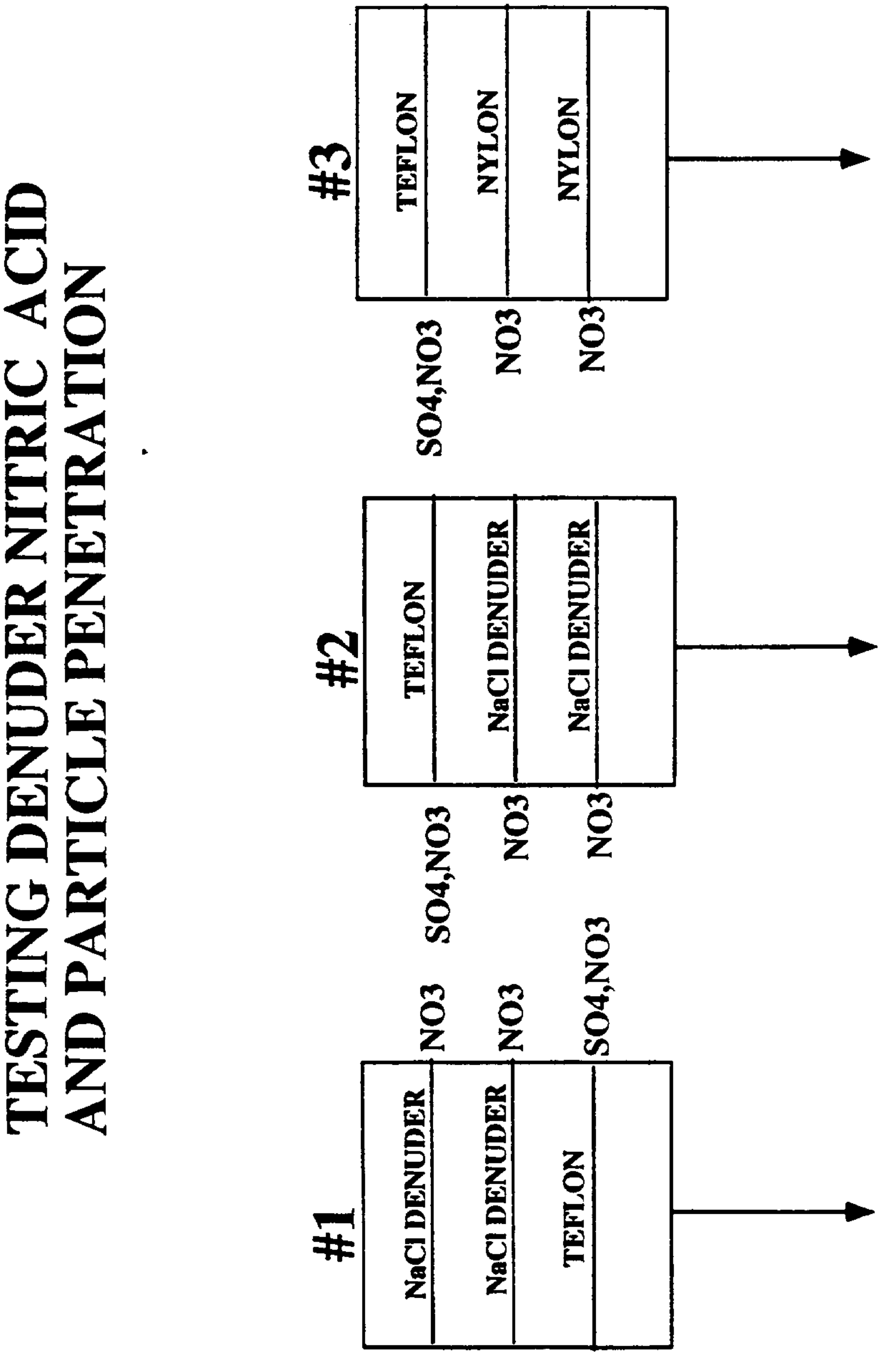

TESTING DENUDER NITRIC ACID AND PARTICLE PENETRATION

Figure 19

CONCLUSIONS

- BASIC DENUDER CONCEPT WORKS
- NaCl IS COATING OF CHOICE FOR NITRIC ACID
- NaCl PRESENTS COLLECTION EFFICIENCY DIFFICULTIES

Figure 20

REMAINING WORK

- TEST DENUDER PARTICLE PENETRATION,THEN RESOLVE NaCl DENUDER COLLECTION EFFICIENCY PROBLEM:
  - MULTIPLE DENUDERS FOR NaCl (Other coatings?)
  - TEST NaCl HNO3 PENETRATION IN AMBIENT AIR
  - TEST MORE DENUDER SUBSTRATES
- TEST HONO PENETRATION THROUGH SAMPLER
- LAB TEST PAN PENETRATION THROUGH SAMPLER
- LAB TEST ACETIC AND FORMIC ACID PENETRATION
- LAB TEST AMMONIA PENETRATION
- LAB TEST OZONE PENETRATION
- FIELD TEST SAMPLER WITH NITRIC ACID, FORMIC ACID, AMMONIA DETERMINED BY FT-IR AND NITRIC ACID ALSO MEASURED BY TDLAS

NEHZAT MOTALLEBI, Moderator

The topic of the next presentation is a new development concerning the size distributions of acidic aerosols and will be presented by Dr. Walter John. Dr. Walter John retired recently from the Department of Health Services in Berkeley.

3. New Developments Concerning the Size Distributions of Acidic Aerosols. Dr. Walter John, Private Consultant.

DR. WALTER JOHN, Private Consultant

My group at the Health Department participated in the ARB Acid Program for about six years and during that time we did a number of things. We developed methods for measurement of acidic gases and particles. We measured the airborne concentrations at a number of locations. We studied dry deposition and, culminating in SCAQS, we measured particle size distributions. That is what I want to concentrate on today.

At the beginning of the acid program 10 years ago, our concept of the particle size distributions was basically that developed by Whitby and his collaborators. For fine particles, that is, particles between 0.1 and 1 micron, there was a peak in size, a mode which was described by a log normal function. These fine particles were largely combustion products, and the aerosol was formed by gas-to-particle conversion. Above 1 micron, there was a coarse particle mode which was generated by mechanical processes such as wind blown dust. Whitby's model was based largely on number distributions. The transformation from number to volume, which is the third moment, involves large errors, and you lose size resolution. Secondly, he had very little chemistry data in the fine particle range which was both particle size-resolved and chemically speciated. Since then, we have had some developments which have made possible improved resolution and chemical speciation. Impactors are now available with cut points somewhat below a 10th of a micron and with high flow rates up to 30 liters per minute. Chemistry can be done on the samples now. As I want to show you today, this leads us to a picture of the particles that is quite different from the Whitby picture.

As we started to develop a method, we used the Berner impactor. We used a monodisperse aerosol to do an accurate calibration of the stage efficiency function. We need high accuracy to be able to use data inversion techniques. The data inversion basically removes the sampling efficiency function from the data and gives you a continuous particle size distribution rather than just a histogram. We also generated ammonium sulfate and ammonium nitrate in the laboratory to make sure that we did not have artifacts from volatilization. We developed a denuder that went upstream from the impactor to remove nitric acid. We did a number of comparisons in the field with other types of samplers. So to make the story short, I think we eliminated the artifacts, and we have a quantitative sample.

During SCAQS, we collected 900 size distributions, and I want to start off with sulfate (Fig. 1). This is a logarithmic plot. The aerodynamic diameter is along the X axis, and the concentration, log concentration, is log diameter, is on the Y axis. We found that all the distributions could be fit by three log normal functions. A log plot is a natural way to show a log normal function, because you can see the mode diameter; you can see the geometric standard deviation, and you can see the concentration. Figure 1 is an average of the parameters during the summer SCAQS study, and I would describe summer SCAQS days as moderately polluted. This is typical in that most of the sulfate is in the middle mode. I named that mode the droplet mode, because we had evidence by looking at the samples that the particles were wet. This mode was unknown to Whitby. The coarse mode I am going to discuss a little later. I do not believe that this is primarily wind blown dust or a resuspended material. This distribution is quite different than what Whitby would have showed you 15 years ago. Before our work, Hering and Friedlander did a study. They measured elemental sulfur particle size distributions in the Los Angeles basin. They noted that on clean days the distribution peaked at a smaller particle size, and on dirty days, it peaked at a higher particle size. They quoted two mass median diameters for these cases. Now during SCAQS we almost always saw both of these modes, the condensation mode and the droplet mode; we saw changes in the proportions between these two modes. I want to point out that quoting mass median diameters is misleading because we have two separate populations here, even where they overlap. These modes reflect different formation processes and so these particles have a different origin in these different modes, and their detailed chemical composition would be different.

Where did these modes come from? The condensation mode is similar to what Whitby said about fine particles, that is gas-to-particle conversion. However, in these types of processes, the rate of particle growth slows down as the particles get bigger. You cannot grow particles much larger than this mode. You then have a problem. How do you make particles as big as the droplet mode, which is about 0.7 microns diameter? A number of people suggested that it would take an aqueous phase reaction, but no one explained how those particles could grow out of the condensation mode. Now last year, Ming and Seinfeld proposed a mechanism to the effect that a subset of particles in the condensation mode get nucleated into fog or low cloud droplets. The number of particles in the droplet mode is about a 10th or less of the particles in the condensation mode, so a small amount of the condensation mode particles are nucleated and grow up to 5-10 microns in size. Then the SO_2 reacts with those droplets, and after sulfate is formed the droplet evaporates back down and winds up here. That is the proposed mechanism. Now, while they give a plausible mechanism for the formation of the droplet mode, they do not provide any other details. For example, how does the nitrate get into those modes? Figure 2 shows the nitrate. This is averaged over summer SCAQS. In the case of nitrate, the average coarse mode is a little misleading because for nitrate, the coarse mode is low near the coast and higher inland. This is an average over three stations, Long Beach, Claremont, and Rubidoux, spanning the basin. You can see they are the same three modes. In fact, we think that the nitrate and the sulfate are internally mixed in the same particles. So how does the nitrate get there? I would like to examine some data in a different way that might give us a clue or suggestion (Fig. 3). On the left hand side, is a frequency plot. This is aerodynamic mode diameter and the number of modes having that diameter. Again, you can see the three modes for sulfate. On the right hand side of Figure 3 is average mode concentration. Let us look at the range of size in the droplet mode. What you see is that larger the diameter of the mode, the higher the concentration. I think this is what you would expect; the sulfate is responsible for forming that droplet mode.

Let us look at the same type of plot for nitrate (Fig. 4). In the case of the nitrate, the frequency plot shows the same three modes; the concentration plot shows only two events at that point (disregard the spike at one micron). Looking at the main part of the distribution, the nitrate particles peak, and they peak at about 0.5 micron. On the droplet mode, the sulfate peaks at 0.7 micron. Half a micron is where the surface mode of an 0.7 micron volume would peak. It suggests to me that the nitric acid is probably reacting with the droplet mode, and the droplet mode is formed by the sulfate, but the nitric acid then reacts with the surface.

Now let us talk about the coarse mode (Fig. 5). I think the coarse mode has not received enough discussion. This figure was made during the "nitric acid shootout" in Claremont some years ago. The nitrate has sort of a flattop distribution, and it extends to above 10 microns. The sodium looks similar to that. This was a period of what we call dry continental air. The air happened to be coming from the east, a Santa Ana condition, which as you know is not very common. What I want to show you is that the size distribution seems to change when the wind comes from the west. This is what we normally saw during SCAQS (Fig. 6). SCAQS days were all very similar. With maritime air, nitrate has a higher concentration. It peaks sharply, and at the right hand side the peak slopes off. I want to discuss a possible mechanism for this, and strangely enough, this reaction was mentioned a few minutes ago (Fig. 7). Nitric acid reacts with sea salt, and yields sodium nitrate plus HCl. In this reference, we described some measurements we made during the nitric acid shootout and also some previous measurements in which we measured all of these components including the HCL. We got a good mass balance accounting for the loss of chloride from the sodium in the sea salt in terms of a sum, chloride in HCl plus the chloride in the fine particles. I did not mention this, but in the droplet mode about 6% of the negative ions are chloride. There was no sodium in the droplet mode, so where does that chloride come from? I think it perhaps comes from this hydrochloric acid. This hydrochloric acid would react with the droplets and wind up as chloride in the particles.

Now I want to continue to derive the particle size distribution from this reaction with sea salt.

Figure 8 shows a simple model. Sodium nitrate is the black and sodium chloride is the white. If we start out with a very small particle, the nitric acid will completely convert the sodium chloride to sodium nitrate. If we go to a larger particle site, we will reach a critical particle size which is completely converted. For larger particles than that critical size, only the surface of the particle will be converted. It does not matter for this calculation whether or not this is mixed into the volume. The question is what proportion of the sodium chloride is converted? Here are some simple equations (Fig. 9). "P" is the fraction, mass of sodium nitrates to mass of sodium chloride. The rate of change of mass of sodium nitrate is the rate of absorption or rate of production of sodium nitrate per unit time per unit area. That is why I use a small m. Multiply that by t (the time) and by the surface area of the sea salt droplet to obtain the mass of sodium nitrates. The mass of sodium chloride is the product of its density and the volume of the particle. This density might be affected a little by the moisture content. For f, we get a factor which is independent of particle size times one over the diameter. That is a constant over diameter. We can evaluate the constant by looking at the fact that at about 3 microns, we can set $f = 1$ and then $f = 3/D$, 3 microns is where the nitrate peaks when we have maritime air. All we have to do to obtain the coarse nitrate particle size distribution at Claremont (Fig. 10), is to take the sodium particle size distribution on the left hand side of the peak since the nitrate distribution will be the same; these particles are completely converted, so they will be the same size. On the right hand side of the peak, we multiply the sodium by one over the diameter of the particle, and that gives us the points shown for calculated nitrate. They follow the measured nitrate nicely. On the left hand side of the coarse nitrate peak we are mass-limited; on the right hand side we are surface-limited. It has the effect of just shifting the right hand side of this distribution.

I have another example with measurements from Berkeley (Fig. 11). In this case, the sodium concentration was higher than the nitrate, and yet we are saying that it was completely converted. I think what we have here is a mixture of air at the sampling site, which was directly opposite the Golden Gate Bridge. We had pure marine air arriving. We also had polluted air from San Francisco arriving. I normalized the sodium, but I got the right shape for the peak. We can derive the particle size distribution for the sea salt reaction from this simple analysis. We have a reaction here that is a significant sink for nitric acid. It is producing hydrochloric acid, and some of it gets into the fine particles as chloride, and so we have acidic gases reacting with some droplets which were nucleated in the nucleation mode and with other droplets which are sea salt, and they remain coarse particles. The others have moved down in the droplet mode into the fine particles.

I want to show the utility of using the mode concept for evaluating effects. Figure 12 shows visibility. This is the light scattering coefficient, bscat per meter, versus aerodynamic diameter. I took the average inorganic mass size distributions from SCAQS and calculated bscat for each mode. The droplet mode dominates the visibility reduction. Unfortunately, the droplet mode is almost exactly positioned at the top of the light scattering curve, which is a terrible coincidence. Also, since the droplet mode appears to be formed through sulfur, then sulfur is the determining factor for the visibility reduction because it puts the mode there. I do not like to give the impression that the droplet mode is always exactly at 0.7 microns. There is some variation. We saw one day in which there was a large growth, so it is not always exactly on the peak of light scattering. If you have an even more polluted day, the sulfate particles can grow beyond the optimum light scattering point.

Figure 13 shows dry deposition, and now the coarse mode dominates the dry deposition because the deposition velocity goes up very steeply with particle size. The deposition velocity also goes up at small particle size because of diffusion. However, there are not enough particles there to increase the deposition flux.

Finally, figure 14 is respirable mass. This is an addition of all the ions together and a plot of the three modes. I plotted the original coarse distribution, and then I showed it as cut by the respirable curve. I am using the ACGIH respirable curve which is what the industrial hygienists use. It is based on an estimate of the fraction of particles that penetrate to the deep lung. This curve has also been adopted by the European Union which is developing their particle standards, and also by the International Standards Organization. It is interesting that in Europe, the same people work on industrial hygiene and indoor air as well as ambient outdoor air. In this country, we pretend that there is a boundary at the wall, and somehow the outside is a different problem than inside. A little less than half of the so-called coarse particles, as far as the inorganic components are concerned, are within the definition of respirable. A 50% cut point on the respirable curve is 4 microns, and it is not a sharp cut; it has a shape to it. This also brings up the question that was mentioned before. The EPA is considering the possibility of adding a fine particle fraction to the monitoring requirement, and so where would you put that cut? The minimum between the droplet and the coarse mode for sulfate is about 2.1 microns based on our average SCAQS data, and for nitrate is about 2.3 microns. If you wanted to put it at the minimum, you would put it somewhere like that. That excludes some of the coarse nitrate particles and sulfate particles which are respirable, so it is a hard choice to make.

To summarize, we have found that the inorganic ionic species are in three size modes. These size modes each reflect a different formation mechanism. I anticipate that the future in atmospheric aerosol research is in combining size resolution with chemical speciation, and I think that the more chemical species we look at, the more modes we will find because each one will have a different formation mechanism and there will be some interactions between various species.

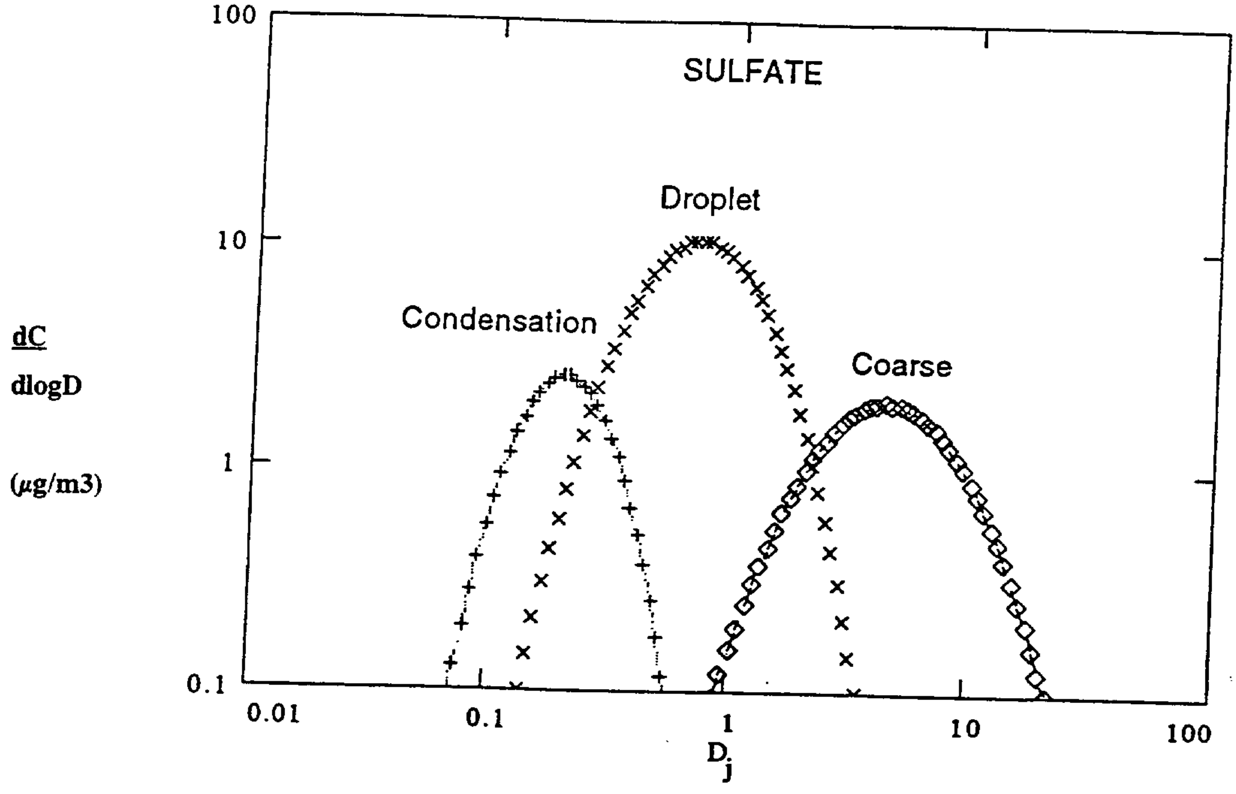
NEHZAT MOTALLEBI, Moderator

Thank you very much. Are there any questions for Dr. John?

Q (AUDIENCE) The coarse sulfate is sea salt?

A (DR. JOHN) Not entirely. In the coarse sulfate, the sea salt is only about 10%, from our data. I think the SO_2 is also reacting with droplets. While we are beginning to get some idea of the mechanism, I do not think we are there yet. We need more measurements and I think we need a lot more modeling to find out. From that point of view, I would point out that we have half a dozen final reports; we have data in the SCAQS Data Bank, and a lot of under-utilized information there that is available for us to try to understand, but I think that it is crucial to know the size distribution of these species.

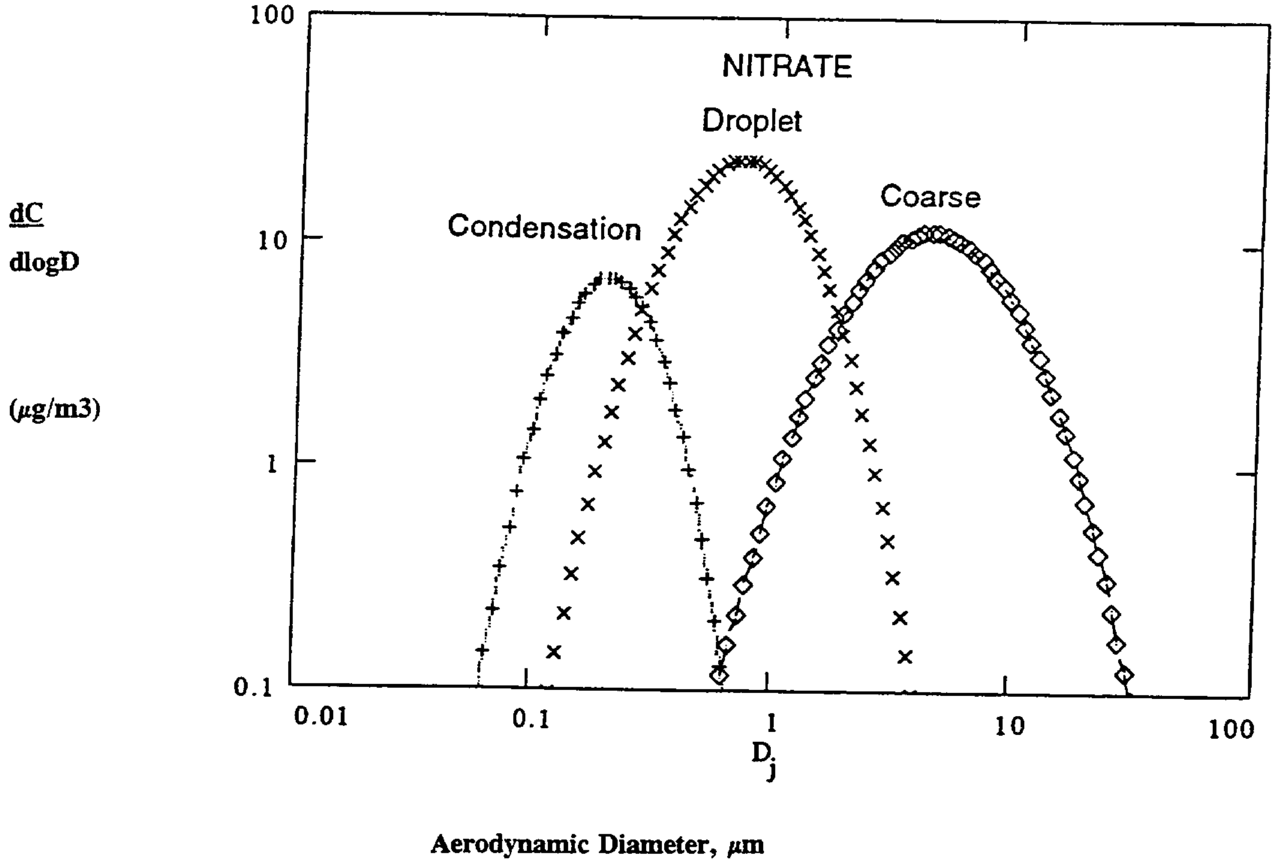
Figure 1



Aerodynamic Diameter, μm

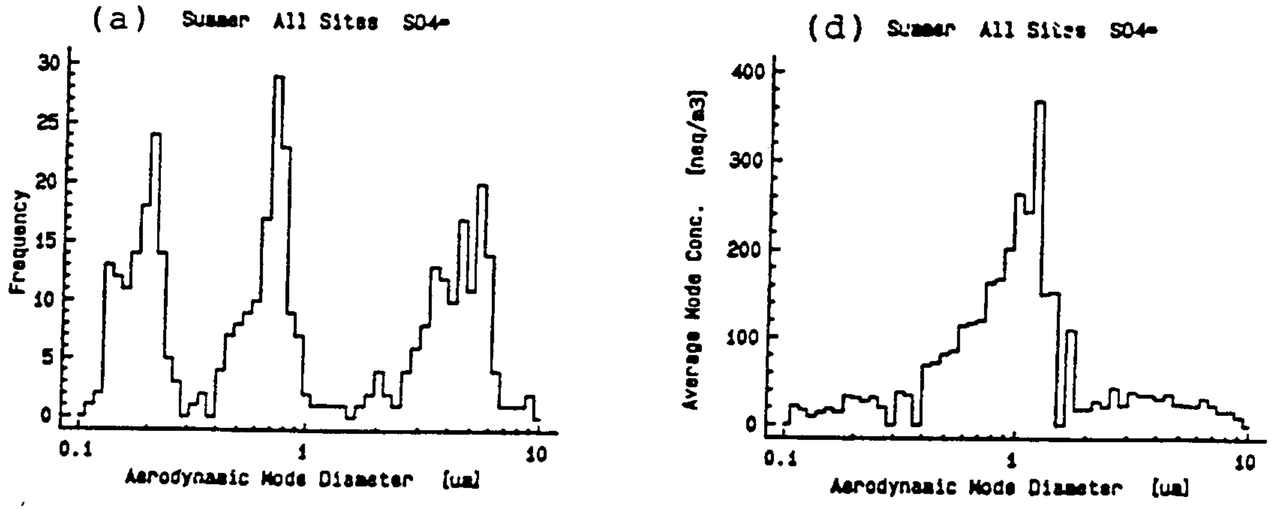
Sulfate size distributions obtained during SCAQS. The lognormal modes are plotted using average values for the parameters.

Figure 2



Nitrate size distributions obtained during SCAQS.

Figure 3

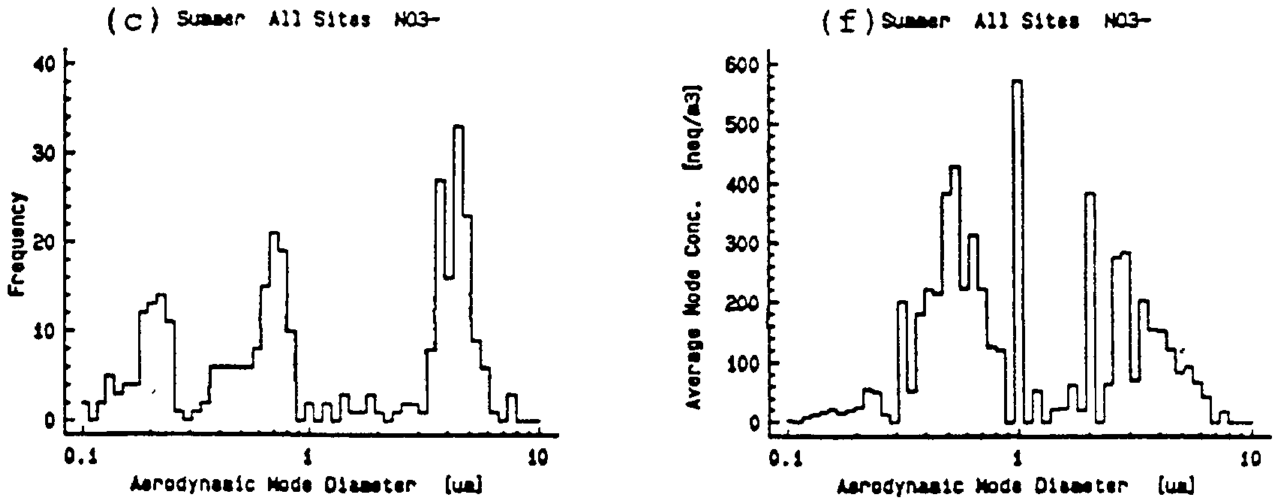


From all sites during summer SCAQS.

(a) frequency (no. of cases) of sulfate modes vs. mode diameter.

(d) average sulfate concentration vs. mode diameter.

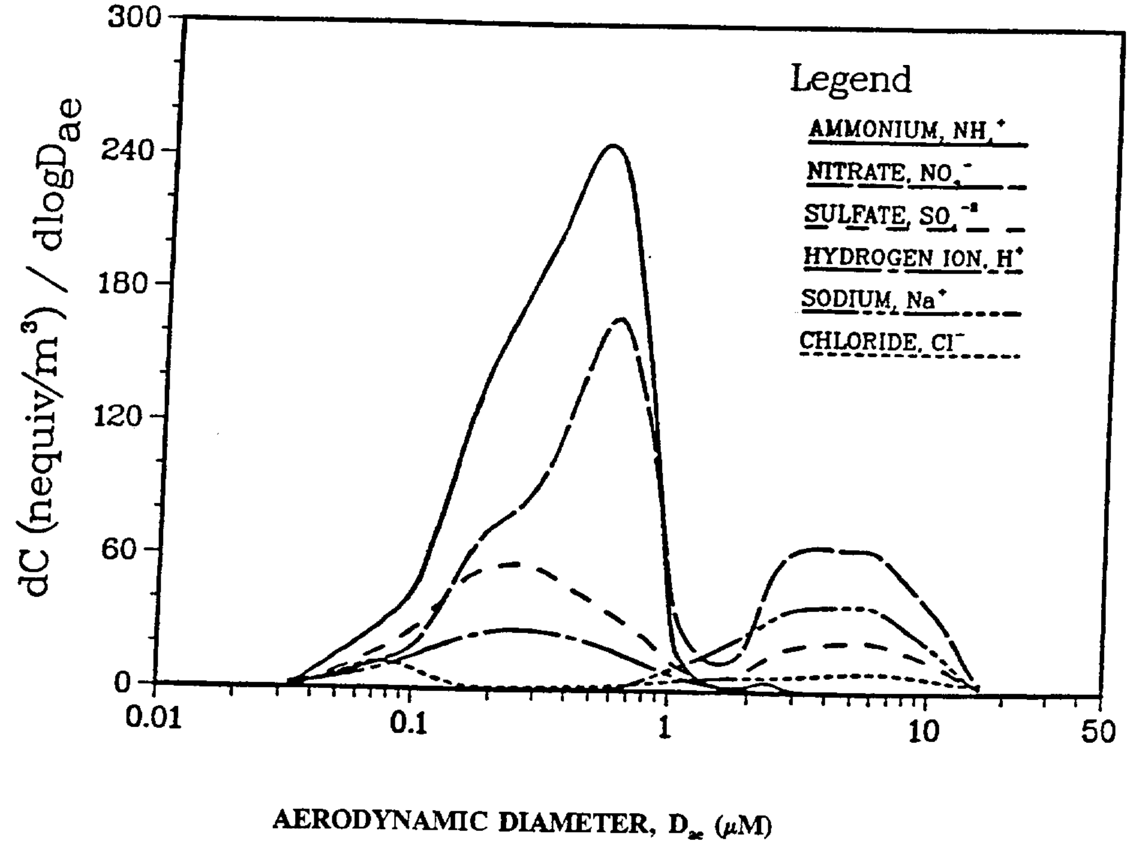
Figure 4



(c) From all sites during summer SCAQS: frequency (no. of cases) of nitrate modes vs. mode diameter.

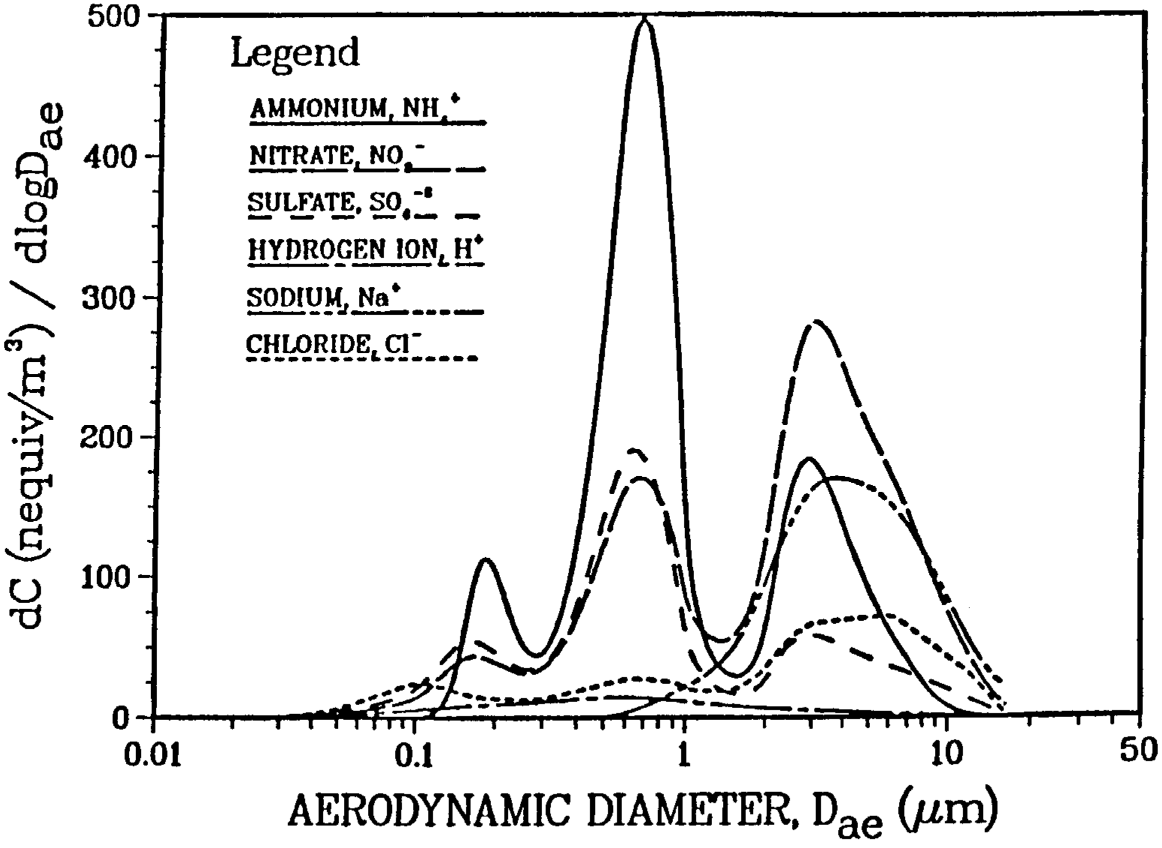
(f) Average nitrate concentration vs. mode diameter.

Figure 5



Major ion size distributions during the initial period of dry continental air (Sept. 13), sampling with both denuder and greased stages. Measurements at Claremont.

Figure 6



Representative size distributions for the period of strong marine sodium influence with both denuder and grease (nighttime, Sept. 16).

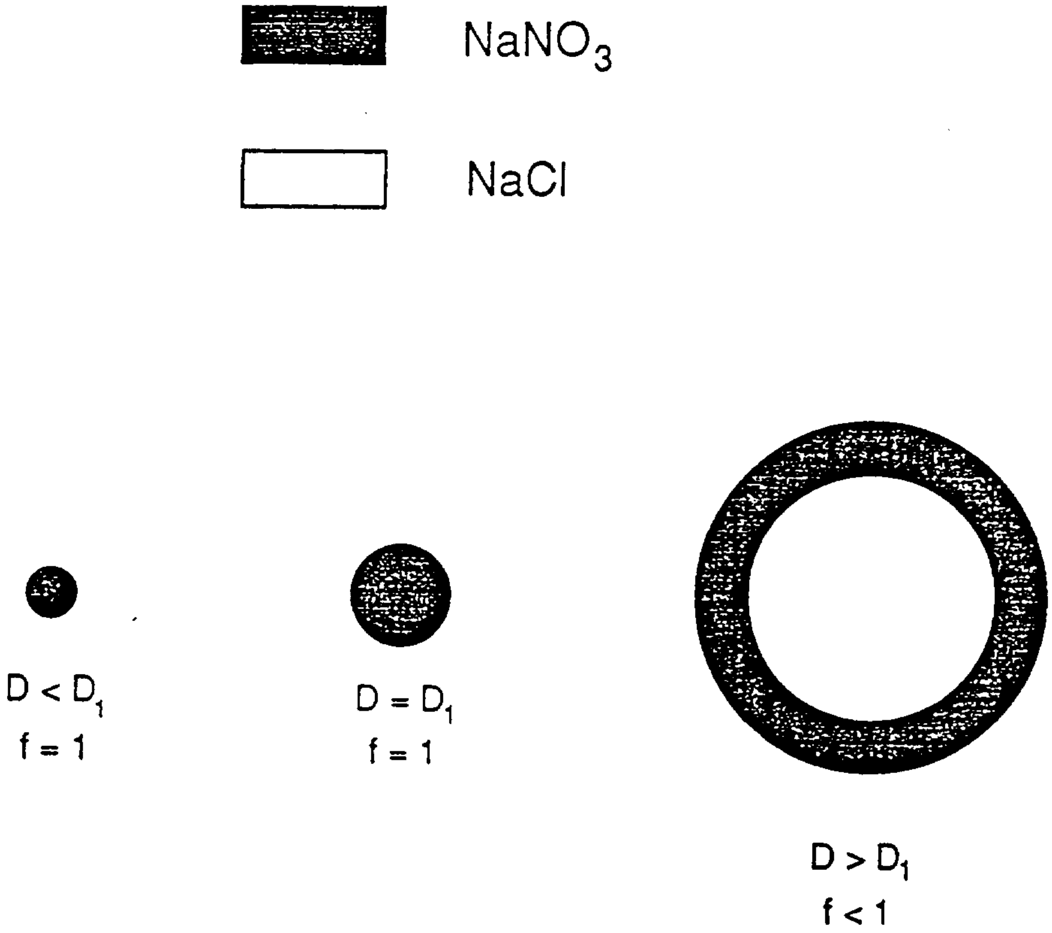
Figure 7

$$HNO_3 + NaCl - NaNO_3 + HCl$$

Reaction of nitric acid with sea salt.

Wall, S.M., John, W. and Ondo, J.L. (1988) Measurement of Aerosol Size Distributions for Nitrate and Major Ionic Species. *Atmos. Environ. 22,* 1649-1656.

Figure 8



Schematic of the conversion of $NaCl$ to $NaNO_3$ by nitric acid. f is the fraction of $NaCl$ convented; D_1 is the largest particle diameter for complete conversion.

$$M_{NaCl}$$

$$M_{NaNO_3} = \frac{dm_{NaNO_3}}{dt} \cdot t \cdot \pi D^2$$

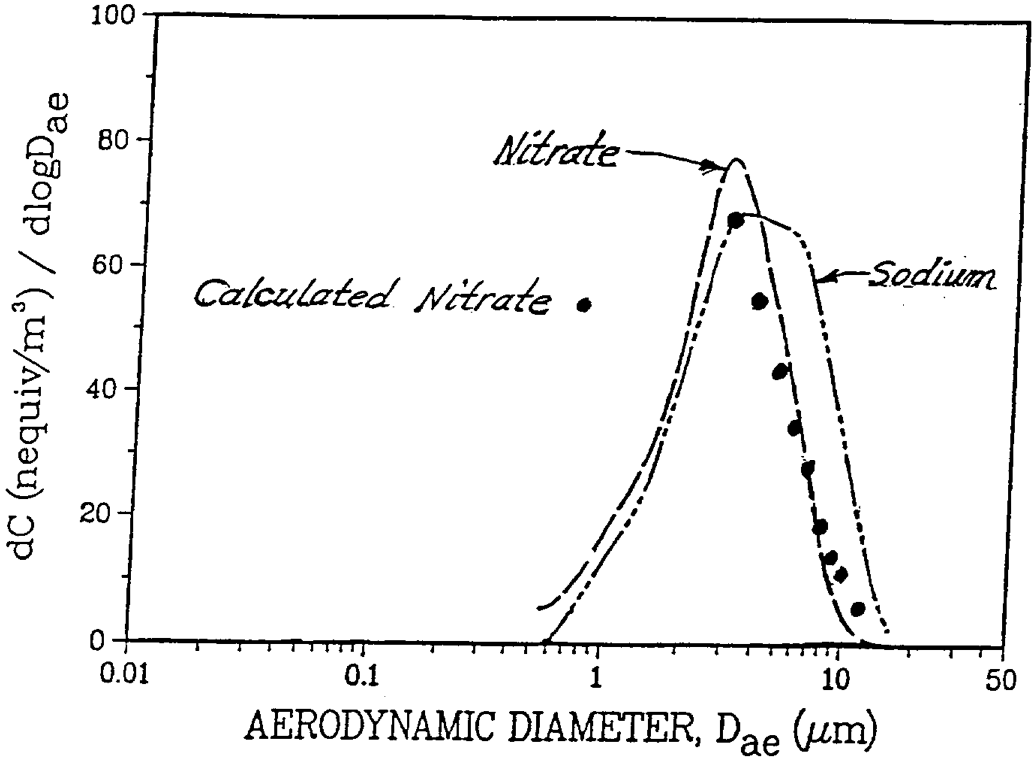
$$M_{NaCl} = \rho_{NaCl} \cdot \frac{\pi}{6} \cdot D^3$$

$$f = \left(\frac{6 \cdot \frac{dm_{NaNO_3}}{dt} \cdot t}{\rho_{NaCl}} \right) \cdot \frac{1}{D} = \frac{a}{D}$$

$$D = 3\mu m, \quad f = 1, \quad f = \frac{3}{D}$$

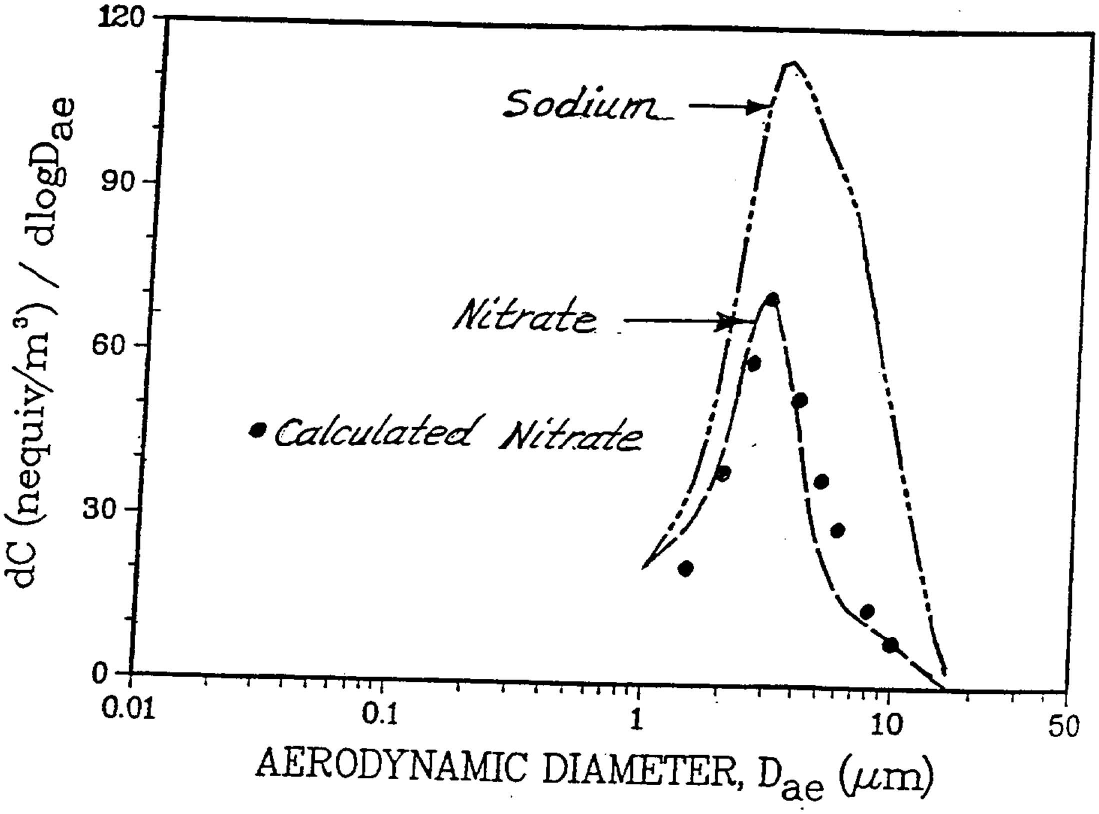
Derivation of the coarse nitrate size distribution from the NaCl size distribution.

Figure 10



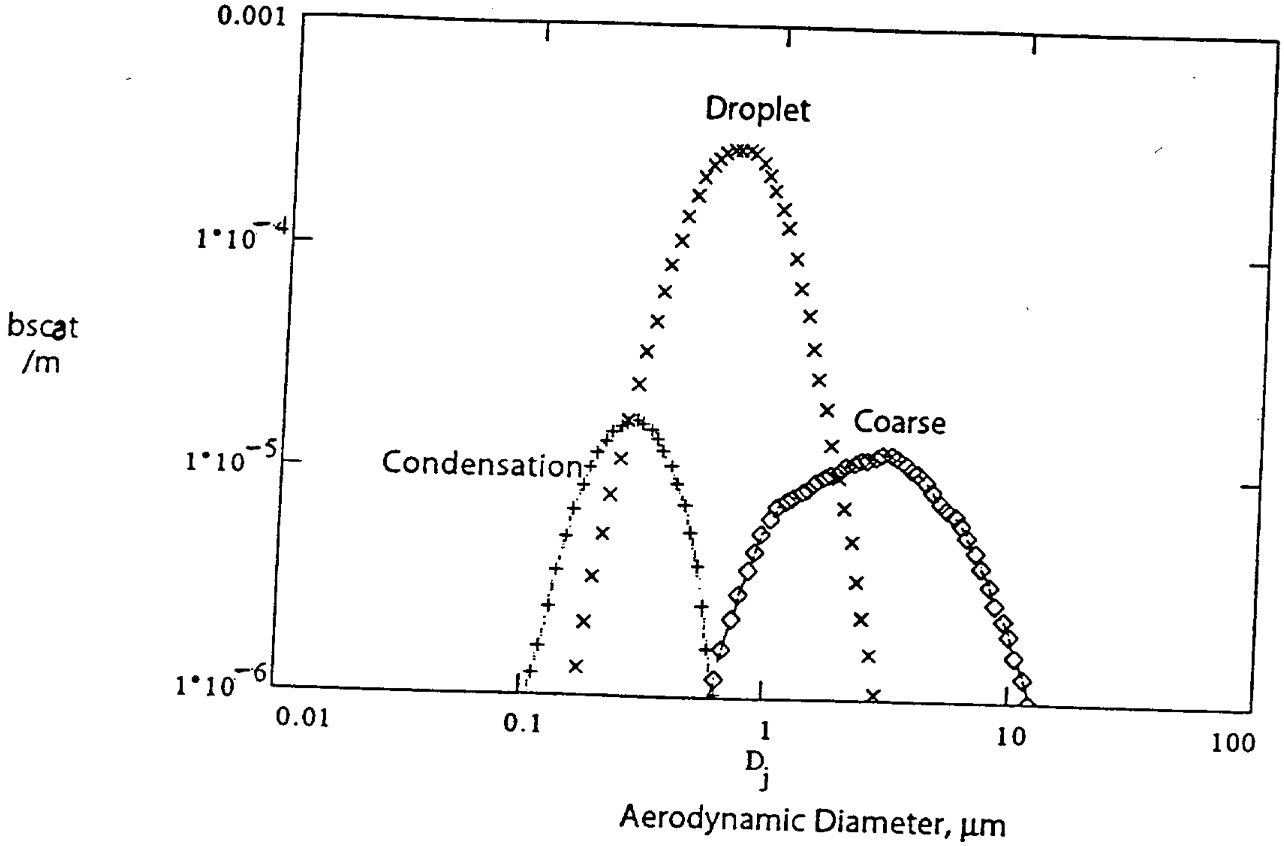
Comparison of the calculated nitrate size distribution to that measured at Claremont.

Figure 11



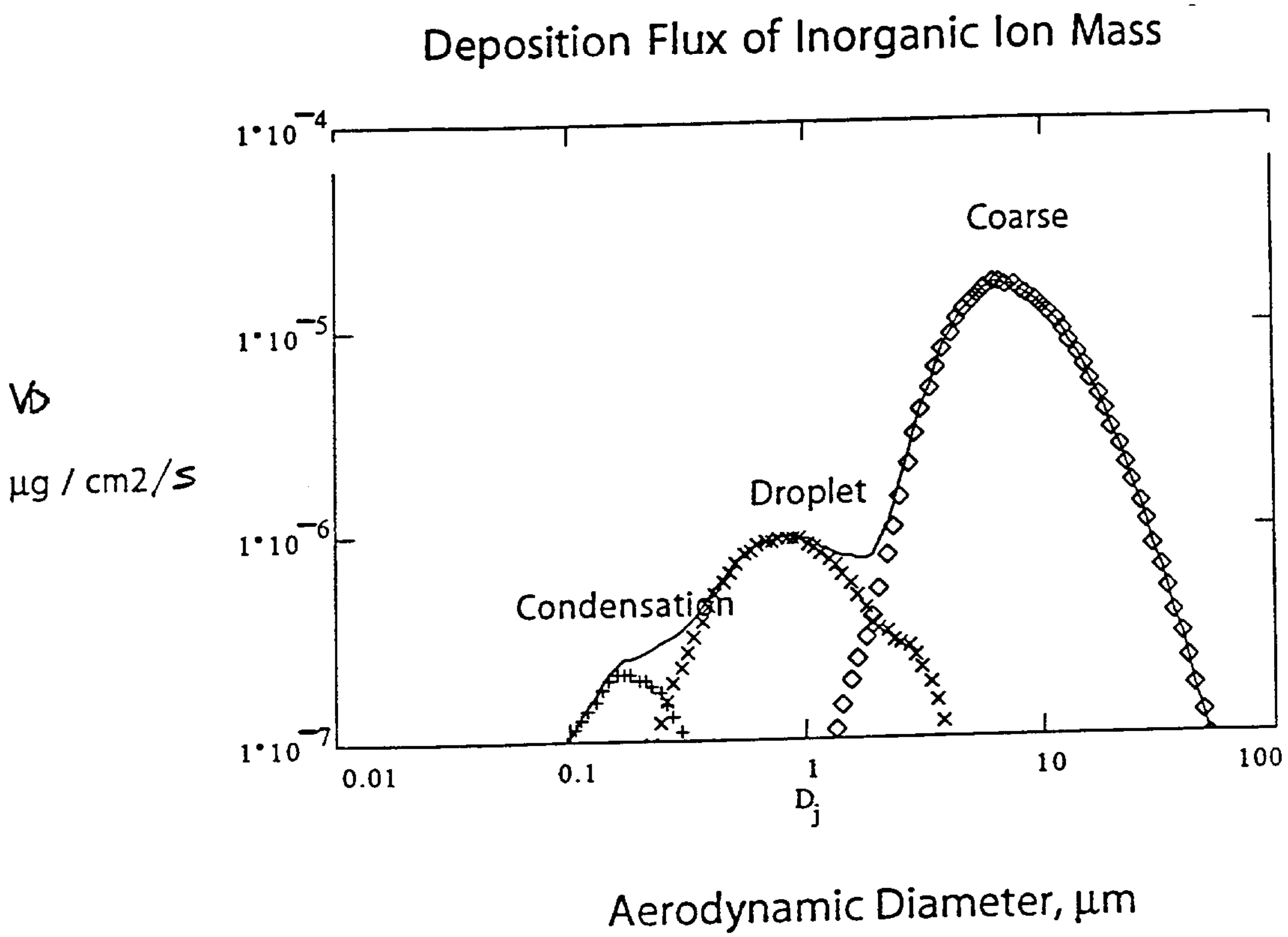
Comparison of the calculated coarse nitrate size distributed to that measured at Berkeley.

Figure 12



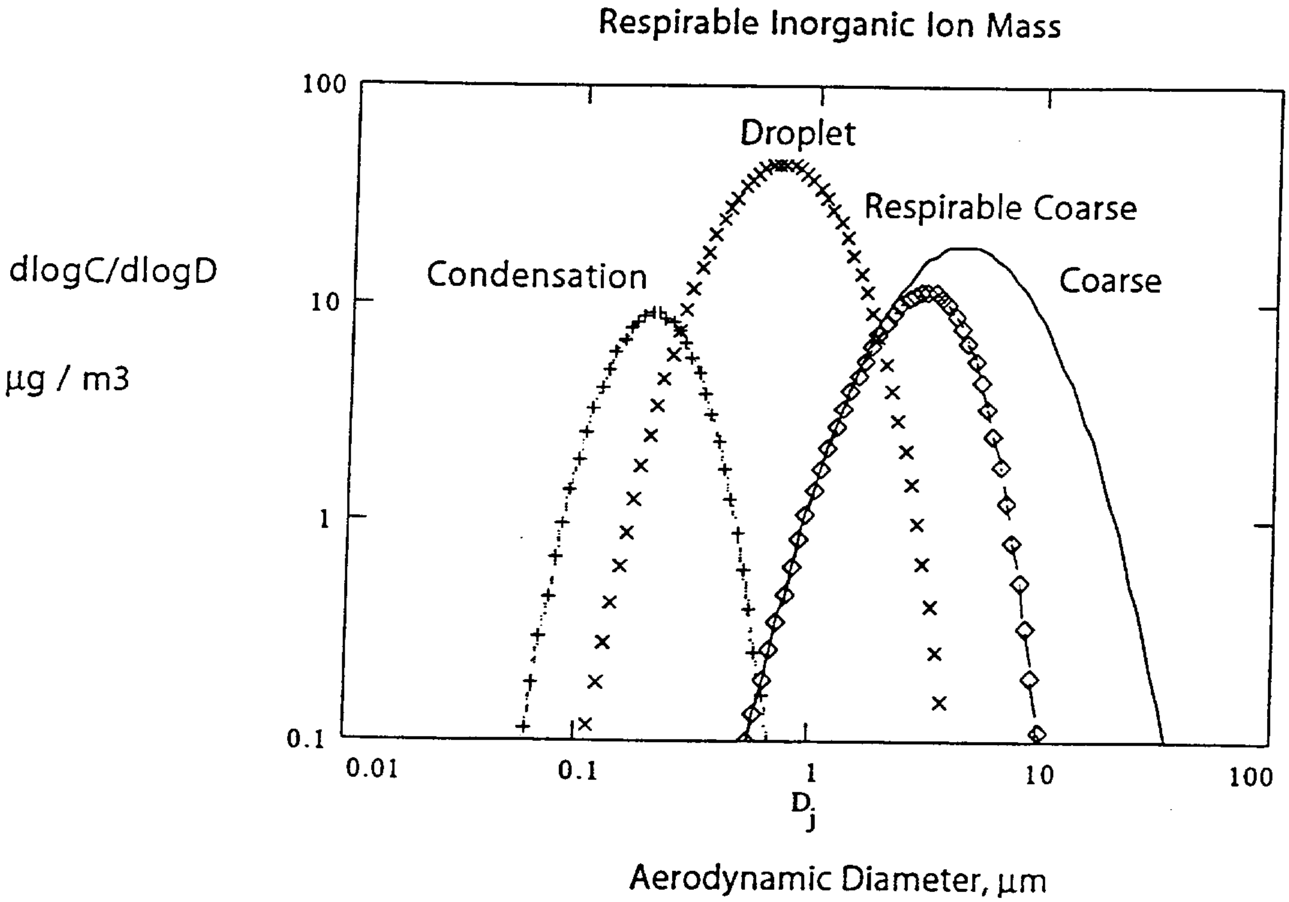
Light scattering coefficient, bscat, calculated from SCAQS data, showing that the droplet made dominates visibility reduction.

Figure 13



Deposition flux of inorganic ions calculated from SCAQS data, showing that the coarse mode dominates deposition.

Figure 14



Respirable inorganic ion concentrations (points) calculated from SCAQS data. While the droplet mode dominates, about half of the coarse mode is respirable.

NEHZAT MOTALLEBI, Moderator

The topic of our next presentation is "Fog and Cloud Chemistry in California" and will be presented by Dr. Michael Hoffman of the California Institute of Technology.

4. Fog and Cloud Chemistry in California. Dr. Michael Hoffmann, California Institute of Technology.

DR. MICHAEL HOFFMAN: California Institute of Technology

Because of the interest and long-term support of the Air Resources Board, my research group tried to unravel some of the details of fog and cloud chemistry. The leader of the advisory board here, Jim Morgan, was the primary impetus to get us involved in field-scale studies of cloud and fog chemistry. Earlier in 1973, I had put forth some ideas that hydrogen peroxide was the dominant oxidant for SO_2 in the atmosphere, and that these reactions took place in water droplets. Back in 1973, that idea was not well received. People at that time thought that sulfur dioxide was primarily converted in the gas phase most likely by hydroxy-radicals. More than 20 years later, there is a consensus that on a global basis, the majority of sulfur dioxide is converted within cloud systems.

This interest, that the Air Resources Board nurtured over the years, really paved the way for understanding the role of clouds and global atmospheric chemistry. In fact, sulfur compounds may provide the condensation nuclei or recycled nuclei, as Walter John pointed out, to form clouds on a global basis, and many researchers are investigating the link between sulfur compounds, cloud formation, and climate feedback. For example, Professor Seinfeld is involved in that area of research. It is difficult to summarize our research over a period of 15 years or more. Many of our studies have ended up in the primary literature. I cannot summarize all of our results, but I will try to give some insight.

We tried to address the size resolution issue back in 1989. In an article that appeared in Atmospheric Environment in 1989, we examined the dependence of chemical composition of coastal stratus clouds on droplet size and distance from the coast. We tried to explore some of the ideas that Walter was stressing; that one gets different chemistries in different droplet size fractions. That is, in fact, what does take place, so I agree with virtually everything that Walter said, and I also agree, with the model proposed by John and his student. In addition, we had quite a few Ph.D. theses that resulted from this work, namely Daniel Jacob, Jed Waldman, Bill Munger, and Jeff Collett. Daniel is now a chaired professor at Harvard, a full professor in atmospheric chemistry, so this work has carried him pretty far. When I was first exposed to atmospheric chemistry and air pollution, I was struck immediately by the so-called disastrous air pollution episodes and what their implications were. It turns out that the during London smog episode, from December 5 to December 9, 1952, there were 4000 excess deaths. This was due to a thick sulfurous smog or fog. There were earlier fogs in London and elsewhere that presaged this particular event, but the unifying theme among all of these disastrous air pollution episodes was the occurrence of fog. These episodes were characterized by high sulfur dioxide, high soot, and fog. In fact, there was a series of articles on fog in the Transactions of the Royal Faraday Society. One entire issue was devoted to fog chemistry and pollution chemistry in 1936. A Belgian professor made the prediction in 1936, that if a fog similar to one that had occurred in Belgium in 1930, were to occur in London, there would be about 3200 excess deaths. This particular phenomenon puzzled people for many years, and thus motivated us to try to explore what was going on in fog that was different from photochemical air pollution without fog. We studied London-type smogs versus Los Angeles-type smogs, even though in Los Angeles, we do have London-like conditions on occasion.

Glen Cass, while working on his Ph.D. thesis at Caltech summarized data available through the Air Quality Management District in the Los Angeles basin. Glen noted that, at least statistically, the sulfate concentrations in the Los Angeles basin at different locations, were the highest during fog episodes or at least when fog was noted at the Los Angeles International Airport. The high sulfate levels seemed to correspond with high relative humidities. These observations motivated us to look at the droplet phase more closely. I first was exposed to this type of data in 1973, and I tried to imagine, what could the humidity contribute to those sets of reactions that convert sulfur dioxide to sulfate in the atmosphere.

The intermediate particle-size distribution, that Walter was talking about, was called the haze aerosol fraction in the past. These droplet-sized haze aerosol particles provide the fog condensation nuclei for heavy fog formation. In addition they process a certain portion of sulfur as S(IV). However, we believe that the larger droplets will be more important for dynamic S(IV) conversion within droplets. When the humidity decreases again, one will get this droplet sized haze aerosol. In a nut shell, one can certainly have gas-to-particle conversion. In the case of sulfur dioxide, hydroxy-radical will oxidize SO_2 to produce in the gas-phase to produce gas- phase sulfuric acid and hydroxy-radical will oxidize nitrogen dioxide to yield nitric acid. These gas-phase acids then react with ammonia. Haze aerosol droplets contain sulfate, nitrate, ammonium ion, and protons, and, with an increase in relative humidity, one can get cloud or fog droplets that are dominated in mass composition by ammonia, nitrate, and sulfate.

Our studies were extended in the early part of 1981 to include the San Joaquin Valley and San Francisco. One of the major challenges, that we faced in the beginning, was development of a method to collect cloud water in order to sample clouds in real time and thus to determine the chemical compensation of clouds and fogs. There were really no good methods available at that time. Many early efforts were devoted to devising instruments that we could use to routinely collect cloud water to avoid contamination, to have a representative sample, and to analyze the collected water in order to obtain a time distribution of the chemical components within a particular cloud or fog event. One of the later types of devices was a flow-through collection device that was closed when not in operation. It was fully automatic so that as soon as it sensed the presence of a cloud or fog, this system would be activated. The doors would open and then the droplets were collected by inertial impaction on Teflon strings that were strung across a rack. In the size-fractionating collectors, we had a number of different collection points, similar to a sequential impaction collector, so we could sample different droplet size fractions. Towards the end of our CARB projects, we employed fully automated systems. The remote sensing device was a light scattering system which responded to cloud droplets. In addition there was a refrigerated and automated sample collection unit.

We started out thinking that we could conveniently collect cloud water with something we called a rotating arm collector. This was essentially a propeller blade that rotated at a certain velocity and collected droplets by inertial impaction. This was much more difficult to operate on a continuous basis, because we had to stop the collector from rotating in order to empty the sample bottle. It worked quite well in the beginning, and much of our earlier data were collected with that collector. There were several occasions when the arm broke off. Sampling at night in urban neighborhoods posed a problem; the sounds of the propeller irritated a lot of people, so we moved to remote locations.

What did we find? We were focused early on determination of the chemical concentrations or composition that one would find in rain. We knew that clouds and fogs should be more concentrated, but we were surprised at how concentrated they were. To give you an idea, many of the concentrations of components in clouds were milliequivalents per liter whereas in acid rain on the east coast, the concentrations in the liquid phase were in the range of microequivalents per liter; these are factors of 100 less in many cases. We noted also that many of the fogs throughout the LA basin and elsewhere were hyper-acidic. They had very low pH values and contained more nitrate than sulfate. Initially, we thought that we would find more sulfate than nitrate, but the fogs were dominated by nitrate. In most other places around the world, the clouds are often dominated by sulfate over nitrate. There was one extreme event at Corona del Mar, where we had readings below pH 2. There was very little acid neutralization at Corona del Mar. Most of the acidity associated with nitric and sulfuric acid was neutralized by ammonia as one moved eastward in the basin, and you see that reflected in the ammonium ion. Along the coast, there were often samples that had very little ammonia.

I agree with Walter's argument, that most of the nitric acid is scavenged after the cloud forms around a condensation nucleus, which may be ammonium sulfate or perhaps a mixture of ammonium nitrate and sea salt. Then the gas phase nitric acid is scavenged as soon as one gets a droplet size distribution characteristic of fog. It is that gas phase nitric acid that is pulled into the droplet and results in the intense acidifications seen in the Los Angeles basin.

We also looked at time series. In Bakersfield, fogs were usually not acidic. However, there were occasions when the acid neutralizing capacity from the cattle feed lots was overwhelmed by the sulfur dioxide emissions, resulting in highly acidic fogs in the Bakersfield area. Oildale is a sulfate dominated system up in the Bakersfield area relative to nitrate, nonetheless a fairly acidic environment.

In San Diego, we observed a different time series for the concentrations of principal components. San Diego also had relatively acidic fog, but when we did the back trajectories on the air mass, this air mass was actually moving from the South Coast Air Basin out to sea, and then it came back in on San Diego. There were relatively low pH's in the fog water that was collected over this period of time. It was a nitrate dominated system which is characteristic of the Los Angeles basin. Using the principles that Sheldon Friedlander had developed, we looked at the trace element composition, and we were able to back calculate the various components in that particular fog or coastal cloud episode in San Diego. The composition was mainly secondary sulfate and secondary nitrate, from the Los Angeles basin. The sea salt component added to the total loading in micrograms per cubic meter.

Let us come back to the London fog episodes. These were episodes in which people died; upwards of 4000 excess deaths occurred during a single event. During a few events they actually measured the acidity in the air by total titration of aerosol samples. This value was listed as sulfuric acid, but it was the titratable acidity in micrograms per cubic meter. If that was the amount of sulfuric acid available in a typical cloud droplet system with a liquid water content of 0.2 grams per cubic meter, the pH values will be below 2. These predicted values can be compared to some of the early episodes in the Los Angeles basin where the acidity consists of sulfuric and nitric acid.

The cloud composition over the Los Angeles basin has been relatively uniform over the years. We have continued to make measurements from about 1981 to the present. In San Pedro, located down along the coast in Los Angeles, we found relatively high concentrations of sulfate. There was nitrate present as well as acetate, formate, hydrogen peroxide, and sulfur dioxide, and this points to some interesting chemistry. Early on, we predicted that sulfur dioxide and hydrogen peroxide should not coexist in the droplet phase. This led us to some interesting chemical discoveries. The pH, even in marine stratus clouds, will be as low as 2.2, and these are clouds coming directly off the ocean. Of course the air mass could have been over the Los Angeles basin the previous day.

Our general conclusions about the factors that lead to either high or low pH conditions are as follows. The primary sources of acidity are NO and SO_2. They are converted to their corresponding acids and incorporated into fog droplets or haze aerosol. Ammonia is scavenged from various sources, and neutralizes the acidity. With an insufficient amount of ammonia available relative to the acid that has been produced, low pH conditions are generated. In those regions where ammonia is high, the acidity is neutralized, and high pH conditions in clouds or fog are observed. In the Bakersfield area, the battle was essentially between the sources of acidity: the steam generation plants used for the tertiary recovery of oil and the agricultural activities in the San Joaquin Valley. In an article that appeared in 1984, I reported some of those very acidic values. The people in Bakersfield and the newspaper reporters were excited that they were being exposed to these very acidic fogs, and then they were really disappointed the next year, when we found that most of the fogs were quite basic.

During that particular period, the pH values during winter were about 5.1 to about 7; Visalia was even higher. The only acidic conditions were found at McKittrick, where there were no cattle feed lots. All the high pH fogs were located in areas where there were many cattle feed lots.

Let us come back to the very early model of what goes on in a cloud or fog system. We were able to determine that most of the chemical composition within cloud systems comes from nucleation scavenging. The haze aerosol promotes the condensation of water when the relative humidity is sufficiently high. In addition, gas phase compounds can transfer into the water phase of droplet aerosols. The sulfur compounds can lead to in situ production of sulfate and protons. The droplets themselves very readily scavenge nitric acid. They also scavenge HCl that was released from the sea salt aerosol reacting with nitric acid. As soon as a cloud forms, it can scavenge back the HCl as Walter pointed out.

In the transition from a dry atmosphere to a humid atmosphere, we can imagine starting out with dry aerosol. This aerosol is the condensation mode, in the range above 0.1 micrometer. Above a certain humidity, the aerosol becomes deliquescent. We form the haze aerosols that you saw in one of the earlier pictures, and then at 100% relative humidity, we get a fog. A lot of the in situ conversion takes place here. When the relative humidity drops, you get this droplet size particle that Walter was talking about.

Over the years, we found a number of interesting facets about the in situ chemistry. Our early thinking in the 70s, was that the principle oxidant of sulfur dioxide in the atmosphere was hydrogen peroxide, and this oxidation should take place in cloud droplets. These field studies allowed us to verify many laboratory studies. The major pathway is a pathway that I had worked out in the early 70s, and it essentially involves the oxidation of aquated sulfur dioxide to produce sulfate. However, as I mentioned, we were finding the co-existence of sulfur dioxide, S(IV) in the liquid phase, and also hydrogen peroxide. Chemically, they should not coexist. Thus we needed to rationalize these experimental field observations. We realized that sulfur dioxide from the gas phase was partitioning into the liquid phase, but so were a wide range of aldehydes, such as formaldehyde, glyoxal, methylglyoxal and hydroxyacetaldehyde. There are many aldehydes that are produced photochemically in the atmosphere. They get scavenged into the droplet phase in addition to formic acid, acetic acid, oxalic acid and so forth. Now, a very interesting thing takes place. This is essentially the "wine bottle" or "beer bottle" reaction. Brewers and vintners add sulfur dioxides to wine and beer in order to trap any aldehydes that are produced through alcohol oxidation. The oxidation of alcohol affects the flavor of red wines, in particular, and also beer. S(IV) and aldehydes form hydroxyalkylsulfonates. We learned from our cloud studies, that these reactions are quite important. We then studied a whole series of these in laboratory experiments both kinetically and thermodynamically. We saw that there was another pathway for acidification in addition to incorporation of sulfuric and nitric acid that was the in situ reaction of sulfur dioxide with aldehydes such as formaldehyde to produce hydroxymethane sulfonate. This pathway ended up producing excess acidity, and it also accounted for the novel coexistence of S(IV) and H_2O_2. S(IV) is thus a combination of aquated sulfur dioxide primarily as bisulfite, hydroxymethane sulfonate, plus other aldehyde-bisulfate species. This chemistry allowed for the very high concentrations of S(IV). We developed analytical methods to actually identify these compounds. Once again, the gas phase chemistry is important to what we see in the liquid phase. You cannot separate the gas phase from the liquid phase because they are very highly intertwined. For instance, the aldehydes that we see in the droplet phase come from the gas phase photo-oxidation via hydroxy radical of toluene and xylene. We see glyoxal, methylglyoxal, and unsaturated aldehydes and a variety of other aldehydes. These all bind sulfur dioxide and lead to the production of acidity.

There was a tremendous amount of work done over the years. We did look at cloud chemistry and snow chemistry up in the Sierra Nevada. In the Sierra Nevada, we had automated collection devices that could operate for a month at a time collecting and documenting fog and cloud frequency. We still have several sampling sites in Yosemite in operation. After several years of intensive study, one could look at the relative composition of rain water in that area, because we also know how much rain fell. Due to higher concentrations in cloud water, impaction at higher elevations resulted in substantially more deposition of nitrate and ammonium, than by rain. In terms of sulfate, rain and cloud water were about equal. Cloud-derived impaction, from clouds moving through the trees introduced a lot of nitrates, sulfates, and various acid components to those environments.

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Cloud, Fog & Snow Chemistry

Professor Michael R. Hoffmann

Environmental Engineering Science
W. M. Keck Laboratories
California Institute of Technology
Pasadena, CA 91125

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NEHZAT MOTALLEBI, Moderator

The topic of the next presentation is "Mathematical Modeling and Control of the Dry Deposition Flux of Nitrogen-Containing Air Pollutants", and will be presented by Dr. Glen Cass of the California Institute of Technology.

5. Mathematical Modeling and Control of the Dry Deposition Flux of Nitrogen-Containing Air Pollutants. Dr. Glen Cass, California Institute of Technology.

DR. GLEN CASS, California Institute of Technology

I have been asked to talk to you this afternoon about one particular study (Fig. 1) that was done as part of our work for the Air Resources Board. We tried to address a question (Fig. 2) that I have not heard addressed yet today: "How are the emission sources coupled to the dry deposition problem, and can we make reasonable predictions about the effects that would occur if the emission source rates were changed?" I am going to proceed through an analysis that we did in which a photochemical airshed model was modified in order to specifically examine its dry flux predictions. Such models can make these predictions, but they are generally not displayed because the models' original purpose was for the prediction of atmospheric pollutant concentrations. This research represents a joint effort among a number of people: Armistead Russell who is now at Carnegie-Mellon University and formerly was a graduate student at Caltech, as well as Darrell Winner, Robert Harley, Kenneth McCue, and myself. At the time of this study, we were all at Caltech. Rob Harley is now at UC Berkeley.

The approach taken in this study (Fig. 3) was to modify the Caltech photochemical airshed model in order to enhance its ability to produce dry deposition flux predictions. This model was originally developed by John Seinfeld's group in order to make ozone and other photochemical smog component concentration predictions in the gas phase. We wanted to modify that model to compute and store a variety of parameters that are of importance to the dry deposition question. Specifically, we wished to compute and store the dry deposition velocities that parameterize the removal mechanisms in these models, to collect and store the spatial and temporal distribution of the dry deposition flux of each of the many derived pollutant species, and to upgrade the dry deposition flux calculation procedures. We wanted in particular to take advantage of high resolution land use data to improve the accuracy of the dry deposition calculation and to track through the model all of the nitrogen-containing species that are derived from either nitrogen oxide emissions or the ammonia emissions from the airshed. This would include NO, NO_2, nitric acid vapor, PAN, aerosol nitrates, and other photochemical oxidants. The model was then applied to test its predictive capabilities in southern California against data sets that have been used to verify gas phase pollutant concentration predictions historically. Next, we used the modified model to examine the effect of emission controls on the deposition flux of nitrogen-containing pollutants. We looked specifically at emission controls that could be applied to stationary sources and emission controls that could be applied to motor vehicles, as well as combinations of mobile and stationary source controls. The improved air quality model was used to assess the effect of different types of emission control procedures on the dry deposition flux for each of the nitrogen-containing air pollutants studied.

The airshed model contains a rather detailed gas phase chemical mechanism (Fig. 4). The nitrogen-containing species within the model interact with each other in the following way. Emissions enter the model principally as nitric oxide (NO), are transformed over time predominantly to nitrogen dioxide (NO_2). The nitrogen dioxide reacts to form nitric acid vapor. During the daytime, the nitric acid vapor is produced by hydroxyl radical attack on NO_2, and at nighttime, by transformations through the nitrate radical and N_2O_5 to form nitric acid vapor. Once the nitric acid vapor has been formed, the model in this particular implementation computes the amount of aerosol nitrate that will exist at equilibrium with the amount of ammonia being carried in the model. In addition, the hydrocarbon chemistry is tracked by the model. The dry deposition calculation proceeds as follows: the atmospheric concentrations predicted by the model at a reference height, typically about 10 meters above the ground, are multiplied by deposition velocity values that are computed theoretically from this calculation, a predicted flux to the surface of the air shed is obtained for each pollutant, which varies as a function of space and time depending on meteorologic conditions and the roughness and the surface properties of a particular grid square. This deposition velocity in turn depends inversely on the summation of a series of resistances to deposition. Two of these resistances are essentially aerodynamic resistances to deposition. They depend on the atmospheric fluid mechanics and the rate at which pollutants can be delivered from high in the atmosphere down close to the ground. In addition, there is a surface resistance that depends on the physical and chemical character of the receiving surface. The maximum deposition velocity for a particular pollutant is the inverse of the summation of the aerodynamic resistances. In other words, with the surface resistance set to 0, you get the maximum possible pollutant delivery that fluid mechanics can provide to your surface. We can calculate that maximum delivery rate according to fluid mechanical principles that essentially come from integrating fluxes through the boundary layer equations as the atmosphere blows across the surface. The surface resistance air model (Fig. 5), depends on field experiments conducted historically to determine pollutant the uptake characteristics of different kinds of surfaces. The surface resistance parameterization in our model begins with the parameterization that was developed for the RADM model as part of the National Acid Precipitation Assessment Program. In that parameterization, we have taken USGS land use maps and subdivided them into more than 30 different types of land uses. Essentially what we have done is to take the USGS maps for the Los Angeles area (the South Coast Air Basin), and examined them at intervals of a few hundred feet at very high resolution to determine the spatial distribution of each of the major types of urban land uses (residential, commercial, industrial, and so forth) and agricultural land uses including crops, pastures, orchards, and vineyards. We have identified where the range land is located, where different kinds of forests are located, where water bodies are located, and where bare land is located.

Figure 5 shows the surface resistance parameterization for a particular time during the summer for sulfur dioxide, with resistances appropriate to the land uses listed. The model varies the surface resistance depending on the solar isolation and the season of the year which is intended to capture stomatal opening and closing effects present at different times of day and temperature effects that occur at different times of the year. The surface resistance data are probably most complete for sulfur dioxide. For other compounds much less information is available. The model estimates the surface resistances for the other pollutants that are carried by the model as being proportional to the surface resistance for SO_2 at the appropriate level of solar isolation and time of the year specified. We have made a few modifications to the procedure used in the RADM model. In particular, we have set our surface resistances for NO to a much higher value than that used by the RADM model because our own experience with our indoor air quality model shows that NO is not removed very quickly at surfaces. The surface resistances for NO, NO_2, ammonia, hydrogen peroxide, aldehyde, nitric acid vapor, nitrate radicals, N_2O_5, and the rest of species in the model are specified as shown in figure 6. Note that the surface resistances for nitric acid are very low. Nitric acid and most of the radical species, we believe, are taken out at nearly a diffusion limited rate.

The dry deposition flux for aerosol nitrate in the present model is based on empirical evaluation of Bill Pierson's experiments at Claremont, where both aerosol nitrates and nitric acid deposition rates were measured. At the time this model was developed more than a half dozen years ago, we did not have Walter John's high resolution size distribution data for the aerosol nitrates. Therefore we could not calculate nitrate dry deposition fluxes as a function of particle size. So we ratioed those fluxes to the fluxes for nitric acid vapor which had been measured.

In addition, we further subdivided the urban land into properties that were paved over and built upon and properties that were not (Fig. 7). In Los Angeles, we have a great deal of landscaped area in urban and residential neighborhoods, but the surface resistances to dry deposition that were used in the RADM model essentially view the city as if it were practically barren land with a very high surface resistance. Obviously, if the land is not paved over or built upon but instead is in grass and landscaping, a more appropriate surface resistance would be for vegetation. We have viewed Los Angeles as if it is a suburban area instead of an urban core and calculated our deposition fluxes to the urban areas as a mixture of hard surfaces, built upon surfaces and landscaped surfaces.

The model was tested by application of data taken in southern California during August of 1982 (Fig. 8). On these days in 1982, our research group conducted a field experiment to measure the gas phase concentrations of ammonia, nitric acid, and aerosol nitrate, in addition to collecting the NO, NO_2, and ozone data that are routinely provided by the South Coast Air Quality Management District. As part of that gas phase measurement and modeling exercise we developed the necessary emission data to support air quality modeling calculations for those days. In order to exercise the model over that period of time, a grid system was laid down over the South Coast Air Basin (Fig. 9). The emission inventories are developed over the entire area mapped in figure 9 that extends from Point Conception out into the desert. The air quality modeling region, however, is the smaller domain in the center of that map and includes the most heavily populated portions of Los Angeles, Orange, Riverside, and San Bernardino counties as well as most of the mountain ranges that surround the air basin. Within that grid area, the emission inventories were developed for ammonia, oxides of nitrogen, hydrocarbons and carbon monoxide (Fig. 10). I want to point out the ammonia inventory in particular because this inventory was prepared for the purpose of modeling ammonia in relationship to aerosol nitrate production. The interesting feature of this inventory is the giant spike in the ammonia emissions that is centered over the Chino area in San Bernardino County overlapping a little into Riverside County. That big spike is due to decomposition of livestock waste from approximately a quarter of a million dairy cattle that are confined in a small geographic area. This spike, although it looks as though it contains all of the ammonia emissions in the air basin, in fact, contains I believe less than a third of the ammonia emissions. Instead the rest of the ammonia is spread at very low release rates all over the area due to release from fertilizer decomposition and many other processes that are contained in the emission inventory. Thus, the livestock are not entirely responsible for producing the ammonia emissions. In addition, the land use data for the same area were mapped and gridded. These land use maps are shown for a few of the more important land use categories in figure 5. The blackness or density of the squares in the land use maps represents the fraction of the land use within a particular grid square devoted to a particular use. You can see that the residential densities are greatest over Los Angeles and northern Orange County, and extend out to the Riverside, and San Bernardino areas. If we look at crop land and pasture, we can see that the agricultural areas are located in Ventura County, in southern Orange County, in the lower part of Riverside County, and to some extent around the Chino area. Land use 32 in Figure 11 shows what is called shrub and brush range land which is the scrubby growth on the sides of most of our mountains. We can see that there is a ring of shrub and brush range land around the backsides of the air basin. We have data on all of the other land uses as well.

The emission data and land use data were applied to the dry deposition model. Atmospheric concentration predictions were computed and compared against atmospheric measurements. Figure 12 shows, for Anaheim, predicted and observed NO_2 concentrations, predicted and observed total nitrate, predicted and observed nitric acid levels, as well as predicted and observed ammonia and aerosol nitrate. Predictions and observations are not in perfect agreement, but they are close. The model also produces predictions of the spatial distribution of the concentrations of each of the pollutants that are being tracked. Figure 13 shows model predictions for 2:00 in the afternoon on the second day of the episode model, which is a time at which the nitrogen dioxide concentrations had dropped from their early morning high values. The peak NO_2 concentration at that time is about the 0.05 ppm, with the highest concentration portion of the HNO_3 cloud centered over eastern Los Angeles County at that time of day. The HNO_3 concentration profile is complicated (Fig. 14). Note that the HNO_3 peak is at 25 ppb at that time. The ammonia vapor peak is a little bit further downwind (Fig. 15). Note also that in addition to the peak in the ammonia concentration in the atmosphere, there is a hole in the nitric acid vapor concentration. This hole in the nitric acid concentrations is downwind of the high ammonia emissions that occur in the Chino livestock area. The model is capable of producing spatially and temporally resolved hour-by-hour predictions of not only the nitrogen-containing species shown in figures 13 through 15 but also NO, PAN, and aerosol nitrate.

The model also produces calculations of the spatial distribution over time of the air pollutant deposition velocities. Figure 16 shows deposition velocity results for NO_2 at 2:00 in the afternoon on the second day of the simulation. NO_2 deposition velocity is predicted spatially, with the peak deposition velocity at about 1 cm per second in the eastern area of the air basin where the NO_2 surface resistance is lowest. In the case of nitric acid vapor, the surface resistance is practically zero everywhere (Figure 17). What matters in the case of HNO_3 is the fluid mechanics of the situation. The winds are blowing faster in the afternoon in the western portion of the air basin and the surface roughness created by all of the urban buildings is higher on the western side of the air basin than on the eastern side. As a result there are differences in the spatial distribution of the deposition velocities at the same time for different pollutants (Figs. 16, 17, and 18).

We then take the atmospheric concentrations distributed in space at that time, and we take the deposition velocity distributed in space at that time, and we calculate the dry pollutant flux. Figure 19 shows the NO_2 flux in milligrams per square meter per hour as a function of position in the air basin. We can see that the NO_2 flux is centered over the same location as the NO_2 atmospheric concentration peak, more or less running about 0.75 milligrams per square meter per hour. This essentially reflects the position of the pollutant cloud at that time. The cloud then of course blows across the air basin. Figures 20 and 21 show the nitric acid and the ammonia dry flux prediction, respectively. Again you can see that the ammonia flux is centered over the position of the ammonia cloud at that time.

What does this mean for the air basin as a whole? We can sum up the dry flux predictions for a moderately polluted day in the middle of the summer (Figure 22). The day studied here has an ozone peak of between 0.2 and 0.3 ppm, far from the worst day of the year but hardly a nice day either. The model predictions show 247 tons per day of nitrogen deposited at the surface and distributed among the delivering species. The largest dry flux is due to the nitric acid vapor flux to the surface. This is something that everyone has remarked on today and that is also predicted by the model (Fig. 22). The other large fluxes are the nitrogen dioxide and ammonia plus ammonium nitrate fluxes . The NO_2 fluxes are a little bit higher in proportion to the nitric acid fluxes than was the case for some of the mountain side data presented by earlier speakers. The reason for this is that NO_2 concentrations are much higher over the populated flat portions of the air basin than they are up in the mountains.

If you add up the dry flux of just the species that are contributed from the NO_X emissions, (NO, NO_2, PAN and nitric acid vapor plus half of the nitrogen contained in aerosol nitrate), you have 170 total tons per day of nitrogen. If you convert that back to equivalent NO_X emissions, it is equivalent to, I believe, around 577 tons per day of NO_X. Now the total emissions of NO_X in the model are around 1100 tons per day. This means that very close to half of the NO_X emissions during this summertime smog episode are removed at the surface of the air basin before the air mass is transported out of the air basin.

Q (AUDIENCE) Do those figures cover the entire grid that you showed us originally on your map?

A (DR. CASS) These figures cover the smaller modeling domain in the center of the map. The only part of the South Coast Air Basin we have excluded is a small fraction of the eastern section of San Bernardino and the eastern section of Riverside County, and we have included within the modeling domain a little bit of extra desert in the northeast. The area modeled is approximately the South Coast Air Basin, not the whole map.

Now having developed a model that seems to be doing a reasonable job of accounting for atmospheric pollutant levels and pollutant deposition fluxes, the next thing that we did was to examine a number of source-specific emission control measures. These control measures are not identical to any particular control plan that has been proposed by the government. Instead, they simply represent groups of controls that logically might be anticipated to be adopted at some point in the future (Fig. 23). In the upper left corner are our base case 1982 emissions. There are a little more than 1100 tons per day of NO_X with the official stated reactive hydrocarbon emission rates of 1200 tons per day at that time and total hydrocarbon emissions of around 2400 tons per day. To the best of our belief, the actual hydrocarbon emissions are higher than this now. About 164 tons per day of ammonia was emitted into the atmosphere of the South Coast Air Basin in 1982.

Nine different combinations of emissions controls on specific sources were studied. The upper left corner of Figure 23 describes a minimal emission control effort: a vehicle inspection and maintenance plan that is not particularly drastic combined with evaporative controls and combustion modifications applied to stationary sources. These are some of the emission controls that were part of the air quality management plan in effect in 1982. The controls stated in the upper left zone of figure 23 would drop the hydrocarbon emissions by a little more than 9% and the NO_X emissions by a little more than 5.4% and make no change in the ammonia emissions. Moving across the diagram of figure 23 from left to right, more stringent motor vehicle controls are added. No particular motor vehicle control hardware is stated. Instead, the effect of reaching various emission rates for the entire light duty fleet and for the entire heavy duty fleet is computed. If the emissions from the light duty fleet ever in fact got to 0.41

grams per mile of hydrocarbons and 0.7 grams per mile of NO_X and if the heavy duty fleet got to 2.6 grams per mile of THC and 10.7 grams per horsepower hour of NO_X, then a 36-37% reduction in both reactive hydrocarbons and NO_X emissions would occur relative to the base case given 1982 traffic volumes. We also looked at what would happen if the NO_X emissions from the fleet were actually dropped to 0.4 grams per mile. This is not to say that you would do this with a 0.7 or 0.4 gram per mile NO_X standard but rather that the motor vehicle fleet would eventually reach those levels either, because we adopt the standards at those levels and maintain the vehicles religiously or because we adopt a standard lower level and allow for deterioration.

We looked at progressively increased emission control supplied to stationary sources in combination with the alternative levels of motor vehicle control indicated in figure 23. At the first level of stationary source control, a relatively inexpensive NO_X control method, noncatalytic ammonia injection or thermal denox as it is sometimes called, was considered. As we go down the rows of figure 23 much more efficient but more expensive oxides of nitrogen control systems are applied to the big stationary sources. In the case of the lowest row of figure 23, we examine selective catalytic reduction as a stationary source NO_X control measure. Stationary source NO_X decreases up to around 18% of total basin emissions were considered. The lower right corner of figure 23 shows the maximum amount of control considered during this study, that is to say all of the major stationary and all of the mobile sources are controlled at the same time. In this case about a 60% NO_X reduction and about a 37% hydrocarbon reduction would occur relative to the base case. This is nowhere near the amount of hydrocarbon control required to meet the ozone standard, but the NO_X emission reductions are rather close to the amount of NO_X reduction that is presently being contemplated in southern California.

What is the effect of those various kinds of controls on the dry flux of each of the pollutant species studied here? Figure 24 shows the percentage reduction in the dry flux of each of the pollutant species modeled. The results are not surprising. The minimal emission control program with a few percent change of hydrocarbon and NO_X produces a few percent change in the dry flux of most of the species in the system. In the far right hand lower corner of the table in figure 24, with the maximum NO_X control plan studied, the 60% NO_X control and 37% or so hydrocarbon control program produces about a 69% reduction in the NO dry flux and a 59% reduction in the NO_2 dry flux. In other words, the NO and NO_2 dry flux reductions are in the same range as the NO_X emission reductions that were achieved. The maximum NO_X reduction program studied produces nitric acid and ammonium nitrate dry flux reductions of 43% and 53%. In other words, nitric acid and ammonium nitrate dry fluxes do not decline by quite as much as the oxides of nitrogen emissions reductions that were achieved. PAN fluxes hardly change at all, and I can tell you that the ozone concentrations simulated with that combination of emission controls does not change a whole lot either, because there are still so many hydrocarbons still going into the system and the NO_X emissions are still running at about 400 tons per day. There is still a fair amount of pollution around. Another feature that is noticed in the cases studied is that the ammonia concentration in the atmosphere goes up when NO_X emissions are reduced even though ammonia emissions remain unchanged. The reason for this is that when you suppress the NO_X emissions and drop the nitric acid vapor formation in the model, you make less ammonium nitrate, but you have not reduced the ammonia emissions. So the ammonia that was once tied up in ammonium nitrate is now back out in the gas phase. The gas phase dry deposition rate for ammonia in the model is considerably higher than the aerosol nitrate dry flux rate. The result of higher atmospheric ammonia concentrations is a higher dry flux as ammonia to the surface of the air basin.

The model can be examined to look at temporal changes in the pollutant deposition flux. Figure 25 shows the flux of nitric acid vapor to the surface as a function of time at downtown Los Angeles. The solid line is the base case simulation with the no emission control calculation while the dashed line shows the case where the oxides of nitrogen are reduced by the maximum amount studied in figures 23 and 24. The two cases more or less track each other. Bringing down NO_X emissions brings down nitric acid vapor in the atmosphere and it brings down the nitric acid dry flux. Figure 26 shows the same comparison for NO_2 before and after control, and Figure 27 summarizes the results for nitrogen compounds.

In conclusion (Figs. 28 and 29), we have developed a grid-based air quality model that has been modified to capture and retain those portions of the photochemical airshed modeling exercise that are most important for studying the dry deposition flux and its control. We have tested that model by application to the South Coast Air Basin under summertime photochemical smog conditions. Under 1982 historical conditions the dry flux of nitrogen containing pollutants was 176 tons N per day derived from NO_X emissions and 72 tons N per day derived from ammonia emissions, and the NO_X dry flux was very close to half of the NO_X emitted within the air basin that day. When we apply the NO_X and RHC controls that were studied here to the sources, NO and NO_2 dry flux reductions occur that are roughly proportional to the NO_X emissions reductions. HNO_3 and NH_4NO_3 aerosol flux reductions achieved are a little less than proportional to the degree NO_X control and the ammonia dry fluxes go up. These are all consistent with the changes to the aerosol nitrate concentrations and gas phase pollutant concentrations that you would expect from the control program alternatives studied here. The model of course can be used to study other control options as well.

Figure 1

MATHEMATICAL MODELING AND CONTROL OF THE DRY DEPOSITION FLUX OF NITROGEN-CONTAINING AIR POLLUTANTS

Armistead G. Russell

Carnegie-Mellon University

Darrell A. Winner
Robert A. Harley
Kenneth F. McCue
Glen R. Cass

California Institute of Technology

Figure 2

PROBLEM

- INTERACTION OF NITROGEN-CONTAINING AIR POLLUTANTS WITH SURFACES LEADS TO
  - MATERIALS DAMAGE
  - EFFECTS ON CROPS AND FORESTS
  - HIGH NITRATE LEVELS IN DRINKING WATER
- EMISSION CONTROLS CAN BE IDENTIFIED THAT WOULD REDUCE NO_x EMISSIONS
- CAN THE EFFECT OF EMISSION CONTROLS ON POLLUTANT DRY DEPOSITION BE PREDICTED

Figure 3

APPROACH

- CALTECH PHOTOCHEMICAL AIRSHED MODEL MODIFIED TO COMPUTE AND STORE
  - DEPOSITION VELOCITIES
  - DRY DEPOSITION FLUX
  - TO 19 DIFFERENT LANDUSE CATEGORIES
  - FOR POLLUTANT SPECIES INCLUDING NO, NO_2, HNO_3, PAN, AEROSOL NITRATE, AND O_3
- MODEL APPLIED TO SOUTHERN CALIFORNIA
- EMISSION CONTROLS STUDIED
  - STATIONARY SOURCES
  - MOTOR VEHICLES
- EFFECT OF CONTROLS ON DRY DEPOSITION FLUX COMPUTED

Figure 4

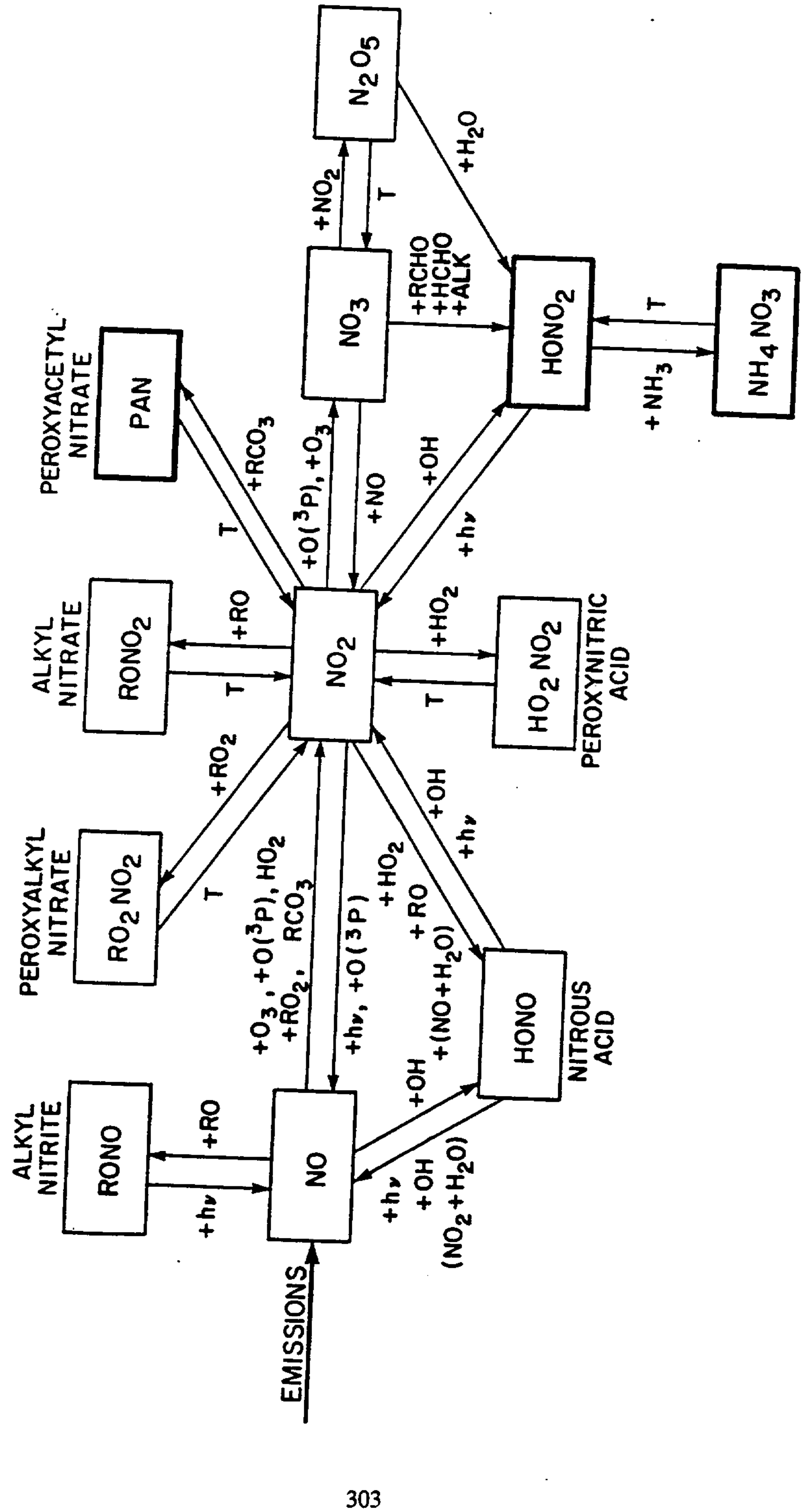

EMISSIONS
NO
ALKYL NITRITE
RONO
+RO
+hν
+O$_3$, +O(^{3}P), HO$_2$
+RO$_2$, RCO$_3$
+hν, +O(^{3}P)
+OH
+(NO+H$_2$O)
+hν
+OH
+OH
(NO$_2$+H$_2$O)
HONO
NITROUS ACID
+HO$_2$
+RO
+OH
+hν
NO$_2$
PEROXYALKYL NITRATE
RO$_2$NO$_2$
+RO$_2$
T
ALKYL NITRATE
RONO$_2$
+RO
T
HO$_2$NO$_2$
PEROXYNITRIC ACID
+HO$_2$
T
PEROXYACETYL NITRATE
PAN
+RCO$_3$
T
+O(^{3}P), +O$_3$
+NO
NO$_3$
+OH
+hν
HONO$_2$
+RCHO
+HCHO
+ALK
+NO$_2$
T
N$_2$O$_5$
+H$_2$O
NH$_4$NO$_3$
+NH$_3$
T

Figure 5

SURFACE RESISTANCE AS A FUNCTION OF LAND USE CATEGORY (SUMMER)

(sec/cm)

	O_3	SO_2
URBAN		
–HIGHRISE URBAN	3.0	10.0
–RESIDENTIAL	3.0	10.0
–COMMERCIAL	3.0	10.0
–INDUSTRIAL	3.0	10.0
–UTILITIES	3.0	10.0
–INDUSTRIAL/COMMERCIAL	3.0	10.0
–MIXED URBAN	3.0	10.0
–OTHER URBAN	3.0	10.0
AGRICULTURAL		
–CROPS AND PASTURE	0.6	0.7
–ORCHARDS, GROVES, VINEYARDS	0.6	0.7
–LIVESTOCK FEEDING	0.6	0.7
–OTHER AGRICULTURAL	0.6	0.7
RANGELAND		
–HERBACEOUS RANGE	0.9	1.0
–SHRUB AND BRUSH RANGE	0.9	1.0
–MIXED RANGE	0.8	1.0
FOREST		
–DECIDUOUS FOREST	0.8	0.6
–EVERGREEN FOREST	1.3	1.5
–MIXED FOREST	1.0	0.7
WATER		
–OCEAN	20.0	0.0
–STREAMS	20.0	0.0
–LAKES	20.0	0.0
–RESERVOIRS	20.0	0.0
–BAYS AND ESTUARIES	20.0	0.0
WETLAND		
–FORESTED WETLAND	1.0	0.7
–NON-FORESTED WETLAND	1.5	0.5
BARREN LAND		
–DRY SALT FLATS	3.0	10.0
–BEACHES	3.0	10.0
–SANDY AREAS	3.0	10.0
–BARE ROCK	1.2	1.5
–QUARRIES, MINES, GRAVEL PITS	3.0	10.0
–TRANSITIONAL AREAS	3.0	10.0

Figure 6

SURFACE RESISTANCE AS A FUNCTION OF POLLUTANT SPECIES

SPECIES	r (sec/cm)
NO	$13.9 \times r_{SO_2}$
NO_2	$1.0 \times r_{SO_2}$
NH_3	$0.2 \times r_{SO_2}$
H_2O_2	$0.1 \times r_{SO_2}$
HCHO	$0.5 \times r_{SO_2}$
RCHO	$2.0 \times r_{SO_2}$
HNO_3	0.01
NO_3	0.01
N_2O_5	0.01
PAN	4.5
HONO	0.4
RNO_4	4.5
RONO	4.5
OTHER	50
AEROSOL NITRATE	$v = 0.182 \times v_{HNO_3}$

Figure 7

FRACTION OF URBAN LAND NOT PAVED OVER AND NOT BUILT UPON

Highrise Urban	0.25
Residential	0.44
Commercial	0.34
Industrial	0.47
Utilities	0.55
Industrial/Commercial	0.40
Mixed Urban	0.43
Other Urban	0.43

Figure 8

APPLICATION

- SOUTHERN CALIFORNIA
- AUGUST 30-31, 1982

Figure 9

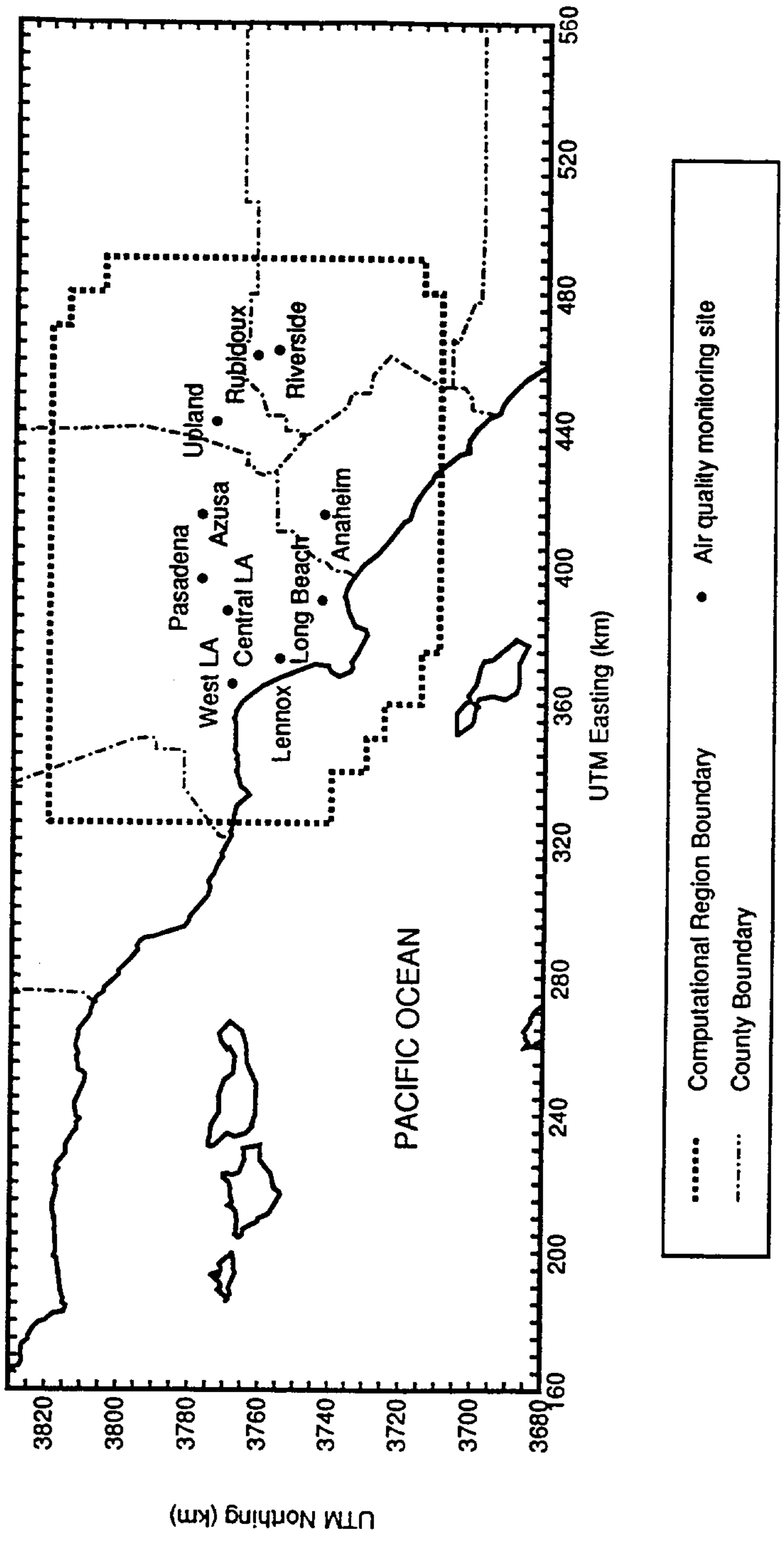

PACIFIC OCEAN
West LA
Pasadena
Central LA
Azusa
Upland
Rubidoux
Riverside
Lennox
Long Beach
Anaheim
UTM Easting (km)
UTM Nothing (km)
160
200
240
280
320
360
400
440
480
520
560
3820
3800
3780
3760
3740
3720
3700
3680
Computational Region Boundary
County Boundary
Air quality monitoring site

Figure 10

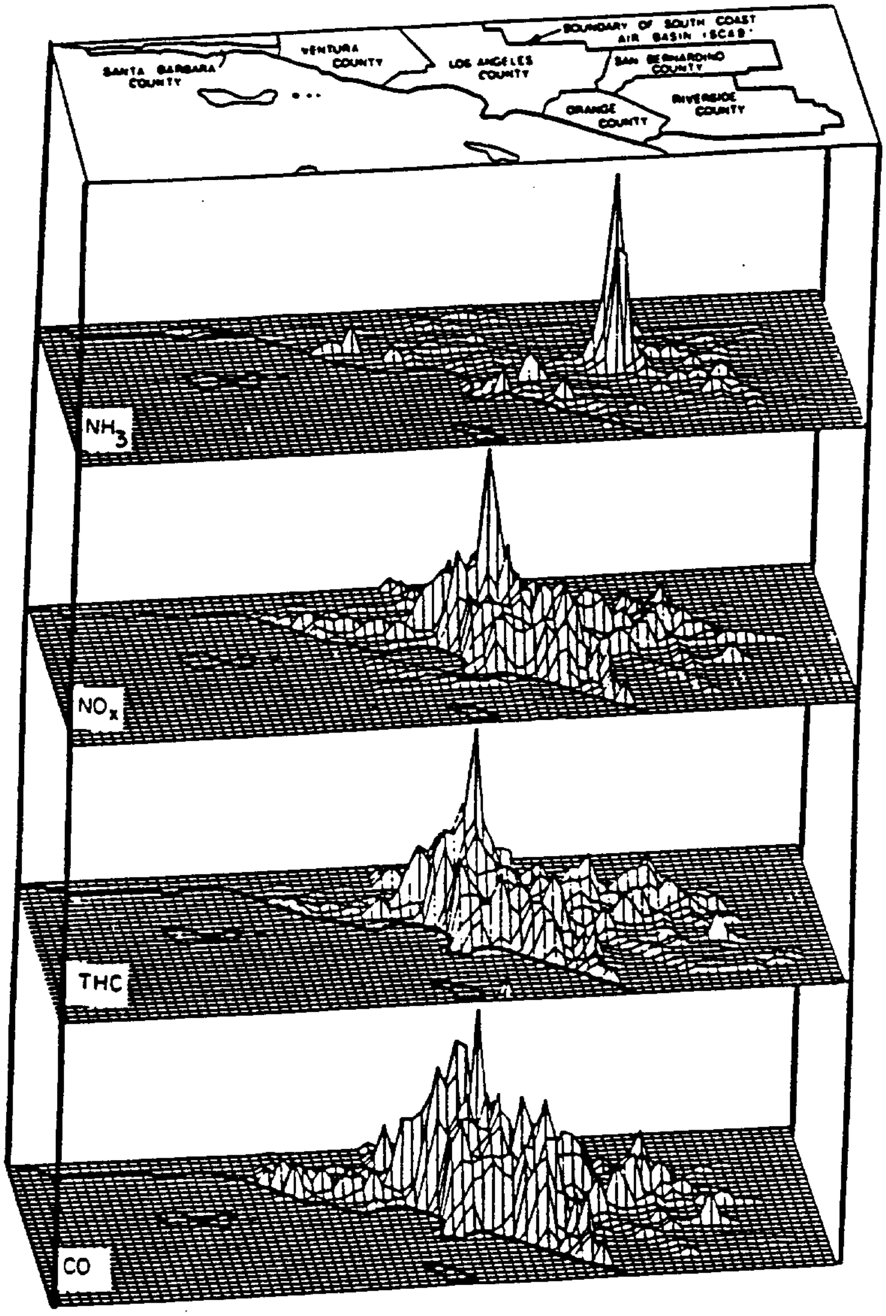
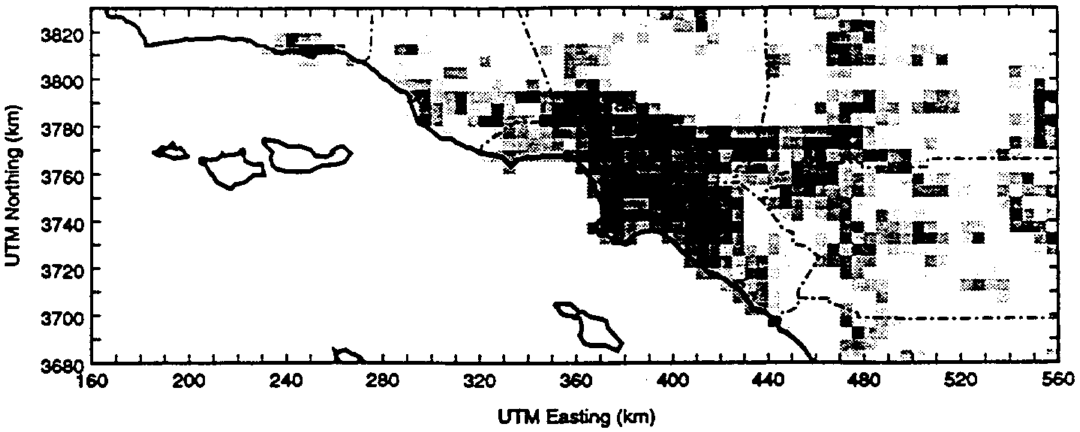
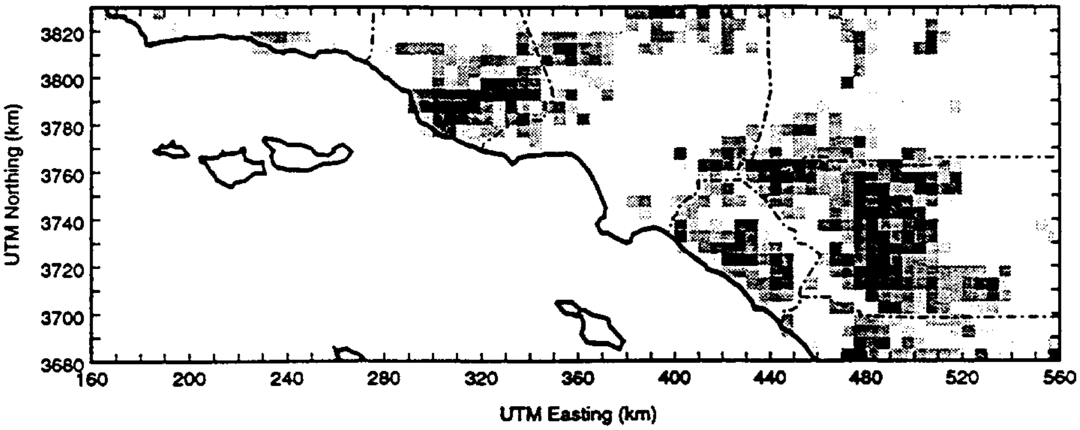

BOUNDARY OF SOUTH COAST AIR BASIN (SCAB)
SANTA BARBARA COUNTY
VENTURA COUNTY
LOS ANGELES COUNTY
SAN BERNARDINO COUNTY
ORANGE COUNTY
RIVERSIDE COUNTY
NH_3
NO_x
THC
CO

Figure 11

LANDUSE 11 RESIDENTAL



LANDUSE 21 CROPLAND AND PASTURE



LANDUSE 32 SHRUB & BRUSH RANGELAND

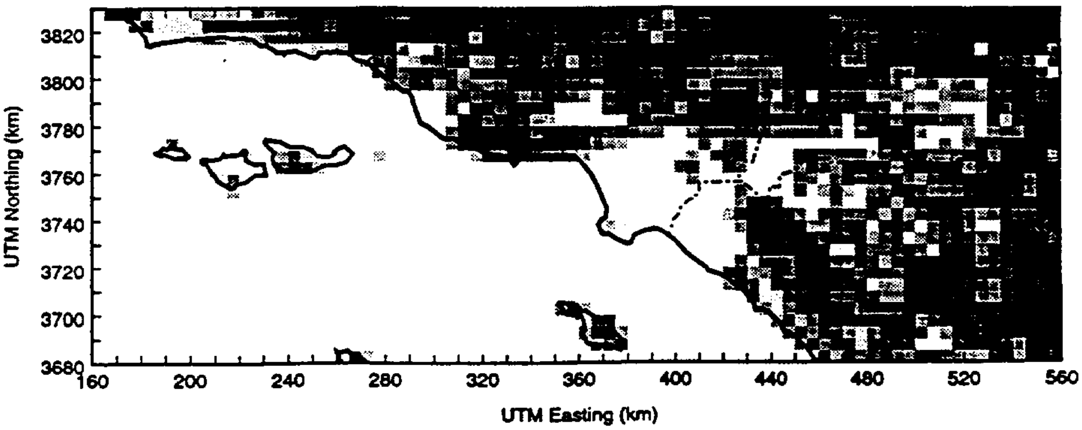
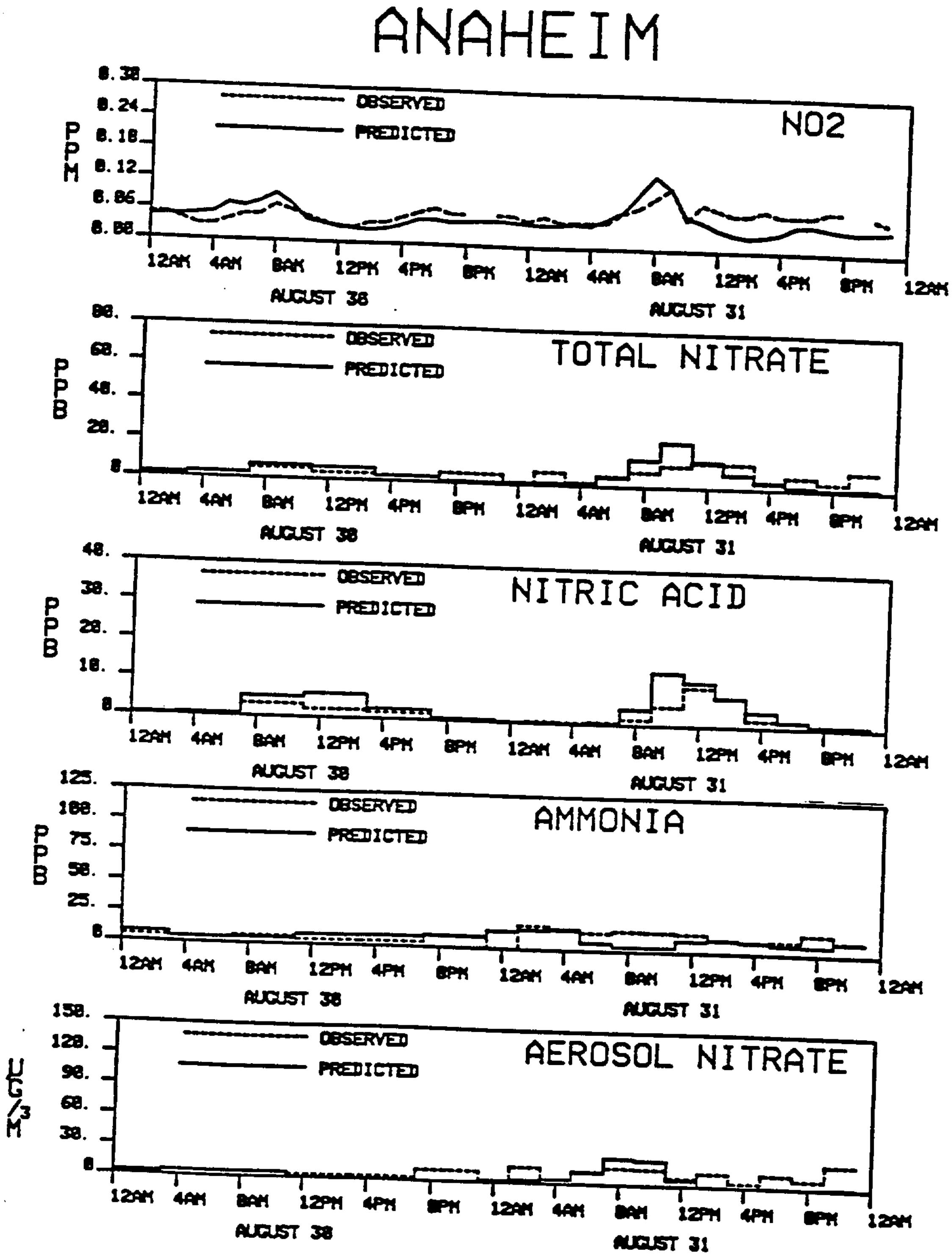


Figure 12



ANAHEIM
NO2
PPM
0.30
0.24
0.18
0.12
0.06
0.00
OBSERVED
PREDICTED
12AM
4AM
8AM
12PM
4PM
8PM
AUGUST 30
AUGUST 31
TOTAL NITRATE
PPB
80.
60.
40.
20.
0.
NITRIC ACID
PPB
40.
30.
20.
10.
0.
AMMONIA
PPB
125.
100.
75.
50.
25.
0.
AEROSOL NITRATE
UG/M3
150.
120.
90.
60.
30.
0.

Figure 13

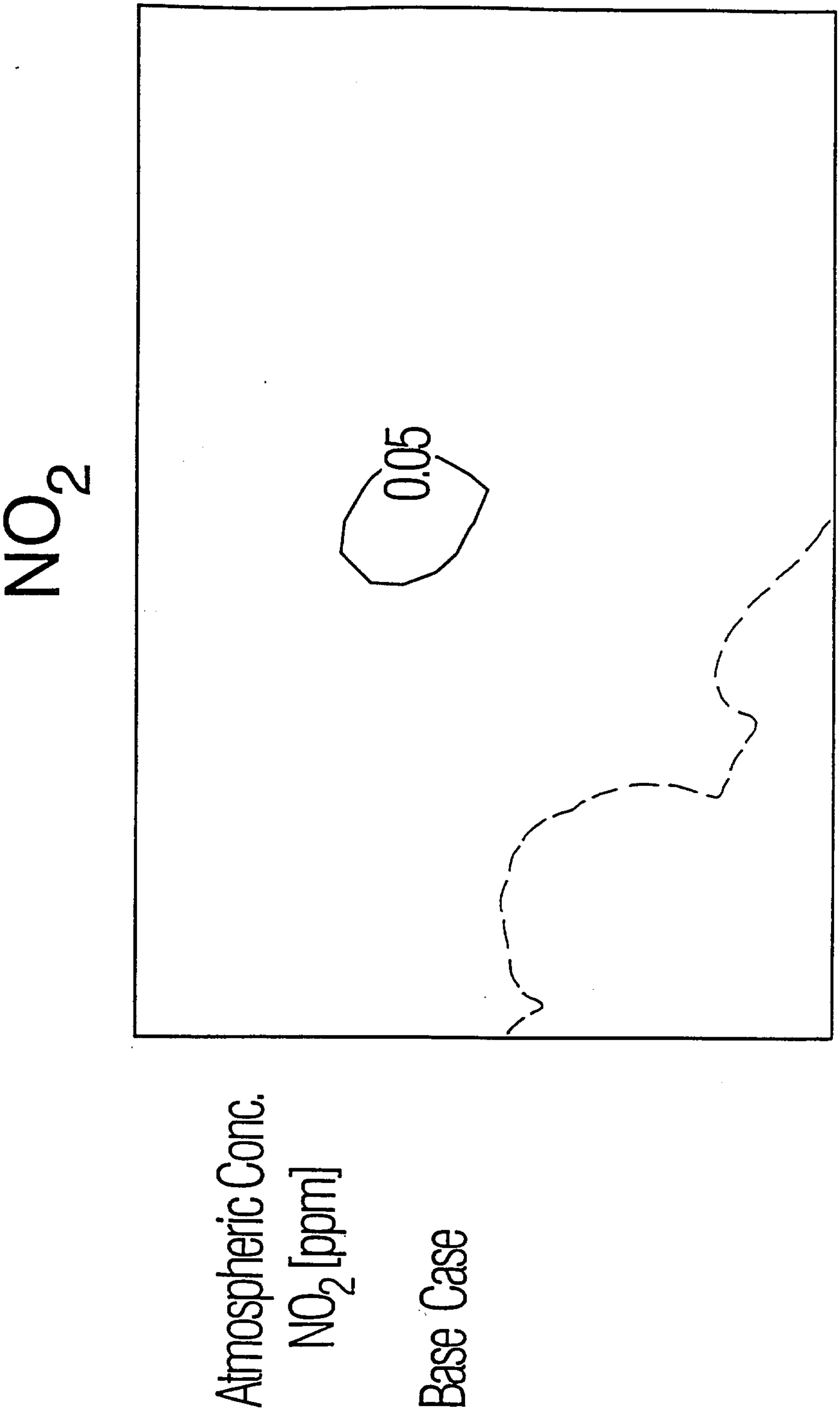


Figure 14

HNO_3

Atmospheric Conc.

HNO_3 [ppb]
Base Case

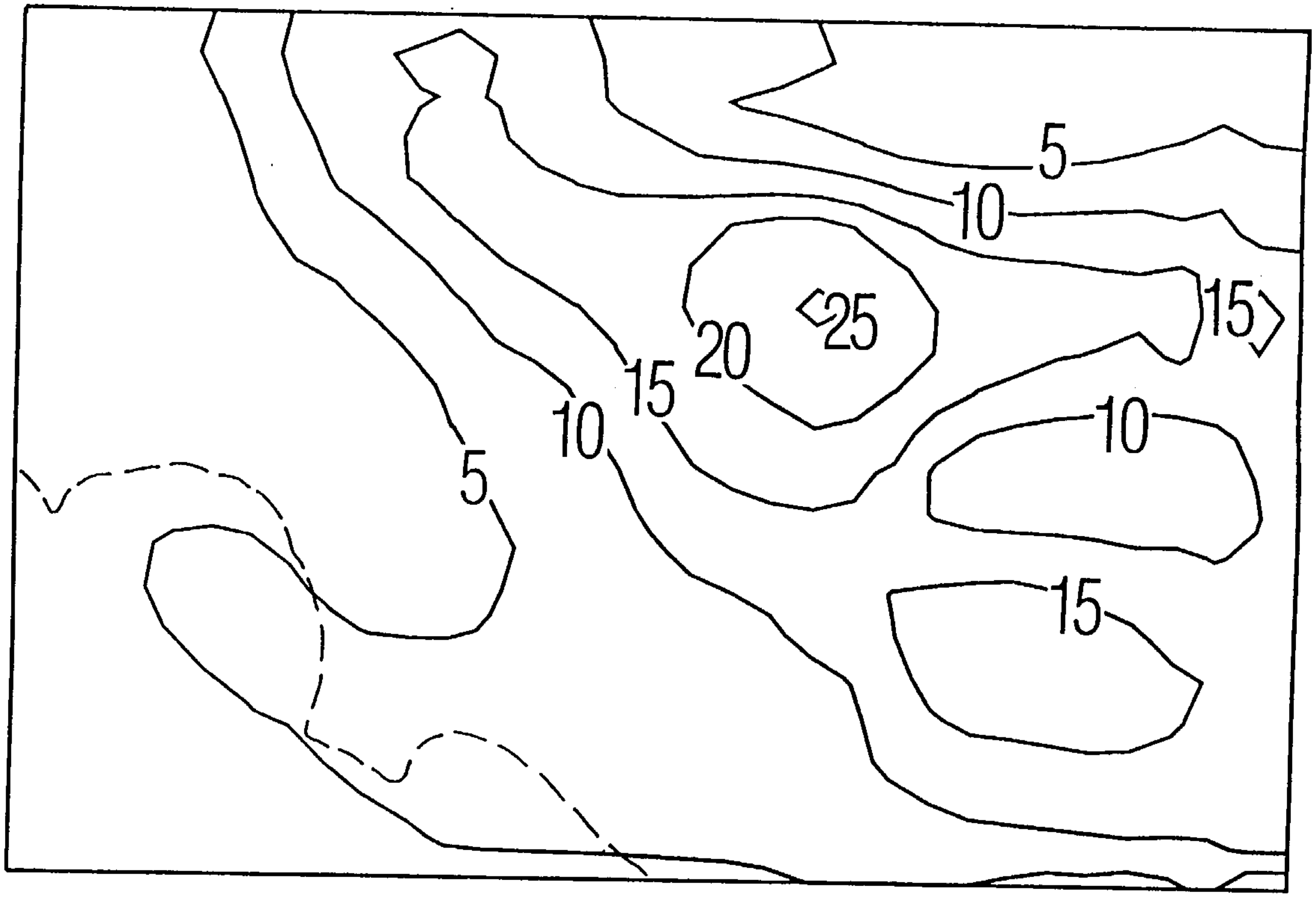
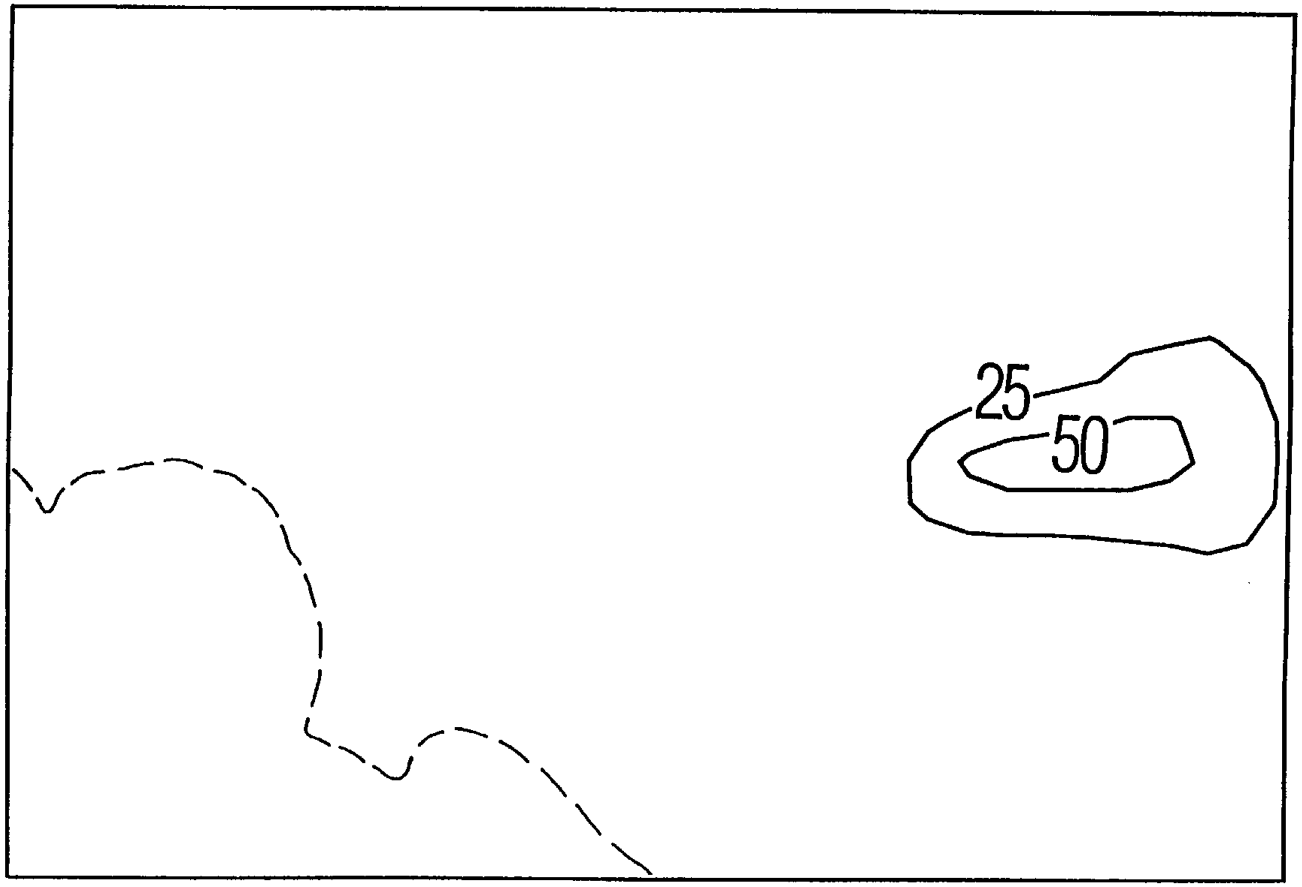


Figure 15

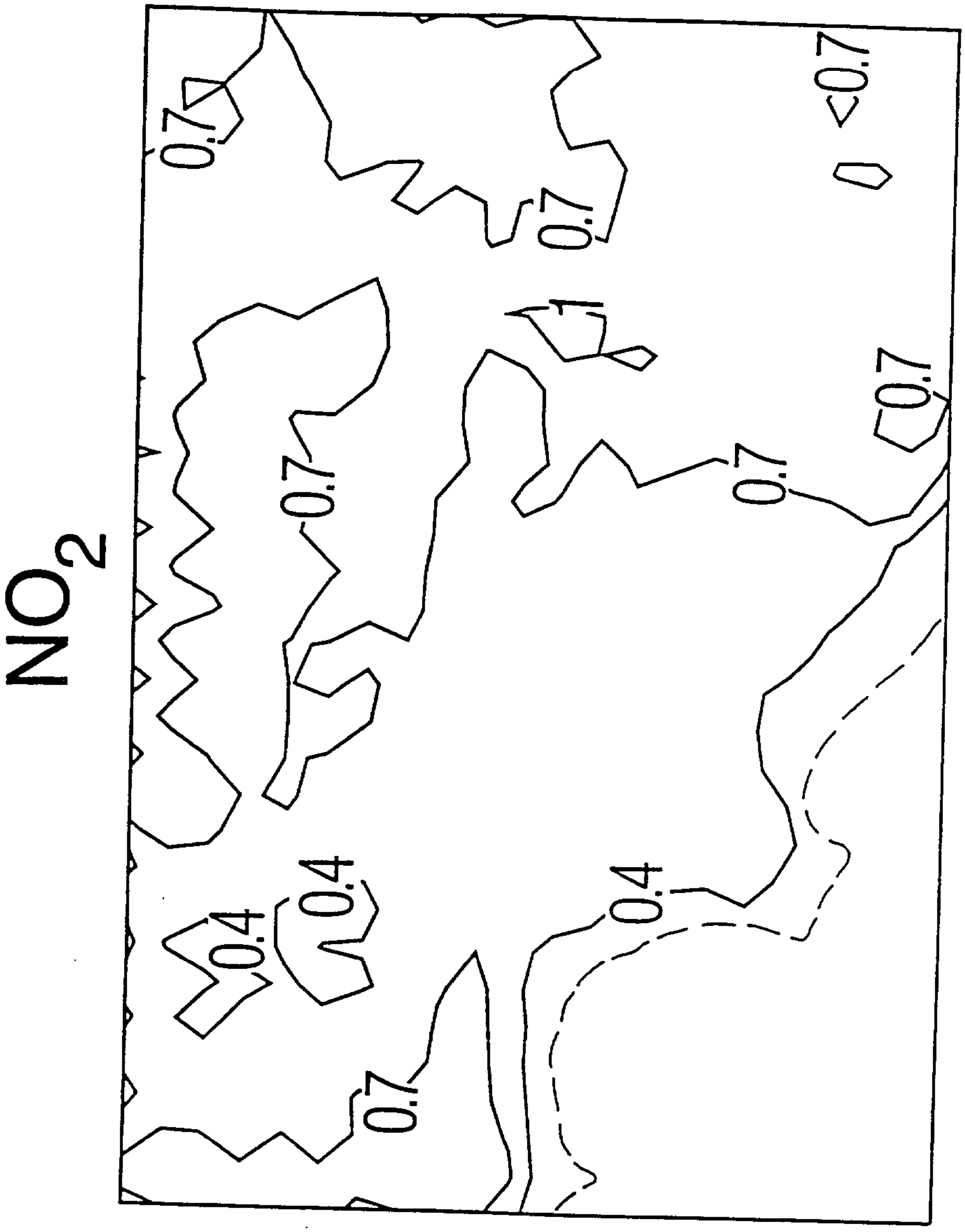
NH_3



Atmospheric Conc.
NH_3 [ppb]

Base Case

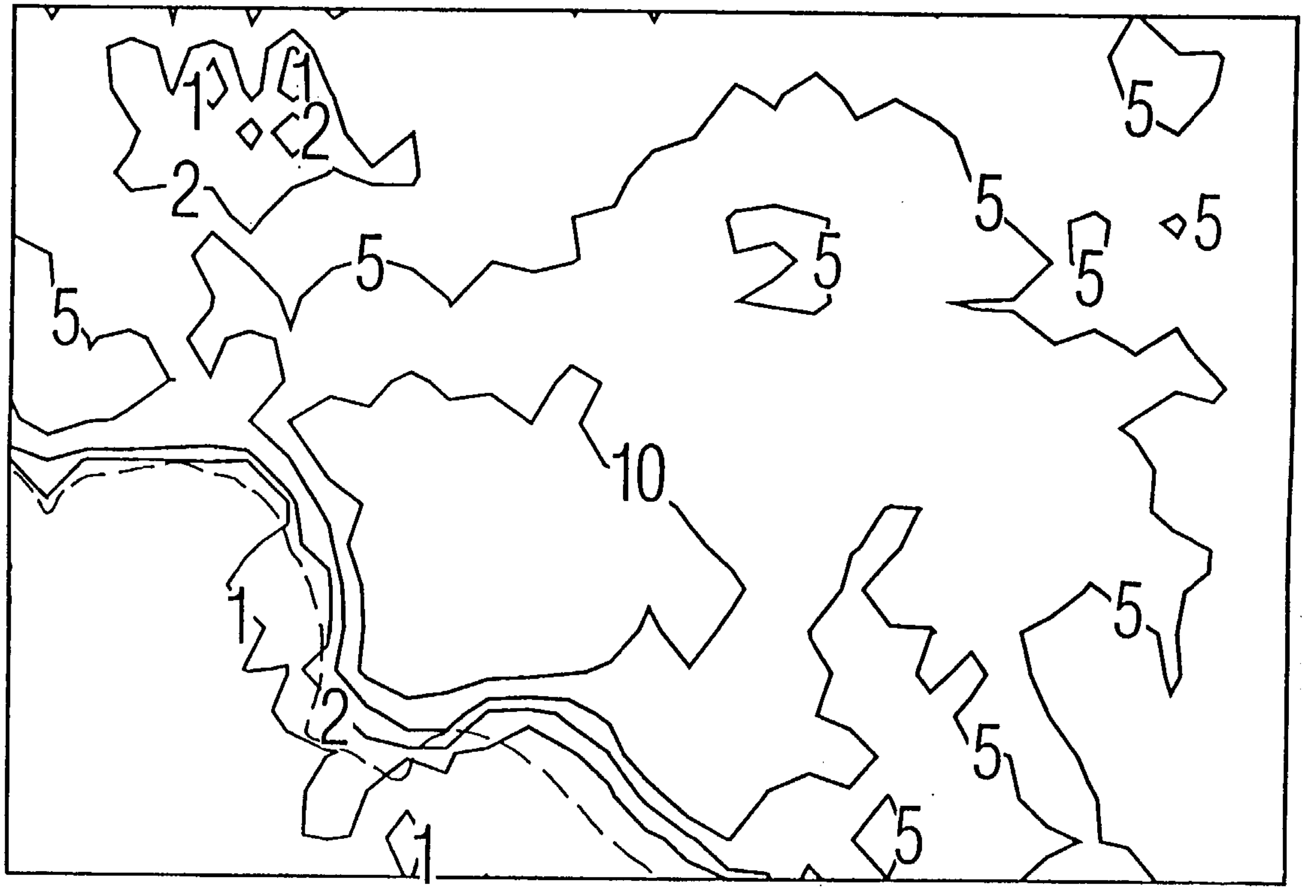
Figure 16



Deposition Velocity
[cm/sec]
Base Case

Figure 17

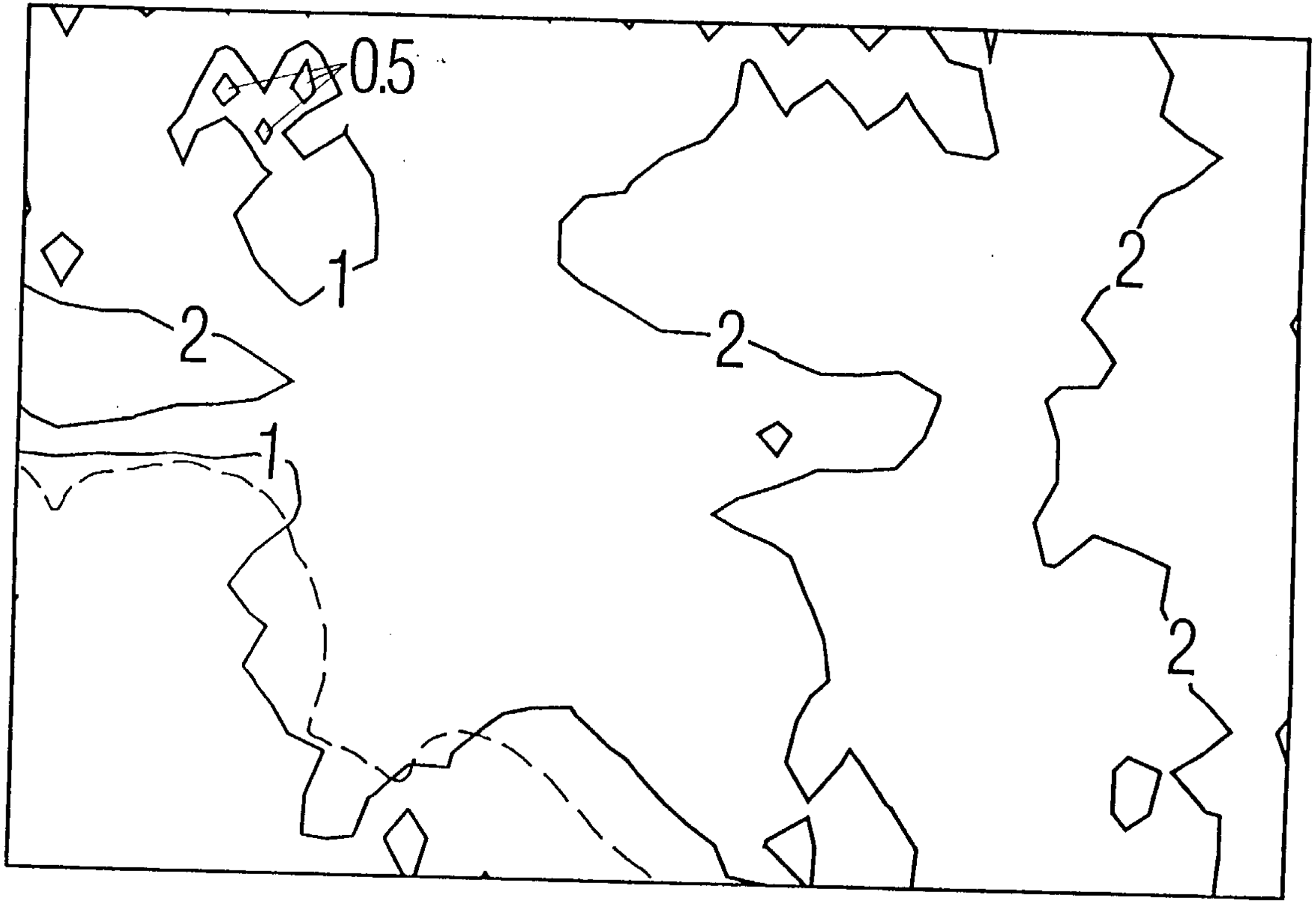
HNO_3



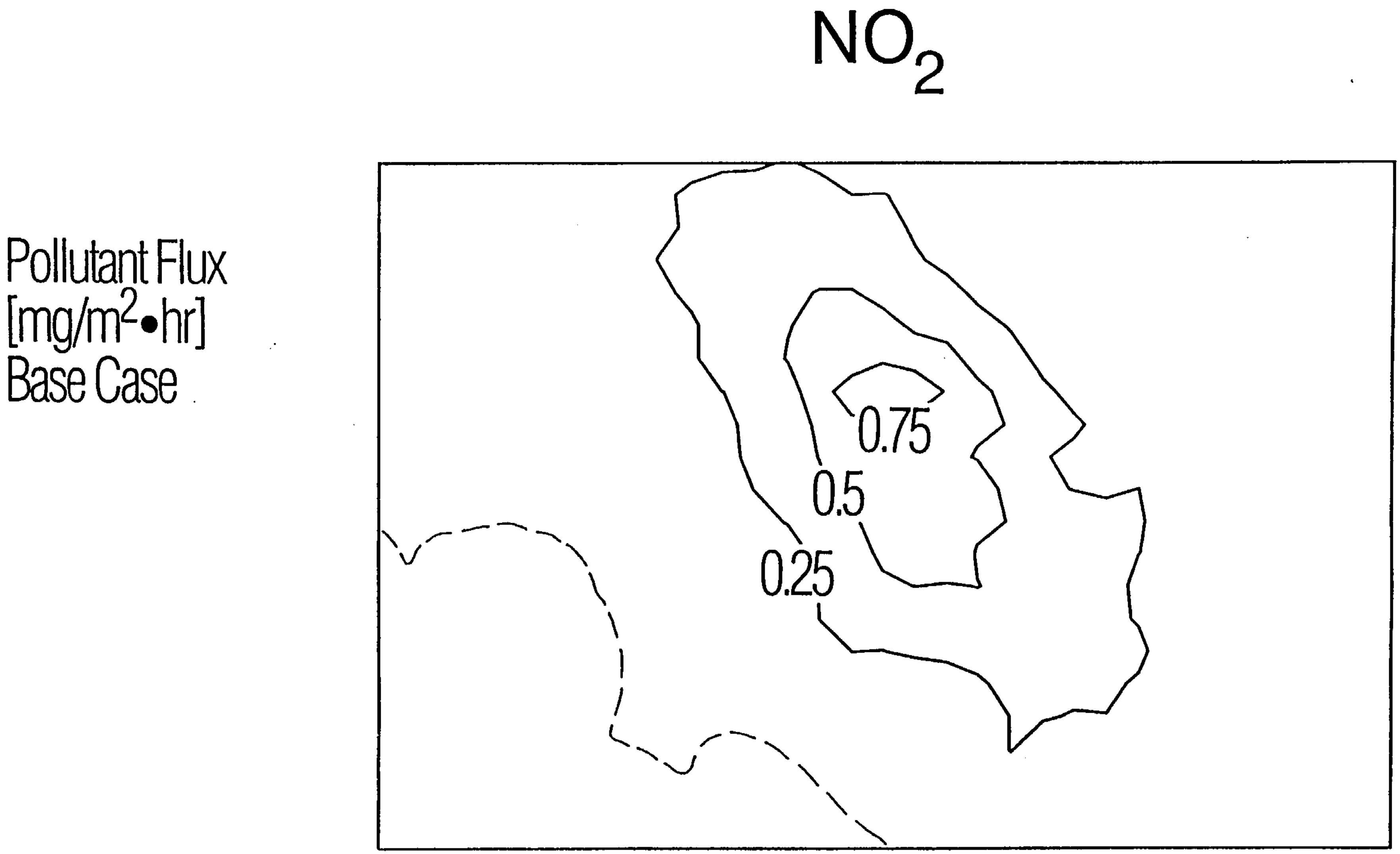
Deposition Velocity
[cm/sec]
Base Case

Figure 18

NH$_3$



Deposition Velocity
[cm/sec]
Base Case



NO_2

Pollutant Flux
[mg/m^2•hr]
Base Case

Figure 19

Figure 20

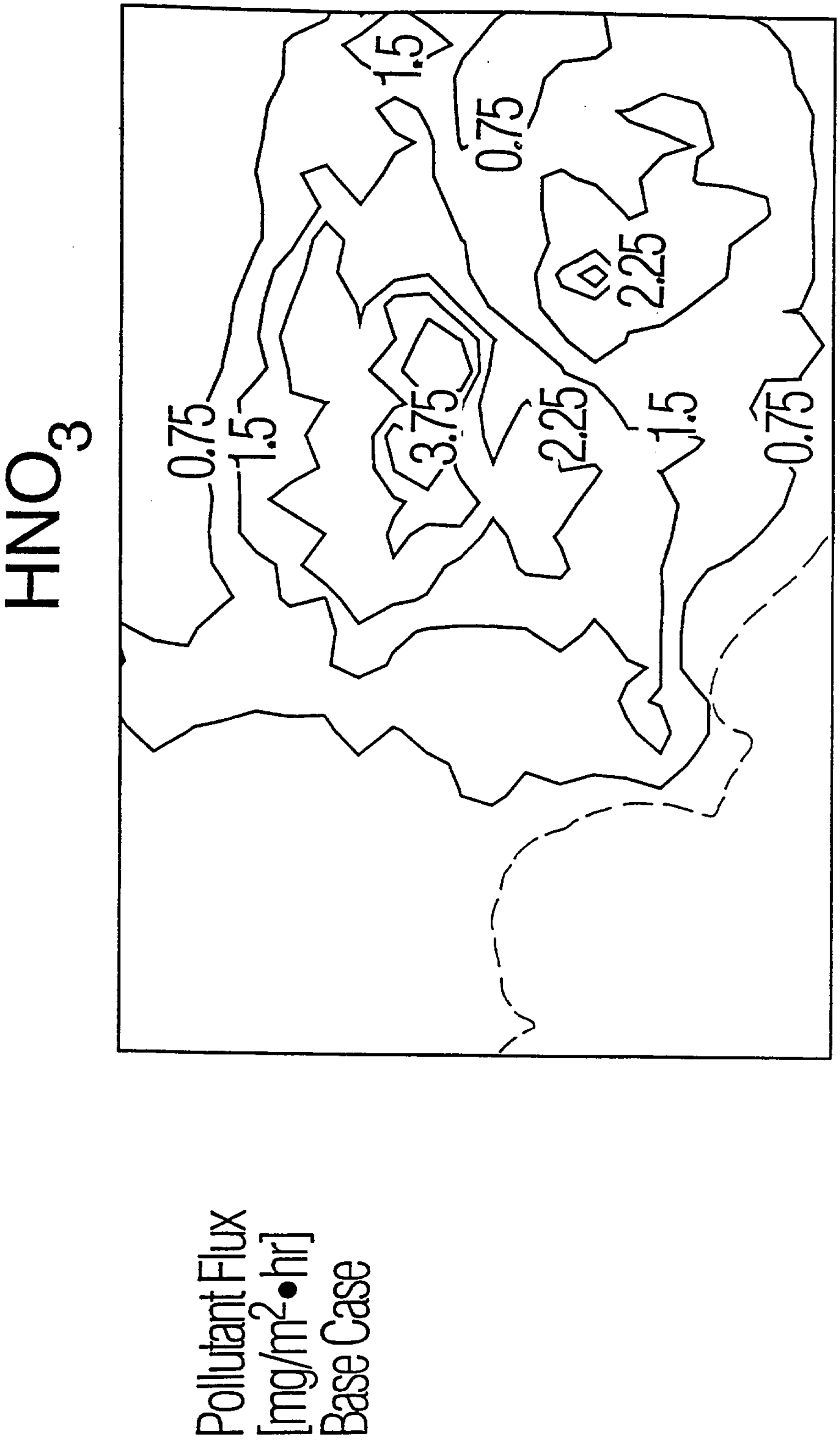

HNO$_3$
0.75
1.5
3.75
2.25
1.5
0.75
1.5
0.75
2.25
Pollutant Flux
[mg/m^2•hr]
Base Case

Figure 21

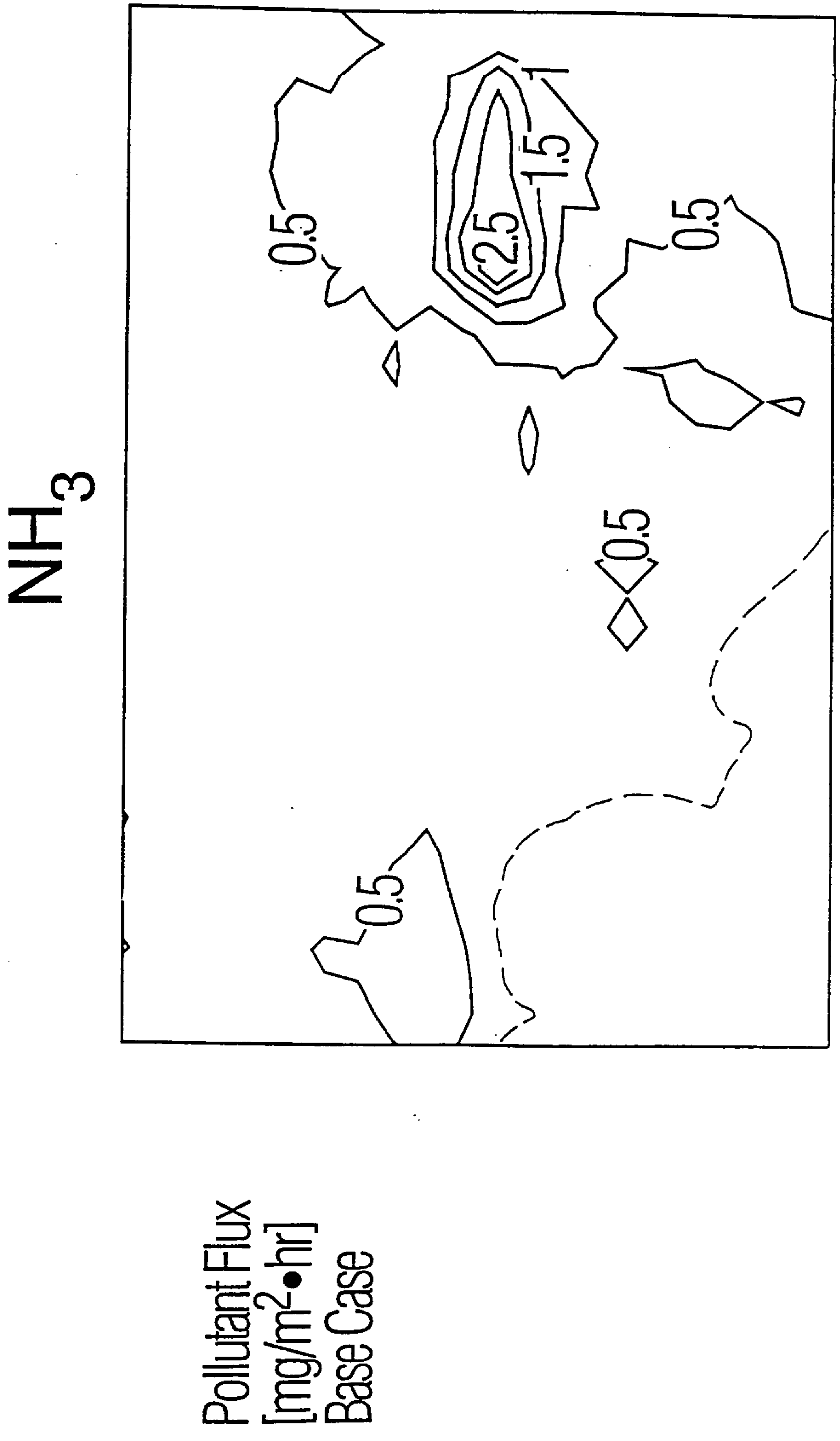


Figure 22

DRY DEPOSITION FLUX TO THE SURFACE OF THE MODELING REGION

BASE CASE CONDITIONS

(Metric tons N/day for August 31, 1982)

Pollutant	Flux
NO	4.8
NO_2	49.1
PAN	7.2
HNO_3	101.4
NH_3	58.7
NH_4NO_3	25.9
TOTAL	247.1

Figure 23

		MOBILE SOURCE CONTROLS		
	BASE CASE 1982 EMISSIONS (tons/day) THC = 2416 RHC = 1224 NO_x = 1120 NH_3 = 164	VEHICLE INSPECTION AND MAINTENANCE	LIGHT DUTY FLEET 0.41 g/mi THC; 0.7g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 10.7g/bhp-hr NO_x	LIGHT DUTY FLEET 0.41g/mi THC; 0.4g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 5.1 g/bhp-hr NO_x
STATIONARY SOURCE CONTROLS	AQMP EVAPORATIVE CONTROLS & COMBUSTION MODIFICATION	CONTROL MEASURES: 1-24 EFFECT ON EMISSIONS: RHC -9.3% NO_x -5.4% NH_3 NO CHANGE	CONTROL MEASURES: 1-28 EFFECT ON EMISSIONS: RHC -37.2% NO_x -36.8% NH_3 +3.9%	CONTROL MEASURES: 1-24,28-31 EFFECT ON EMISSIONS: RHC -37.2% NO_x -47.6% NH_3 +3.9%
	AQMP + NON-CATALYTIC AMMONIA INJECTION	CONTROL MEASURES: 1-18,20,24,32-36 EFFECT ON EMISSIONS: RHC -9.3% NO_x -10.0% NH_3 +8.7%	CONTROL MEASURES: 1-18,20,24-28,32-36 EFFECT ON EMISSIONS: RHC -37.2% NO_x -41.2% NH_3 +12.7%	CONTROL MEASURES: 1-18,20,24,28-36 EFFECT ON EMISSIONS: RHC -37.2% NO_x -52.2% NH_3 +12.7%
	AQMP + SELECTIVE CATALYTIC REDUCTION	CONTROL MEASURES: 1-18,20,24,37-42 EFFECT ON EMISSIONS: RHC -9.3% NO_x -18.4% NH_3 +0.7%	CONTROL MEASURES: 1-18,20,24-28,37-42 EFFECT ON EMISSIONS: RHC -37.2% NO_x -49.6% NH_3 +4.7%	CONTROL MEASURES: 1-18,20,24,28-31,37-42 EFFECT ON EMISSIONS: RHC -37.2% NO_x -60.6% NH_3 +4.7%

Figure 24

Changes in Flux to Surface of Modeling Region (Percent)

BASE CASE		MOBILE SOURCE CONTROLS		
		VEHICLE INSPECTION AND MAINTENANCE	**VEHICLE FLEET MEETS:** LIGHT DUTY FLEET 0.41 g/mi THC 0.7g/mi NO_X HEAVY DUTY FLEET 2.65 g/mi THC 10.7 g/bhp-hr NO_X	**VEHICLE FLEET MEETS:** LIGHT DUTY FLEET 0.41 g/mi THC 0.7g/mi NO_X HEAVY DUTY FLEET 2.65 g/mi THC 5.1 g/bhp-hr NO_X
EVAPORATIVE CONTROLS AND COMBUSTION MODIFICATION	NO	-7%	-42%	-54%
	NO_2	-5%	-39%	-51%
	PAN	-2%	-11%	-9%
	HNO_3	-3%	-28%	-36%
	NH_3	+2%	+17%	+22%
	NH_4NO_3	-4%	-30%	-43%
NON-CATALYTIC AMMONIA INJECTION	NO	-11%	-46%	-58%
	NO_2	-7%	-41%	-55%
	PAN	-1%	-11%	-9%
	HNO_3	-7%	-32%	-39%
	NH_3	+7%	+23%	+28%
	NH_4NO_3	-1%	-29%	-43%
SELECTIVE CATALYTIC REDUCTION	NO	-26%	-58%	-69%
	NO_2	-14%	-47%	-59%
	PAN	+2%	-9%	-9%
	HNO_3	-10%	-35%	-43%
	NH_3	+6%	+22%	+27%
	NH_4NO_3	-11%	-40%	-53%

Figure 25

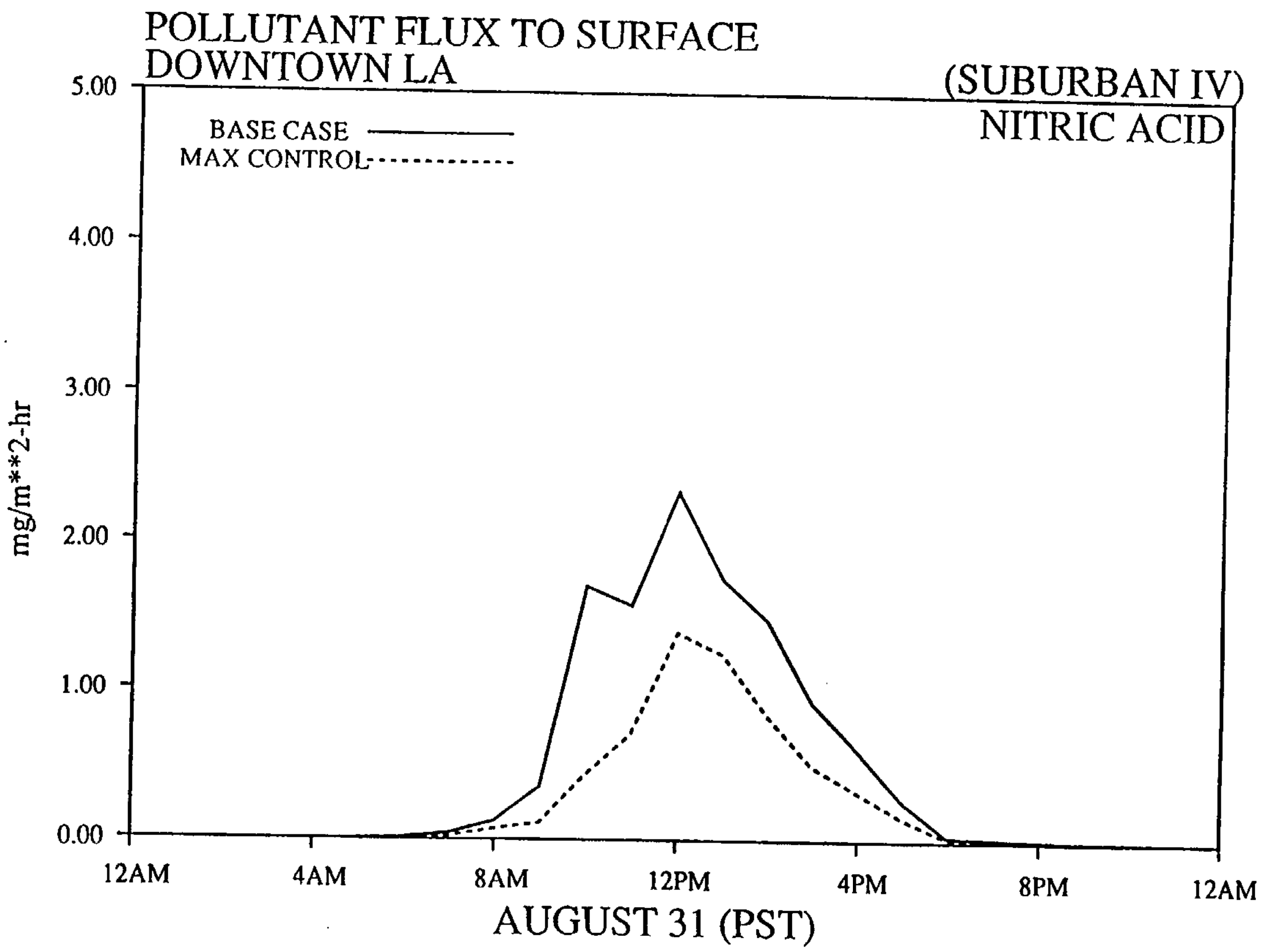
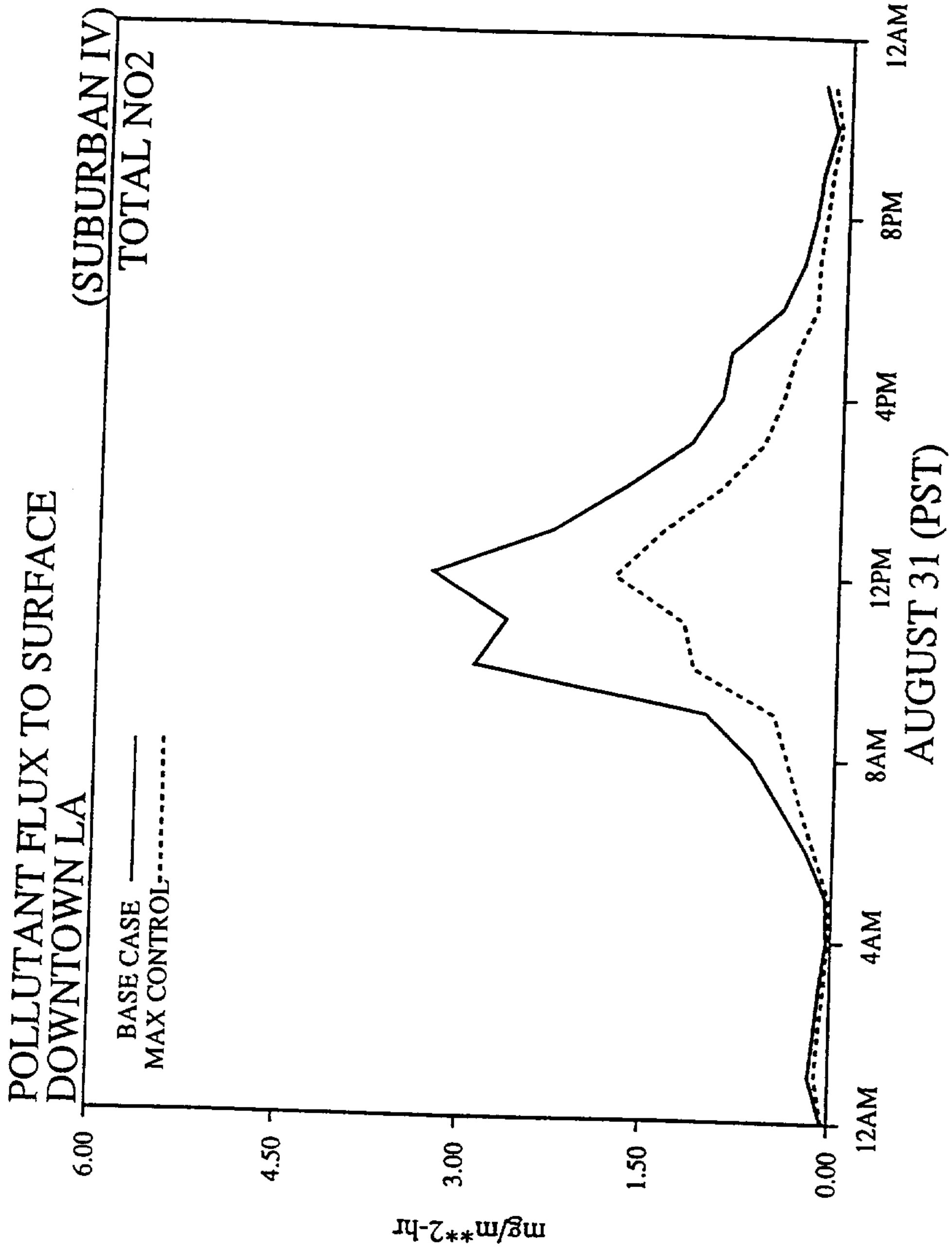

POLLUTANT FLUX TO SURFACE
DOWNTOWN LA
(SUBURBAN IV)
NITRIC ACID
BASE CASE
MAX CONTROL
mg/m**2-hr
5.00
4.00
3.00
2.00
1.00
0.00
12AM
4AM
8AM
12PM
4PM
8PM
12AM
AUGUST 31 (PST)

Figure 26


POLLUTANT FLUX TO SURFACE
DOWNTOWN LA
(SUBURBAN IV)
TOTAL NO2
BASE CASE
MAX CONTROL
mg/m**2-hr
6.00
4.50
3.00
1.50
0.00
12AM
4AM
8AM
12PM
4PM
8PM
12AM
AUGUST 31 (PST)

DRY DEPOSITION FLUX TO THE SURFACE OF THE MODELING REGION

Maximum Control Case Studied
(37% RHC control; 61% NO_x control)

(Metric tons N/day for August 31, 1982)

Pollutant	Flux	vs Base Case
NO	2	- 69 %
NO_2	20	- 59 %
PAN	7	- 9 %
HNO_3	58	- 43 %
NH_3	75	+ 27 %
NH_4NO_3	12	- 53 %
TOTAL	174	

Figure 28

CONCLUSIONS

AN EULERIAN GRID-BASED AIR QUALITY MODEL HAS BEEN MODIFIED TO COMPUTE THE POLLUTANT DRY DEPOSITION FLUX AS A FUNCTION OF LAND USE

THE MODEL WAS TESTED BY APPLICATION TO THE SOUTH COAST AIR BASIN

UNDER THE SUMMERTIME PHOTOCHEMICAL SMOG CONDITIONS STUDIED, THE DRY FLUX OF NITROGEN-CONTAINING POLLUTANTS WAS

176 tons/day N from NO_x emissions

(5 from NO, 49 from NO_2, 7 from PAN
101 from HNO_3, 13 from aerosol nitrate)

72 tons/day N from NH_3 emissions

(59 from NH_3, 13 from NH_4^+)

Figure 29

CONCLUSIONS

WHEN THE NO_x AND RHC CONTROLS STUDIED HERE ARE APPLIED TO THE SOURCES:

NO AND NO_2 FLUXES ARE REDUCED ROUGHLY IN PROPORTION TO NO_x CONTROL;

HNO_3 AND NH_4NO_3 DECLINE A LITTLE LESS THAN THE NO_x;

NH_3 FLUXES INCREASE WHEN NO_x CONTROLS ARE APPLIED

(this behavior is consistent with that expected as NO_x emissions are reduced: HNO_3 concentrations decline, less aerosol nitrate is formed; with less aerosol nitrate more of the NH_3 remains in the gas phase while some of the emission controls increase NH_3 emissions slightly, thus NH_3 dry flux goes up)

NEHZAT MOTALLEBI, Moderator

The topic of the final presentation for this session is "Development of Urban and Regional Acid Deposition Models for California" and will be presented by Dr. John Seinfeld of the California Institute of Technology.

6. Development of Urban and Regional Acid Deposition Models for California. Dr. John Seinfeld, California Institute of Technology.

DR. JOHN SEINFELD, California Institute of Technology

This presentation is really of a work in progress. You will see we are by no means finished. This is a joint effort with Frederick Lurman and Stefan Musarra at Sonoma Technology, Anthony Wexler at the University of Delaware, Spiros Pandis at Carnegie-Mellon and myself (Fig. 1).

The goal (Fig. 2) is to develop a three dimensional photochemical air quality model that predicts size resolved aerosol chemical composition, and I also have fog water and fog water processes. Glen just talked in some detail about gas phase photochemical models, and these have been around for about 20 years. They have had extensive development. We are trying here to take the next major step in three dimensional air quality modeling to include the aerosol and the droplet phase. I will tell you today about our progress in that direction.

Figure 3 is a flow chart of how such an effort would fit together. At the top is the gas phase model that Glen Cass just talked about. Glen also has ammonium nitrate included as well as the usual gas phase chemistry with diffusion and advection processes. This would be coupled to the new aerosol part of the model which will have inorganic species, gas to particle conversion, secondary organics, and all of the things that we understand at present to be happening chemically and physically to the aerosol. Finally, we have an aqueous phase model. I will discuss some preliminary results, and these are the things that Michael Hoffmann talked about in terms of aqueous chemistry and microphysics. Ultimately, this is all coupled together to produce a complete picture of the full system.

Because the urban air shed model has been the standard regulatory tool, it was chosen as the host air quality model to develop new aerosol models and a new fog water aqueous phase model. Use of the SAPRC photochemical mechanism from Bill Carter and Roger Atkinson to incorporate what we know about secondary organic aerosol formation is still quite sketchy. This incorporates the updated deposition algorithms like Glen Cass just talked about and the available emission inventories.

Now what are the processes (Fig. 4)? As you might certainly expect from what we heard today, the physics and chemistry becomes quite a bit more complicated, depending on what we put in particles and droplets. There are of course emissions and deposition, and now, there is condensation as well as evaporation, and advection. There is some settling for very large particles, and turbulent diffusion. Fortunately, it can be shown that at ambient particle concentration levels in the south coast air basin, coagulation is very slow, some nucleation likely occurred from either sulfuric acid or organics. The emissions into such a model would be the usual gas phase. These are the species in the SAPRC mechanism, particulate matter (chemically resolved if possible), sulfate, sodium, and others. We fit profiles or size distributions to the source emissions.

The aerosol part of the model, which is a little like the one Michael showed, includes primary organic emissions, gas phase photochemistry leading to low vapor pressure products of organics that can condense and form secondary organics, SO_2, formation of gas phase sulfuric acid, nitric acid, and ammonia. The initial results assume that there is a thermodynamic equilibrium, but we have shown in other work that the time scale to establish that equilibrium is not always fast. Thus, there may be cases where you do not actually have equilibrium attained. The gas aerosol chemical species are shown in figure 5 and include the usual gas phase species and additional gases because these are important in the aqueous phase, and various solids depending on the relative humidity and the relative amounts of the different components. These come out of the aqueous or solid phase system of sulfate, nitrate, ammonium, sodium, and chloride.

Q (AUDIENCE) A minor question. What is the source of the particulate sulfate emissions?

A (DR. SEINFELD) I do not remember the numbers, but it is probably small, and stems from combustion processes where you might have some catalytic oxidation.

In the fog droplet aqueous phase (Fig. 6), the chemical mechanism developed here involving all these is really derived from Michael's work over many years. One aspect that we have worked on experimentally for a number of years is to determine the yield to secondary organic aerosols from various classes of organics (Fig. 7). These are the yields that were used in our calculations. These yields depend on hydrocarbon and NO_X ratios and a variety of things. It is really not correct to talk about a single yield. It is expressed in terms of micrograms per cubic meter per ppm reactive compound or one of these classes of organics. There are more significant figures in these estimates than there ought to be.

How does the size resolved aerosol calculation work? If you are moving along in the airshed, you generate condensable organic vapors, nitric acid, and all the rest. We assume that there is an equilibration for the volatile species like nitric acid and ammonia between the gas and aerosol phases and we do a mass transport calculation to allocate these across the size distribution. This might represent the primary emissions in the three size categories in the ARB inventory (Fig. 8), and the calculation here should have about 10 size distributions. This grows and evolves either as a result of direct condensation, if it is not volatile, or by equilibrium for volatile species.

Figure 9 shows internally mixed aerosol dynamic equations. In keeping with the additional complication, the basic equation which underlies the model computes the amount of mass of species contained in a size range. This will be broken into a number of bins that evolve by advection and affect the gases equally and include some settling for large particles. Evaporation is new. Diffusion is the same for the gas and particle emission; there are possibly internal chemical reactions if there are sources for nucleation, and this would ordinarily be in the boundary position of dry deposition. The derivation of this is in a 1994 paper in Atmospheric Environment. Numerically, this is solved by what is called "operative splitting" in which you solve the east-west part of the problem, then the north-south part of the problem, and then the vertical with the gas phase chemistry together. So actually the aerosol dynamics can be put in as just another operator.

On the droplet side, deposition can occur in gases, droplets, and particles. I am going to show a first calculation for how the aerosol and the droplet phase interact, and this illustrates some of the phenomena that Michael was talking about. In a simulation of fog formation, each of these intervals is 10 minutes, and the first 10 bins are aerosol particle sizes. For sulfate distribution, we see that the relative humidity in the fog and relative humidity before the fog rises. The aerosol is taking up water, the humidity is rising, and the sulfate is pulled along. There is virtually no additional sulfate formation occurring at this point. When you get activation, most of the sulfate that forms does so within about the first 10 minutes in the fog. In fact, there was no formaldehyde there to have hydroxymethane sulfonate, which would have tied up the sulfate and allowed the hydrogen peroxide and the sulfate to coexist. These droplets then grow and reach a peak, the saturation of the fog starts going down, and you can see some of the particles evaporating. Then, you see the droplet mode that Walter John talked about. Right at the end of the fog, all except the very largest particles are evaporating.

It is also interesting to see what fog processing does to a chemical species. Consider a tracer that starts out uniformly in the aerosol. As the aerosol picks up water with increasing humidity, we can see how this inert tracer is carried along in the fog and then is shifted back as the water evaporates from the fog. It is an interesting way to look at the processing.

I will show some preliminary results with the aerosol part of the 3D code. I will use simulations of two South Coast Air Basin episodes (Fig. 10). We have PM 2.5 nitrate in Anaheim, Burbank, and downtown Los Angeles. Figure 11 is PM 2.5 in Hawthorne, Long Beach, and Riverside. Figure 12 shows PM 2.5 ammonium in Anaheim, Burbank and downtown LA in that same period. These are the kind of results that have to be looked at very carefully to determine whether or not the model is going wrong. For example, Figure 13 shows something that was not picked up, PM 2.5 ammonium in Riverside. This would be expected from what Glen just showed us. Whether that is a problem with the inventory or with the nitric acid is not clear. Figure 15 is PM 2.5 sulfate at the same places over that period. Figure 16 shows the June 23-25 episode. Figure 17 is aerosol organic carbon PM 2.5 in

Anaheim, Azusa, Burbank, and downtown Los Angeles in that June episode. There are lots of data like this that have to be examined very carefully. It is simply too early to assess the degree of validity. The important point is that we now have a working three dimensional model that includes size-resolved, aerosol chemical composition, and size resolved fog water chemistry. As you might expect, it is computationally somewhat slow, but you are asking it to do a lot.

Future areas of work (Fig. 19) include primary particle emission inventories. We have all scratched our heads for a long time on gas phase organic inventories. We know the state that they are still in, and you can imagine the state of primary particles. The acquisition of data bases, such as the SCAQS data base and the sort of data Walter showed, are going to be very valuable. The aerosol forming capabilities of primary organics is something that we are studying to try to get better numbers. Then there is the problem with external mixing that Walter referred to, and it has not yet really been approached in models of this type.

Figure 1

Development of a Three-Dimensional Photochemical Model With Aerosol and Fogwater Processes

Frederick W. Lurmann
Stefan Musarra
Sonoma Technology Inc.

Anthony S. Wexler
Department of Mechanical Engineering
University of Delaware

Spiros N. Pandis
Department of Chemical Engineering
Carnegie Mellon University

John H. Seinfeld
Department of Chemical Engineering
California Institute of Technology

Objective

Develop a 3-dimensional photochemical air quality model that accurately predicts aerosol chemical composition, aerosol size distributions, and PM_{10} mass concentrations during pollution episodes.

Purpose

Assessment of effects of emission control strategies on ozone, NO_2, PM_{10}, acidic species, and visibility.

Figure 3

Overview of the Approach

- Use the UAM as the host air quality model
- Develop and incorporate new aerosol modules
- Develop a new fogwater/aqueous phase model
- Incorporate the SAPRC90 photochemical mechanism
- Incorporate secondary organic aerosol formation
- Incorporate updated deposition algorithms
- Incorporate current PM emissions data
- Evaluate and refine model performance using the SCAQS data

Figure 4

ATMOSPHERIC PROCESSES

- ADVECTION
- TURBULENT DIFFUSION
- EMISSIONS
- DEPOSITION
- CHEMICAL REACTIONS
- CONDENSATION
- EVAPORATION
- NUCLEATION
- COAGULATION (neglected)

Figure 5

Gas / Aerosol Chemical Species

Photochemical Species

NO, NO_2, Ozone, ROG
HNO_3, PAN, H_2O_2, etc.

Additional Gases

- Sulfur Dioxide
- Sulfuric Acid
- Condensable Organics
- Formic Acid
- Acetic Acid
- Hydrochloric Acid
- Ammonia

Solid PM Species

- Sodium Sulfate
- Ammonium Sulfate
- Sodium Chloride
- Ammonium Chloride
- Sodium Nitrate
- Ammonium Nitrate
- Sodium Bisulfate
- Ammonium Bisulfate
- Letovicite
- Elemental Carbon
- Organic Carbon
- Other PM (crustal)

PM Components

- Sodium
- Protons
- Ammonium
- Nitrate
- Chloride
- Sulfate
- Elemental Carbon
- Organic Carbon
- Other PM (crustal)
- Water
- S(IV)
- H_2O_2

Liquid PM Species

- Sodium Sulfate
- Ammonium Sulfate
- Sodium Chloride
- Ammonium Chloride
- Sodium Nitrate
- Ammonium Nitrate
- Sulfuric Acid
- Nitric Acid
- Hydrochloric Acid
- Water
- S(IV)
- H_2O_2

Figure 6

Fog Droplet Aqueous-Phase Species

$SO_2 \cdot H_2O$, HSO_3^-, $SO_3^=$
H_2SO_4, HSO_4^-, $SO_4^=$
HNO_2, NO_2^-
HNO_3, NO_3^-
$CO_2 \cdot H_2O$, HCO_3^-, $CO_3^=$
H_2O_2, HO_2^-
$HCHO$, $H_2C(OH)_2$
$HCOOH$, H_2COO^-
NO
NO_2
O_3
$CH_3C(O)O_2NO_2$
$CH_3C(O)OOH$
CH_3OOH
HCl, Cl^-
OH
HO_2, O_2^-
NO_3
NH_4OH, NH_4^+
CH_3OH
H^+, OH^-
Fe^{3+}
Mn^{2+}
Na^+
Cl_2^-, Cl, $ClOH^-$
SO_4^-, SO_5^-, HSO_5^-
$HOCH_2SO_3^-$, $^-OCH_2SO_3^-$
CO_3^-

Figure 7

Secondary Organic Aerosol Yields

Species	Description	Molecular Weight	Aerosol Yield[1]
ALK1	Less reactive alkanes ($k_{OH} \leq 10,000\ ppm^{-1}min^{-1}$)	4.5	1.4
ALK2	More reactive alkanes ($k_{OH} > 10,000\ ppm^{-1}min^{-1}$)	7.4	144.
ARO1	Less reactive aromatics ($k_{OH} \leq 20,000\ ppm^{-1}min^{-1}$)	7.1	402.
ARO2	More reactive aromatics ($k_{OH} > 20,000\ ppm^{-1}min^{-1}$)	8.5	416.
CRES	Cresols and other alkyl phenols	7.	221.
OLE1	Less reactive alkenes ($k_{OH} \leq 75,000\ ppm^{-1}min^{-1}$)	3.7	9.5
OLE2	More reactive alkenes ($k_{OH} > 75,000\ ppm^{-1}min^{-1}$)	5.0	30.
OLE3	Biogenic alkenes	6.9	311.
HCHO	Formaldehyde	1.	0.
CCHO	Acetaldehyde	2.	0.
RCHO	Propionaldehyde and higher aldehdyes	3.	0.
MEK	Methyl ethyl ketone and lumped higher ketones	4.	0.
MGLY	Methyl glyoxal	3.	0.
MEOH	Methanol	1.	0.
ETOH	Ethanol	2.	0.
MTBE	Methyl tertiary butyl ether	5.	0.
ETHE	Ethene	2.	0.

[1] Aerosol yields are in $\mu g\ m^{-3}\ ppm^{-1}$ and are from Pandis et al., (1992)

Figure 8

EMISSIONS

Gas-Phase

- ROG (15 species)
- NO, NO_2, and HNO_2
- CO
- SO_2
- NH_3

Particulate Matter

- SO_4
- Na
- Cl
- OC
- EC
- Other (Crustal)

- ARB PM composition profiles

- ARB PM size profiles (<1, 1-2.5, 2.5-10, >10 μm)

- Twomey fit 3-section profiles to 8-section profiles

0.04 - 0.08 μm	0.62 - 1.25 μm
0.08 - 0.15 μm	1.25 - 2.5 μm
0.15 - 0.31 μm	2.5 - 5 μm
0.31 - 0.62 μm	5 - 10 μm

Figure 9

Internally Mixed Aerosol Dynamic Equations

$$
\begin{aligned}
&\frac{\partial q_i(m,x,t)}{\partial t} && \textit{(local rate of change)}\\
&+(\overline{V}(x,t) - V_s(m)k)\cdot\nabla q_i(m,x,t) && \textit{(spatial advection and gravitational settling)}\\
&= H_i(m,x,t)\, q(m,x,t) \; - \; \frac{\partial(mq_iH)}{\partial m} && \textit{(condensation / evaporation)}\\
&+ \; \nabla\cdot(K(x,t)\,\nabla\, q_i(m,x,t)) && \textit{(spatial diffusion)}\\
&+ \; E_i(m,x,t) && \textit{(emissions)}\\
&+ \; R_i(m,x,t) && \textit{(chemical reaction)}\\
&+ \; N_i(m,x,t) && \textit{(nucleation)}\\
&+ \; D_i(m,x,t) && \textit{(dry deposition)}
\end{aligned}
$$

where:

$q(m,x,t)$ = *the total mass distribution such that* $q_i(m,x,t)dm$ *is the mass concentration of species i* ($i=1,s$) *in the mass range* $[m,m+dm]$ *and* $\Sigma q_i = q$,
m_i = *the mass of species i in a particle of total mass* $m = \Sigma m_i$,
H_i = $(1/m)dm_i/dt$ = *the inverse of the characteristic time for particle growth due to condensation or evaporation,* $H = \Sigma H_k$,
x = *the spatial coordinate,*
t = *the temporal coordinate,*
V = *the wind velocity vector,*
V_s = *the gravitational settling velocity,*
K = *the turbulent diffusion tensor,*
E = *the emission rate,*
R = *the rate due to aerosol-phase chemical reactions,*
N = *the nucleation rate, and*
D = *the dry deposition rate.*

Figure 10

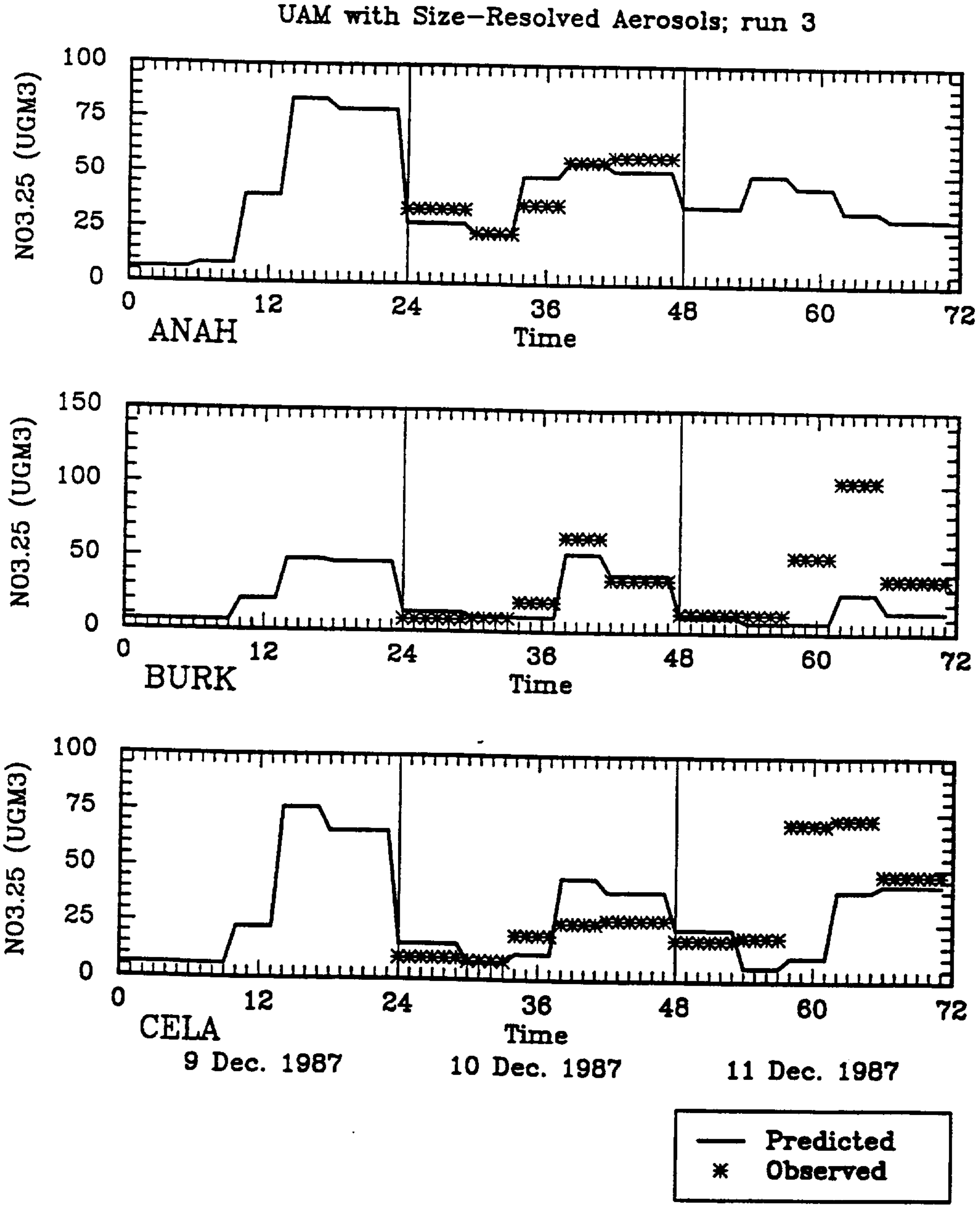

UAM with Size-Resolved Aerosols; run 3
NO3.25 (UGM3)
100
75
50
25
0
0
12
24
36
48
60
72
ANAH
Time
NO3.25 (UGM3)
150
100
50
0
BURK
Time
NO3.25 (UGM3)
CELA
Time
9 Dec. 1987
10 Dec. 1987
11 Dec. 1987
Predicted
Observed

Figure 11

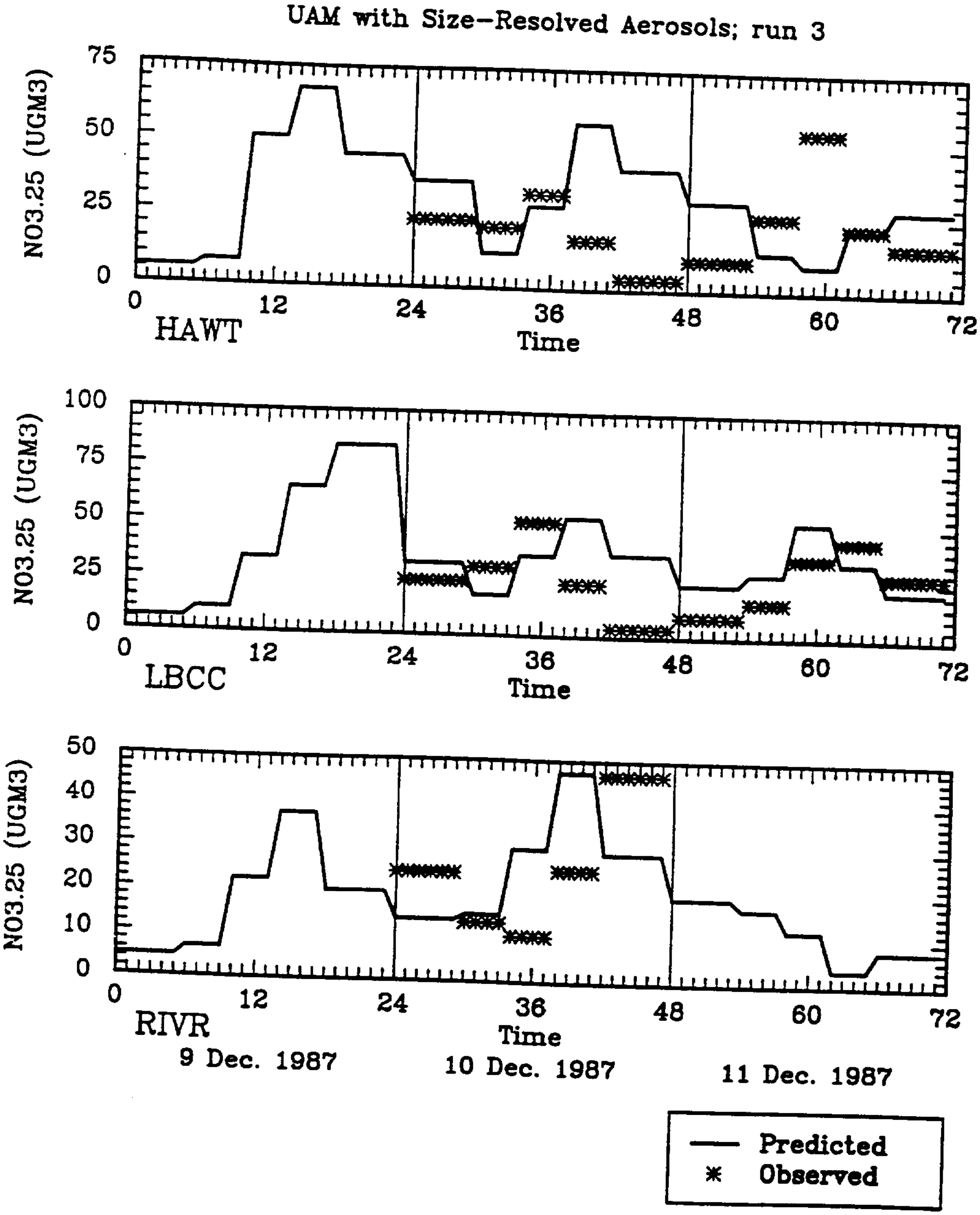
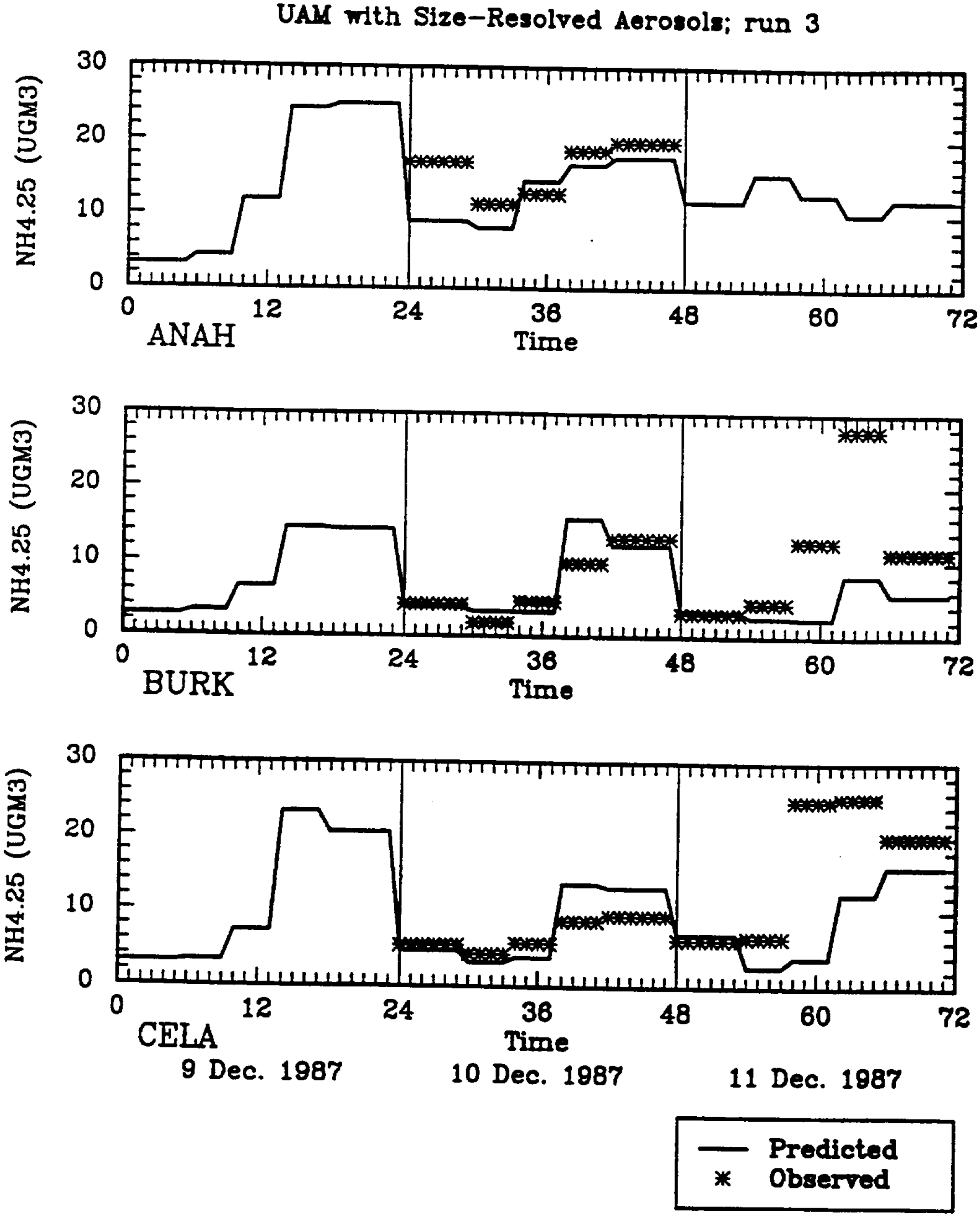

UAM with Size-Resolved Aerosols; run 3
NO3.25 (UGM3)
75
50
25
0
0
12
24
36
48
60
72
HAWT
Time
NO3.25 (UGM3)
100
75
50
25
0
0
12
24
36
48
60
72
LBCC
Time
NO3.25 (UGM3)
50
40
30
20
10
0
0
12
24
36
48
60
72
RIVR
Time
9 Dec. 1987
10 Dec. 1987
11 Dec. 1987
Predicted
Observed

Figure 12



UAM with Size-Resolved Aerosols; run 3
NH4.25 (UGM3)
30
20
10
0
0
12
24
36
48
60
72
Time
ANAH
BURK
CELA
9 Dec. 1987
10 Dec. 1987
11 Dec. 1987
Predicted
Observed

Figure 13

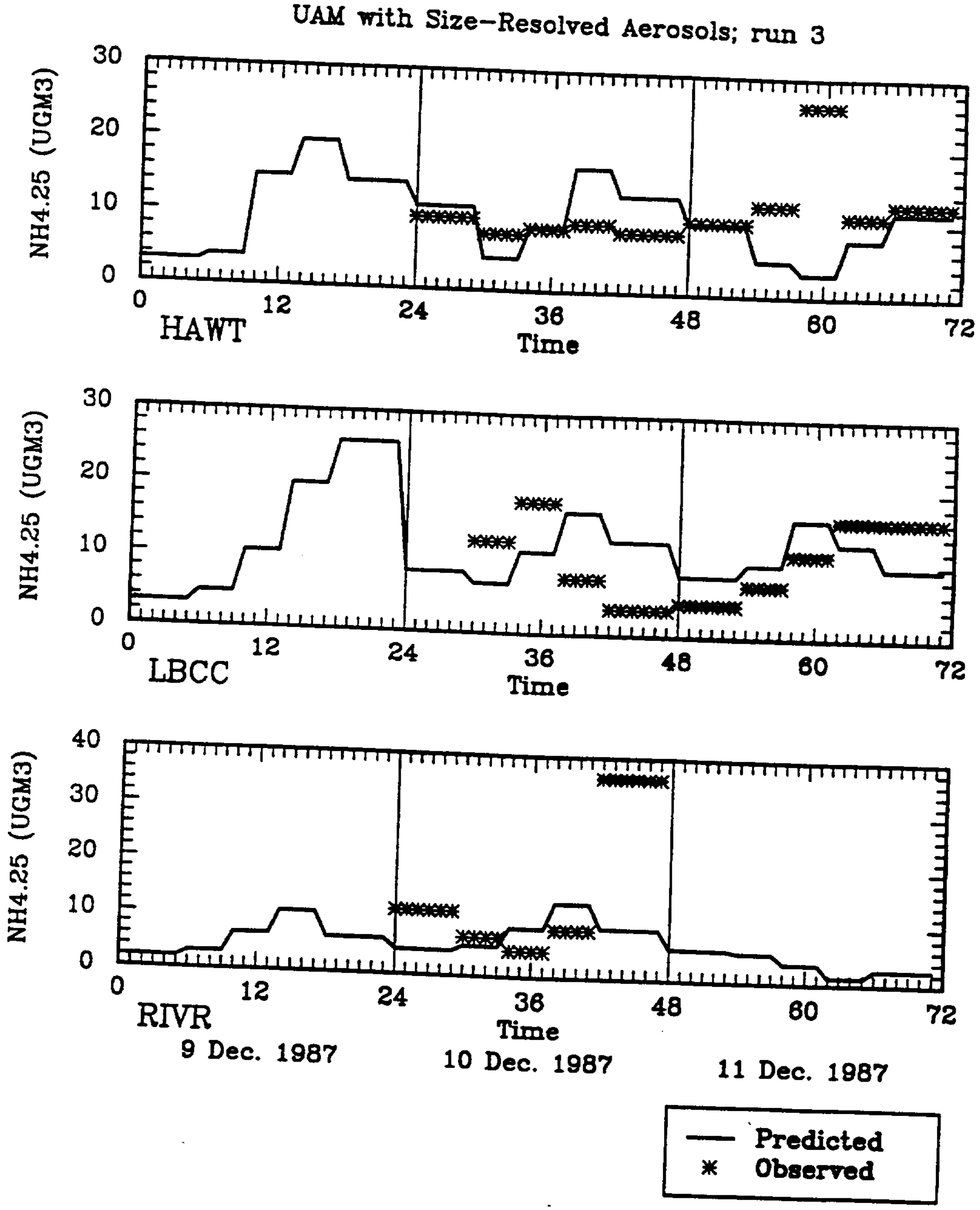
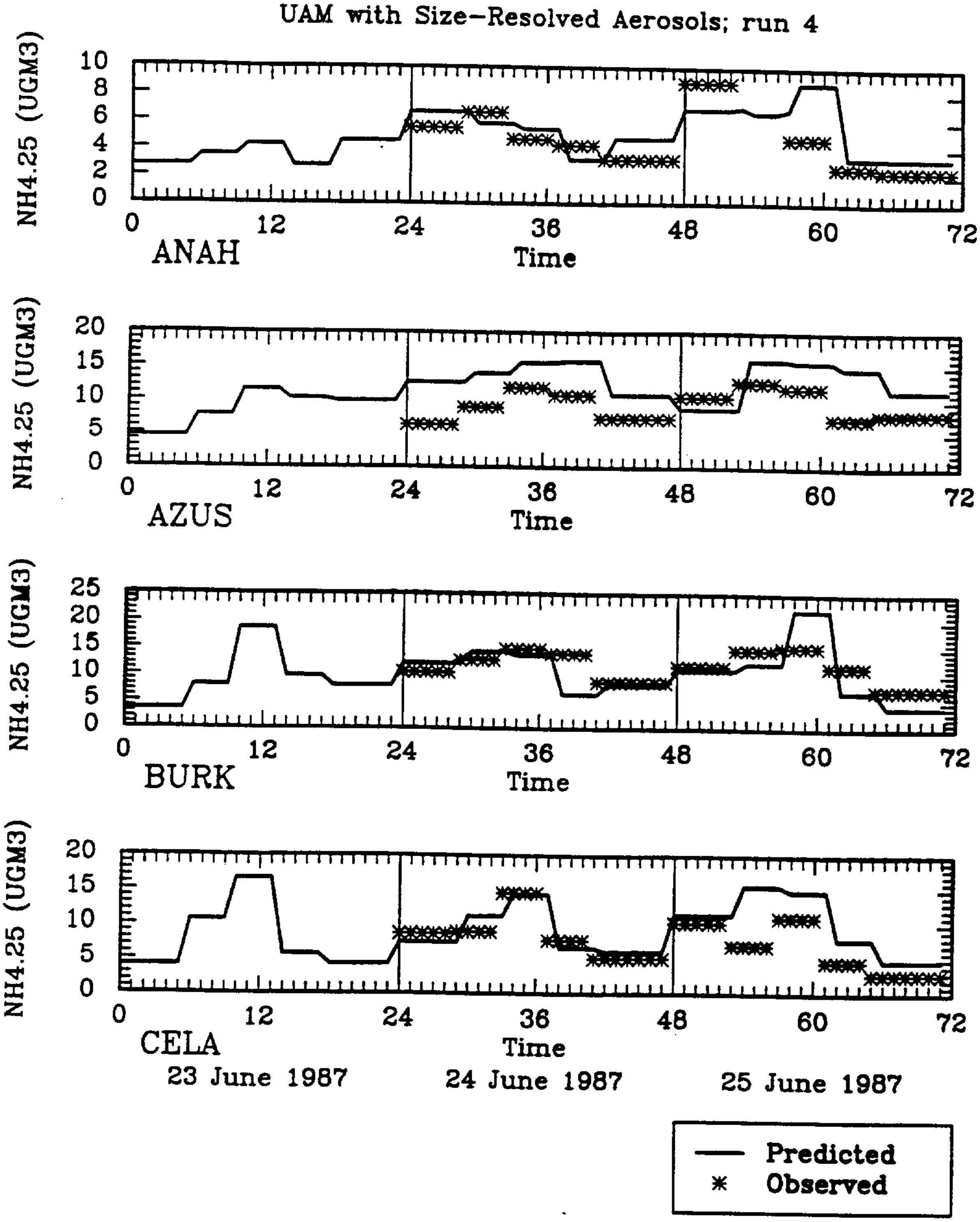

UAM with Size–Resolved Aerosols; run 3
NH4.25 (UGM3)
30
20
10
0
0
12
24
36
48
60
72
Time
HAWT
LBCC
40
RIVR
9 Dec. 1987
10 Dec. 1987
11 Dec. 1987
Predicted
Observed

Figure 14



UAM with Size-Resolved Aerosols; run 4
NH4.25 (UGM3)
10
8
6
4
2
0
0
12
24
36
48
60
72
ANAH
Time
NH4.25 (UGM3)
20
15
10
5
0
0
12
24
36
48
60
72
AZUS
Time
NH4.25 (UGM3)
25
20
15
10
5
0
0
12
24
36
48
60
72
BURK
Time
NH4.25 (UGM3)
20
15
10
5
0
0
12
24
36
48
60
72
CELA
Time
23 June 1987
24 June 1987
25 June 1987
Predicted
Observed

Figure 15

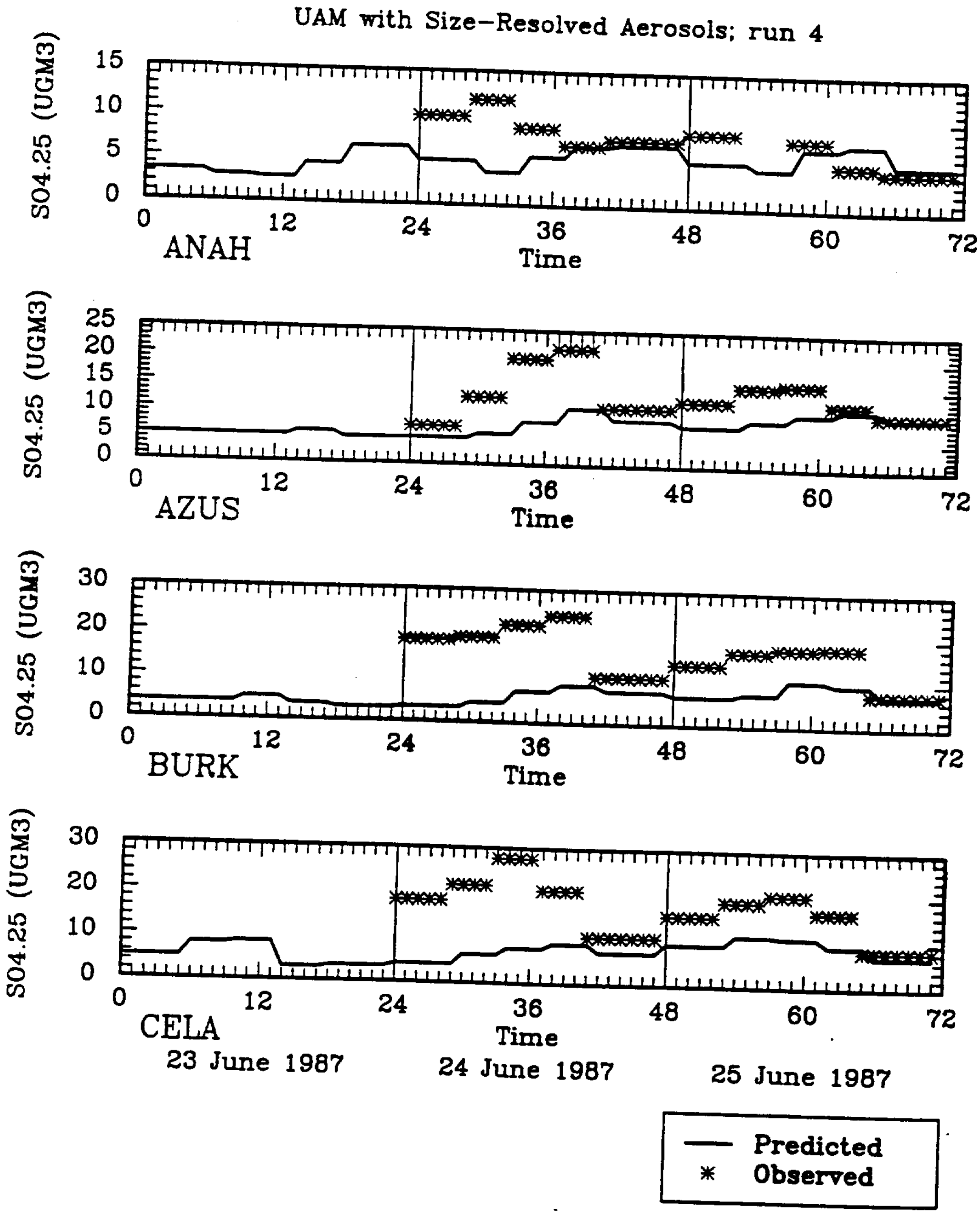

UAM with Size-Resolved Aerosols; run 4
SO4.25 (UGM3)
15
10
5
0
0
12
24
36
48
60
72
ANAH
Time
SO4.25 (UGM3)
25
20
15
10
5
0
0
12
24
36
48
60
72
AZUS
Time
SO4.25 (UGM3)
30
20
10
0
0
12
24
36
48
60
72
BURK
Time
SO4.25 (UGM3)
30
20
10
0
0
12
24
36
48
60
72
CELA
Time
23 June 1987
24 June 1987
25 June 1987
Predicted
Observed

Figure 16

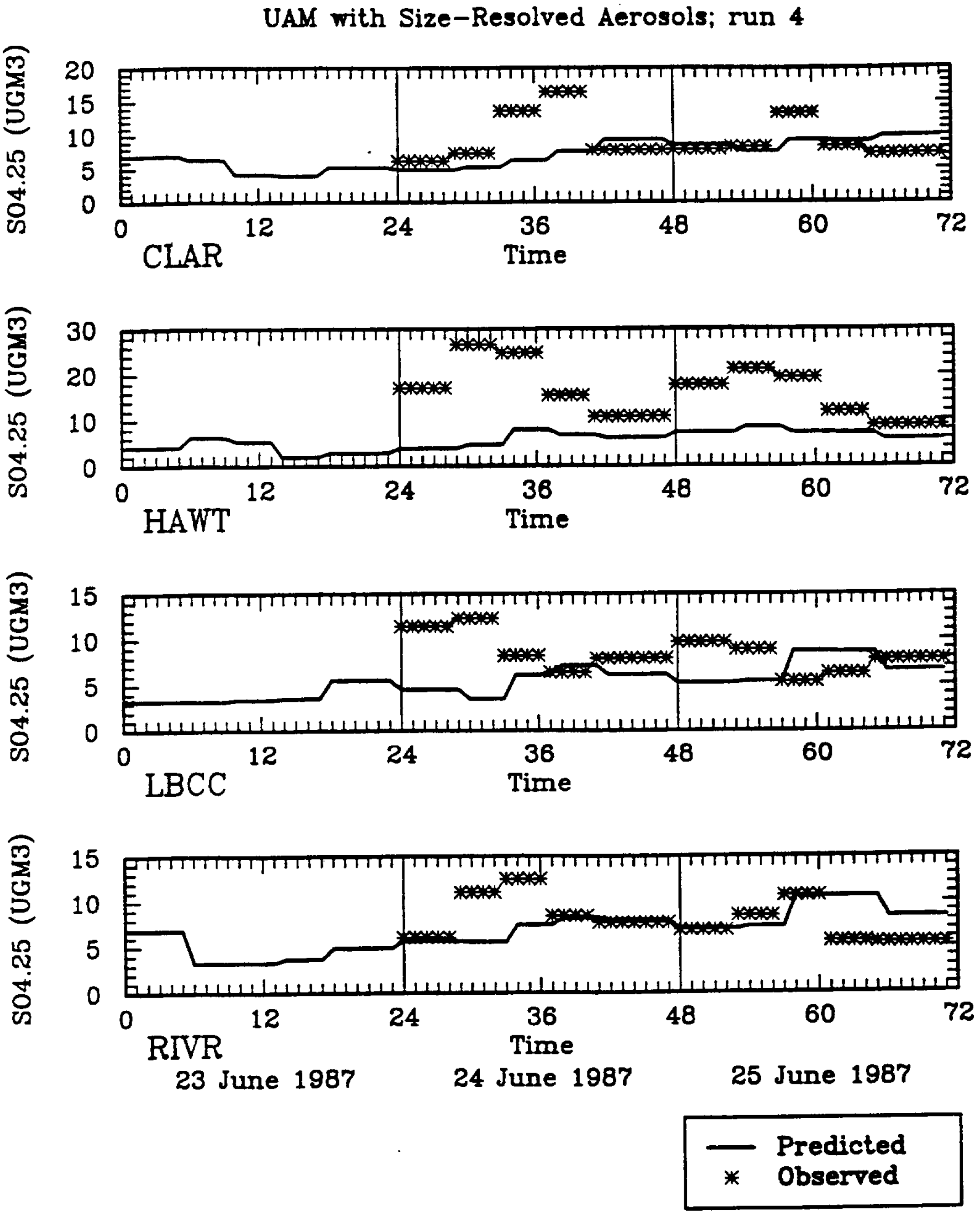

UAM with Size-Resolved Aerosols; run 4
SO4.25 (UGM3)
20
15
10
5
0
0
12
24
36
48
60
72
Time
CLAR
SO4.25 (UGM3)
30
20
10
0
Time
HAWT
SO4.25 (UGM3)
15
10
5
0
Time
LBCC
SO4.25 (UGM3)
15
10
5
0
Time
RIVR
23 June 1987
24 June 1987
25 June 1987
Predicted
Observed

Figure 17

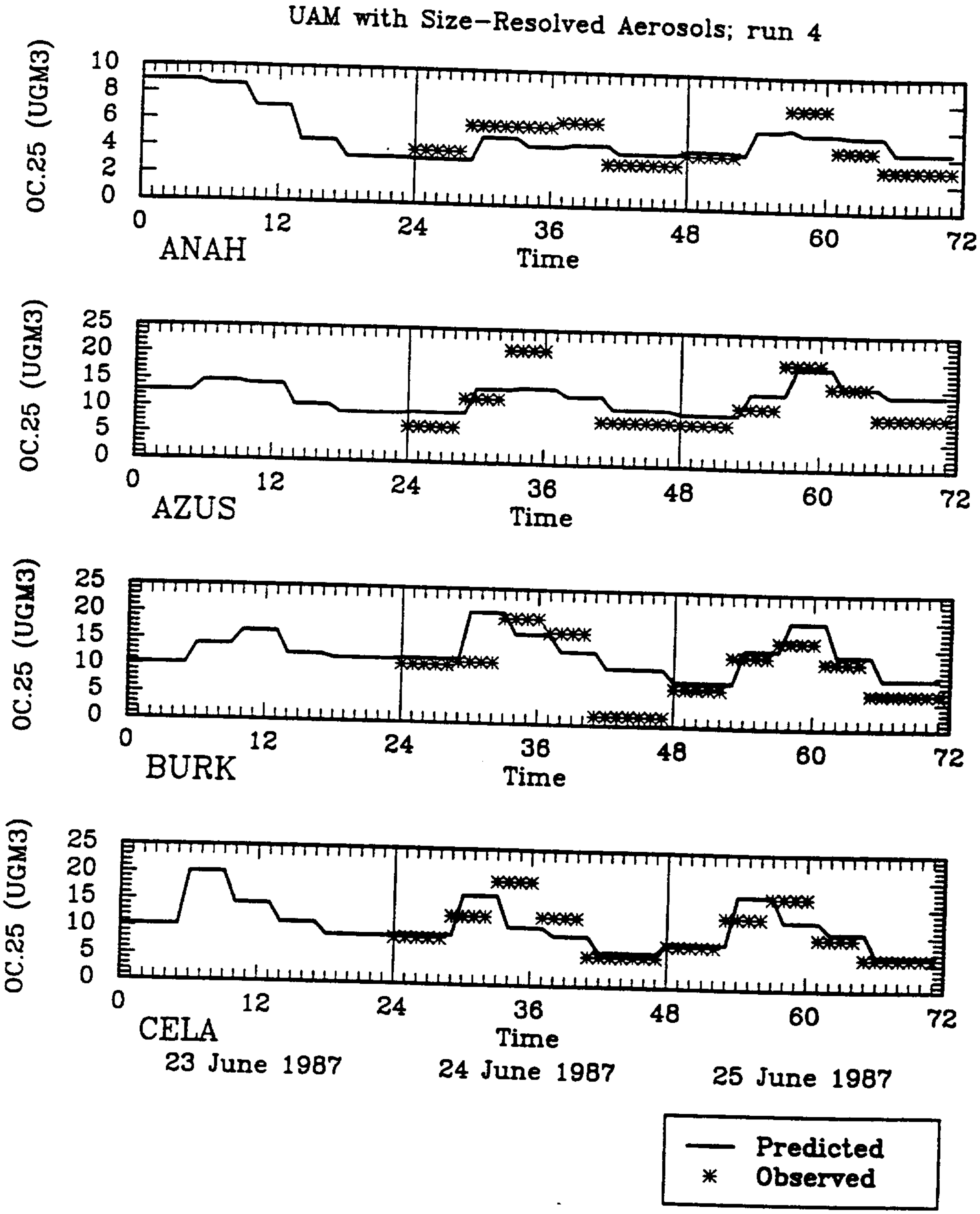

UAM with Size-Resolved Aerosols; run 4
OC.25 (UGM3)
10
8
6
4
2
0
0
12
24
36
48
60
72
ANAH
Time
OC.25 (UGM3)
25
20
15
10
5
0
AZUS
Time
OC.25 (UGM3)
BURK
Time
OC.25 (UGM3)
CELA
Time
23 June 1987
24 June 1987
25 June 1987
Predicted
Observed

Figure 18

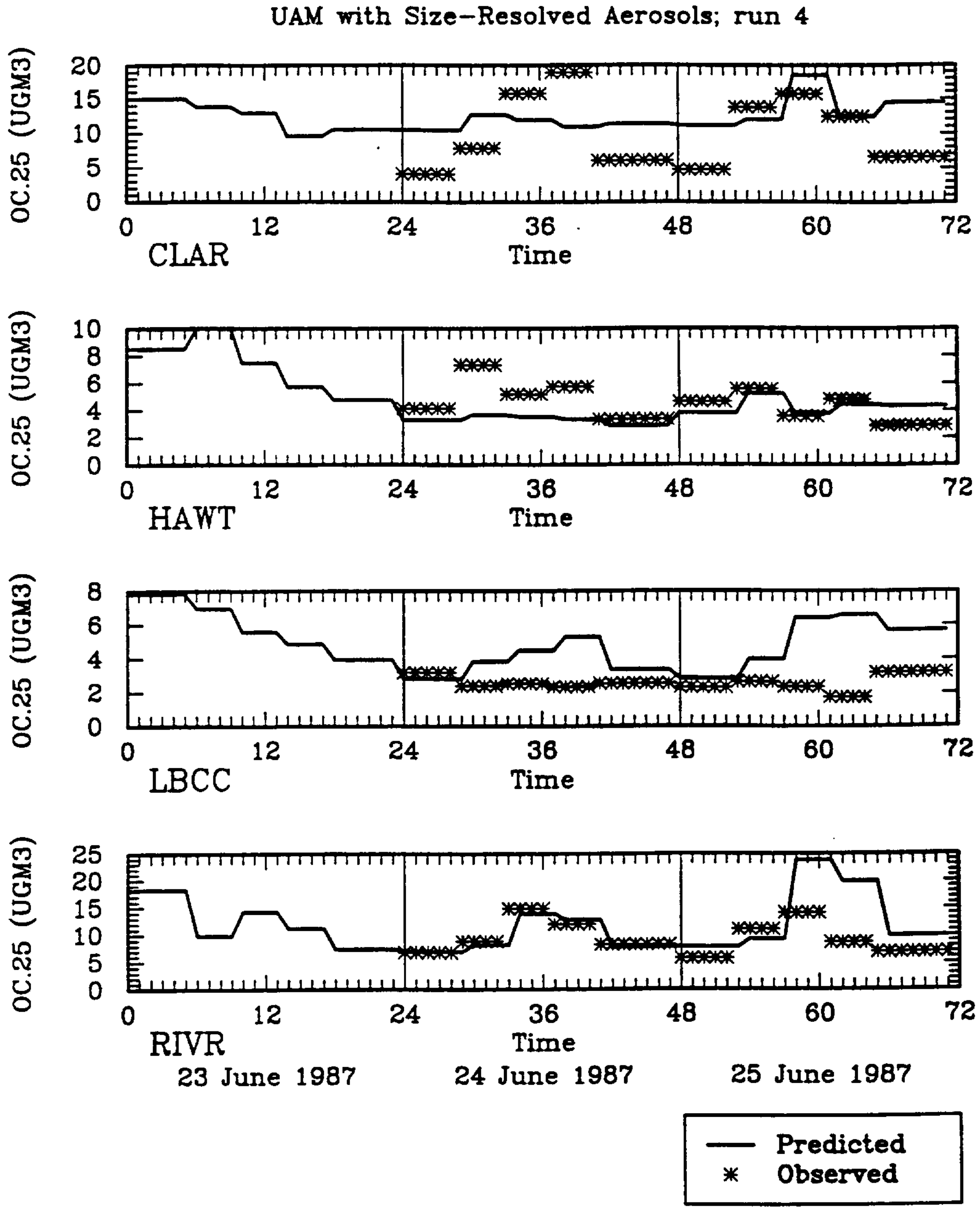

UAM with Size-Resolved Aerosols; run 4
OC.25 (UGM3)
CLAR
HAWT
LBCC
RIVR
Time
0
12
24
36
48
60
72
23 June 1987
24 June 1987
25 June 1987
Predicted
Observed

Figure 19

FUTURE NEEDS

1. Primary particle emissions inventions – submicron, chemically – resolved, if possible
2. Acquisition of size – and chemically – resolved aerosol data bases for model evaluation
3. Acquisition of data on aerosol – forming capabilities of primary VOCs
4. Improvements in numerical performance of coupled gas/aerosol and gas/aerosol/cloud models
5. Treatment of external mixing in the aerosol population by aerosol models

FRIDAY, JANUARY 27, 1995

SESSION 3. AQUATIC ECOSYSTEMS.

OPENING REMARKS

DR. JOHN HOLMES

I would like to welcome you to the second day the Atmospheric Acidity Protection Program Assessment Workshop. My name is John Holmes, and I am the Chief of the research division of the Air Resources Board. I should apologize at the outset for not having been here yesterday. I had a meeting with the Board in Sacramento that I had not originally planned to attend, and I did not get here until late yesterday afternoon. I walked into the lobby at 6:30 and discovered that the meeting had just finished and the place was a buzz with the talk about the papers that had been presented during the day. There were many complimentary remarks, even raves, from the people whom I talked to. What an excellent day it was, so I am certainly looking forward to a repeat performance from the speakers we have asked to be here today.

I want to express my appreciation and the board's appreciation to all the researchers who have helped us carry out this program over the last 10-12 years. We went into this enterprise not knowing very much at all about what the legislature had asked us to do. We were in effect bailed out very early on by the researchers we have here in California. We are very lucky to have them. We were also given immeasurable help by the scientific advisory committee on acid deposition. I want to pay a special tribute to them, many of whom are here this morning, Paul Miller, Freeman Allen, Ralph Perhac, and the fellow who has kept me out of trouble and kept me on the right track for the last 12 years, Professor James Morgan from Caltech. Dr. Morgan is going to introduce the rest of the program, and I will let you get started.

DR. JAMES MORGAN

Let us get right to it. Every minute is precious as you will find out.

DR. STEPHEN BROWN, Moderator

Good morning, my name is Steve Brown. I am working in the aquatic ecosystem program at the Board. We have seven speakers this morning to speak about the aquatic ecosystems in the Sierra Nevada. Our first speaker is Dr. John Melack from the University of California Santa Barbara. The title of his talk is "Atmospheric Deposition and Catchment Solute Balances as Assessments of Acidity in the Sierra Nevada".

1. Atmospheric Deposition and Catchment Solute Balances as Assessments of Acidity in the Sierra Nevada. Dr. John Melack, UC Santa Barbara.

DR. JOHN MELACK, UC Santa Barbara

Let me start by saying to John Holmes that the researchers in California have appreciated the support through the years from the ARB. I think it is been a mutually beneficial process to have long term support to study important questions and environmental issues in California. The ARB has been a very good organization to work with both administratively and scientifically.

As the first speaker in the series on the aquatic effects, I will spend the first five minutes or so providing some context of where we were in the mid 1980s; then I will discuss a more recent study. The Sierra Nevada in California is the first barrier to moisture transport across the continent. It collects great volumes of snow in the winter and supplies much of California with its water. At the same time the mountains collect solutes that are dissolved in that precipitation, and those solutes run into the valleys and affect the local aquatic environments.

The initial work through ARB support was in the southern Sierra Nevada in Sequoia National Park. That choice was driven largely by the concern to study the most likely location for impact from acid deposition, which would be at the southern end of the central valley given the air paths. Subsequently, we expanded the studies to include most of the whole range. I will first discuss the area around Emerald Lake and then more regional assessments of the whole Sierra Nevada range.

It is important to comment at the outset that the Sierra Nevada streams and lakes are among the most dilute waters that you can find anywhere in the world. If there was acid deposition in California, these streams should be highly responsive to changes in deposition. It was that logic which drove us to consider those environments, in chemical terms, hydrologic terms, and biological terms. Working in these environments is challenging. These mountains are approximately 3000 meters above sea level as were most of the basins that we studied. They are not easily accessible and must be reached by foot or on skis. It is this relatively remote location that makes them important as repositories for long term transport of atmospheric pollutants.

Emerald Lake is a typical Sierra Nevada lake. It is about 2 hectares in area and well suited to a variety of experimental studies as well as basic measurements of hydrology, biology, and hydrochemistry.

The original work at Emerald Lake was done in 1985, 1986, and 1987. We sampled rain and snow intensively, year-round, and saw a very strong distinction between the relatively dilute snow fall and relatively concentrated summer rains. Snow had nitrate and ammonia concentrations in the realm of about 2 microequivalents per liter. This was due largely to the passage of large frontal systems across the state of California that emerged from the Pacific Ocean and, therefore, carry very clean air into

California. Contrasting that with the summer situation, we largely but not exclusively have convective storms which pick up a lot more pollutants, and have ammonia and nitrate values more than 10 times higher than the snow has in the winter.

The work in the lake showed the importance, for at least nitrate, of what is referred to as an ionic pulse. We showed that as the discharge begins to rise, there is a large increase in the concentration of nitrate above the background concentration in the snow. Although the snow is relatively dilute, there is a concentration effect that occurs in the snow, and this leads to an ionic pulse which has a slight acidifying effect on the lake in the early stage of the snow melt. Another way to see that effect is in the time series from 1983 through 1987 from Emerald Lake itself. The acid neutralizing capacity (ANC) is essentially all due to bicarbonate. During the initial phase of the snow melt dilution, some acidification occurs, as do depressions of ANC to just a few microequivalents per liter. There is one point of 0 ANC resulting from a very intense rainstorm that occurred in July, it is not just snow melt that causes these depressions, but also rare large rainstorms.

The general pattern is dilution and acidification occurring during this initial phase of the year when the snow is melting. Concurrently with that, depressions in the pH occur. Later, when Scott Cooper talks, he will point out the connection between some of these pH values and the biological response that is likely to occur based on experimental data at pHs in the realm of 5.6 to 5.8. The lake itself varies from about 6.6 to about 5.6 over the annual cycle depending on the year.

Emerald Lake, to the extent that is typical, shows the Sierra Nevada lakes are subjected to mildly acidic snow with very low concentrations of solutes and summer rainstorms which are usually small in volume but high in solutes. An ionic pulse occurs in the spring, which, in conjunction with the dilution by snow melt, leads to depressions in acid neutralizing capacity and depressions in pH.

One last result we will infer from a variety of studies at Emerald Lake are the mechanisms, the chemical mechanisms, which neutralize the effect of acidic deposition. The primary source of the acid neutralizing capacity is weathering reactions which occur in these basins, and there is a strong correspondence between the release of cations and the generation of acid neutralizing capacity. There is some production of acidity through nitrification, at least in some cases, oxidation of sulfate, and some consumption of acidity through nitrate consumption or denitrification.

Starting in 1989, which is water year 1990, we began sampling atmospheric deposition above approximately 3000 meters at 11 sites throughout the Sierra Nevada (Fig. 1). The sites ranged from south of Emerald Lake in Mineral King to the north end of Lake Tahoe. This series of stations was sampled over the course of four water years. The quantity and chemical composition of precipitation was measured over the course of these four years (Fig. 2). Wet atmospheric deposition was sampled as events in the spring, summer, and fall and it was collected as aggregate winter precipitation by sampling the snowpack of maximum accumulation. All the major solutes were measured, and we put a lot of emphasis on quality control. The snow samples are very dilute, and traditional chemical methods analyzing major solutes become trace element analyses. Therefore, we put a lot of effort and emphasis on the veracity of our data. The plan was to sample the whole high elevation Sierra Nevada, and I think we did that as much as was logistically feasible.

The winter precipitation varied considerably during these four years (Fig. 3), which is good, because it gives us a range of conditions. The winters of the water years of 1990 and 1991 were relatively dry in California. We received between 300 and 1000 millimeters of water equivalents in the snowpack. 1991 was more or less normal, ranging between 500 and 1500 millimeters. 1993 was a fairly wet year; we received up to 2.5 meters of water equivalence in the snowpack. The actual snow chemistry was surprisingly similar among these four years (Fig. 4). The pH was typically between 5.3 and 5.5. The ammonia and nitrate concentrations were between 1.5 and 4.5 μEq L^{-1} and sulfate was a little less. We did measure organic ions, acetate and formate, and they tended to be low, usually less than a micro equivalent per liter. These values, if you compare them to sites around the world, would classify the Sierra Nevada as near the lower end in terms of concentration.

To illustrate the range in these data, they are plotted in figure 5 as histograms for the four year period and show the frequency of occurrence of pH values. The values cluster around 5.4-5.5, which is only mildly acidic and not indicative of any major atmospheric pollutant input. The majority of samples for nitrate are around 2 microequivalents per liter (Fig. 6).

In the spring and autumn (Fig. 7), we set out recording tipping bucket rain gauges and Aerochemetrics rain collectors, to collect wet deposition. We used snow boards and buckets to collect wet snow early and late in the year when we could not operate Aerochemetrics collectors. As you might well imagine, collecting samples from all these sites on an event basis was labor intensive.

The non-winter precipitation chemistry was more variable than that for snow (Fig. 8). The spring and autumn storms tend to be more dilute than the summer rains. Not surprisingly the smaller storms had high concentrations relative to the larger storms. The mean pH in summer was 4.66 (Fig. 9). The lowest pH we measured was 3.86. By most criteria, the summer rains would be deemed acid rain. The spring and autumn rains had a pH of about 5, acidic but less acidic than the main summer rains.

One has to consider more than just concentrations, so I will now discuss atmospheric loadings. These combine the concentration and the actual amount of water that falls. When you combine the summer and winter conditions, you find the northern Sierra Nevada receives a greater loading of solutes which corresponds largely to the larger volume of water that falls in the northern Sierra Nevada. However, loading per unit precipitation is actually greater in the south (Fig. 10). The total deposition is higher in the north because of the larger water volume, but the actual concentration of solutes tends to be higher in the south.

The range of values are summarized in figure 11. The units are equivalents per hectare per year; for hydrogen, ammonium, and nitrate, that is equivalent to moles per hectare per year. These values are all on the very low end of loadings. If you examine the NDP data network, the lowest numbers typically reported are similar to our highest numbers. For example, the recent published summaries show low values of around 70 equivalent of ammonium. Again, I emphasize that not only the concentrations but the annual loadings are low by the standards of North American deposition, which is biased toward the more polluted east.

To make comparisons of deposition more quantitative, we have combined data from the California Cooperative Snow Survey which includes several hundred stations in various sectors of the Sierra Nevada, and we produced latitudinal plots (Fig. 12) of the deposition. These are based on California Snow Survey snow courses at about 2500 meters. For four water years, the average water deposited in these latitudinal zones is shown. We used our subset of stations in those regions to provide a regional perspective on how the deposition changes latitudinally in the Sierra Nevada. Slightly larger deposition occurs in the northern regions compared to the southern regions.

In the Rockies, where there are regional surveys of snow chemistry, considerable variability is associated with regional transect. There are some hot spots in the Rockies where there are major sources of pollution. We do not see evidence of any major local sources disturbing the general trends in California, but I think the data does deserve further analysis to look for more subtle effects.

Now I want to switch from atmospheric deposition to the lakes themselves. In addition to the stations where we measured deposition, we also conducted over the same period studies in seven complete catchments (Fig. 13). We measured the deposition of snow and rain, extrapolated through the catchment, and at the same time, we measured stream discharge and a variety of meteorologic factors, and calculated water balance and mass balances. The lakes include Emerald Lake, some lakes near Emerald Lake, and a series of lakes that extended to near the southern end of Lake Tahoe.

Figure 14 summarizes the watershed characteristics and geographical background. The lakes vary in size from only 23 hectares in the case of Lost Lake to 424 hectares in the case of Ruby Lake. The relief varies from a little over 160 meters to as much as 750 meters or so in Ruby Lake. The altitudes of the lakes are generally around 3000 meters, and, with the exception of Lost Lake, they are all high altitude alpine settings. We monitored the discharge continuously with pressure transducers (Fig. 15). We sampled the chemistry in the outflow streams bimonthly during most of the year except during the period of snow melt when we sampled weekly. These measurements were then combined to produce the annual export of solutes, that is, the concentration times the discharge, to determine the export of solutes from these catchments. At the same time, we measured a variety of meteorologic properties in these catchments (Fig. 16) or nearby these catchments. We then were able to calculate the sublimation and evapo-transpiration terms which are critical to doing a water balance.

The hardest part of doing the mass balances was the evaporation calculation. Figure 17 shows a series of histograms of water balances for 1990-1993 water years for Emerald Lake. The first histogram is the rainfall, expressed as thousands of millimeters of water. The second histogram is the snowfall. The third is the outflow of water. The fourth is the combination of sublimation and evaporation-transpiration, and the last one is the residual which reflects both errors in all the other measurements, or, in some cases, it reflects the fact that the official water year ended before the water had drained from that years snowpack. Hence, the larger apparent error in 1993 is not an error. The net result of this analysis gives us considerable confidence in the water balances. With the exception of 1993, we are within 5-10% of a water balance, and by most standards, that would be judged as quite good. This constrains the accuracy of subsequent mass balance estimates.

Figure 18 illustrates the mass flux of ANC in equivalents per hectare per year. In the case of ANC, there is essentially no loading from the atmosphere so the outflow is the yield. The main purpose of showing this is not to compare loading with yield, but to point out that over the course of these five years, the mass yield of ANC varied from about 120 to about 320 equivalents per hectare per year. This is important because when we try to make generalizations, both regionally or temporally, we need to have some sense of variability. The same kind of analysis has been done for all seven catchments, but as those of you who are reading the reports know, describing seven catchments for five years is hard to read and even harder to present. I selected Emerald Lake as the example, although I should emphasize that these data do exist for other lakes as well.

Figure 19 illustrates the mass fluxes for hydrogen. The first histogram is the loading of hydrogen, the second is the outflow, and the third is yield. These negative yields imply that there is more consumption in the catchment than there is input. There is some output, but the watersheds are consuming the hydrogen that is deposited on them from the atmosphere, and there are no internal processes which are contributing enough to result in a net mass flux out. This is a sign that catchments are able to buffer the inputs of acidity they are receiving. The same analysis has been done for all seven catchments and you see the same pattern; the hydrogen ion has a negative yield implying consumption.

Ammonium (Fig. 20) can be important, and Diana Engle will discuss more about that. If you nitrify the ammonium, you actually create acidity. Figure 20 shows that not quite all, but most of the ammonium that enters in is retained in the system. The retention implies that it is being used biologically, which implies that there is an acidification of the watershed associated with this retention of ammonium. Further analysis shows ammonium retention in all seven watersheds. This implies that the process of nitrification has the potential to contribute to the acidity in all these alpine catchments.

Although we have seen fairly wide variations in snowfall, there is an increasing interest in long-term trends in global change. One likely effect in places like the western United States is a change in the fraction of rain in the precipitation. Given our data on rain chemistry, if you were to greatly increase the proportion of the rain either in the autumn or in the spring, that would change the loading of atmospheric solutes. I want to offer a challenge to think not just in terms of these last five years, but to think how these data might be used in a broader context looking ahead 50 years.

DR. STEPHEN BROWN

Any questions for Dr. Melack?

Q (AUDIENCE) First a comment more then a question. You said if the rain increases, we may increase the problem, but that implies that if the rain decreases, we will decrease the problem. I think we ought to keep a balance there as well.

A (DR. MELACK) All the evidence suggests that if you do have global warming, it would increase the proportion of rain. I am not saying that it will necessarily increase precipitation; I am saying there will be more rain relative to snow.

Q (AUDIENCE) Two questions then. You gave some pH values for snow for the spring rains, and for the summer rains. If you consider a total volume and a weighted estimate of pH over a period of a year, about what would it be factoring in all the water from the atmosphere including snow, rain, et cetera? Just some rough idea.

A (DR. MELACK) It is about 5.3, as regional average.

Q (AUDIENCE) Okay, the second question and my final one. You mentioned that the retention of the ammonia would suggest an increased acidification.

A (DR. MELACK) Yes. I said that biological uptake which is a well known process, will result in acidification. However, if you look at that set of histograms, compared to the neutralizing effect of weathering reactions, potential acidification is still a smaller number.

Q (AUDIENCE) I am impressed with the value of your data base for tracking the trends of acidic deposition in the Sierra Nevada in the future. This a baseline data set. Is there now or will there be a protocol manual which has details and method and quality assurance procedures available for future researchers that might want to follow in the same sort of sampling?

A (DR. MELACK) The answer is yes, but it is a staged process. In an earlier stage, in the late 1980's, we did a manual for these things, and we subsequently improved upon that. In the most recent annual report, the material that you are reviewing right now, we included a lot of details on how we did our QA-QC and how we did our chemical analysis. Now it could be extracted and turned into a protocol manual. I should hasten to add, though, that there is a problem with what we did compared to what is typically done with routine programs. If you recall, in the protocols of the ARB or EPA, they usually sample once a week on Tuesday at 9:00 in the morning. We did not do that. We sampled on an event basis in remote sites. That puts a very different constraint on the availability of staff and people. Secondly, sampling at 3000 meters in the Sierra Nevada requires a different set of skills than are typically available. Although we can produce such a manual, I think it is hard to expect that to be implemented by the standard approaches that have been used to date.

Q (AUDIENCE) It is always helpful to have some comparisons of watersheds of interest in California to those in other parts of the world about which we know, historically speaking, a good deal more. How would you characterize the generation of acid neutralizing capacity in the Sierra Nevada with values for Scandinavia, for example, or northeastern Canada or northeastern United States? In broad terms, I realize it is a difficult to produce, but it seems to me it is an important issue. In order to place California in perspective, we have to see the source of the neutralizing capacity as an annual term in relationship to the forest function and the input of acidity.

A (DR. MELACK) I agree broadly, but not completely. There is a book published in 1991 which is a regional case study analysis of all of North America. There are nice summary tables for all the major regions in North America that answer in quantitative terms exactly what you are asking. The answer, however, is not that simple. Florida, for example, has peculiar hydrology and you end up with a lot of acid lakes in Florida, more than you might expect given its deposition. If you go to the northeast, there is some high deposition in the Catskills and in the Adirondacks in relatively dilute water systems. The nitrogen load, which has increased so dramatically in that part of the country, has caused nitrogen saturation. Although the basic chemistry is similar, there is a large change in the dominance of the processes. I think you could argue that nitrogen dynamics and sulfur loading are much more important in the eastern regions and some parts of Scandinavia then in the Sierra Nevada where we are still in a more pristine situation. In the Sierra Nevada, the cation exchange and the weathering reactions with some small contribution from the nitrogen cycle are our primary mechanisms. I would refer you to the book, which was edited by Don Charles, as an excellent source of information on the regional comparisons.

Q (AUDIENCE) John, you have an incredible set of data. In 1983, the ANC apparently went to near zero. Based on the information that you have collected over these years, do you think that is going to happen again.

A (DR. MELACK) That was one of these very rare events somewhat analogous to what is happened in Santa Barbara last week, very intense rain on a particular catchment. The answer to your question is yes. It will happen again. It will be very brief as it was then, and it is very much of a function of a local intense rainstorm. There is a greater concern, which is still quite hypothetical given the fact that the snow is such a dominant influence on the chemistry of these systems. If for whatever mechanism you could imagine, you increased the atmospheric concentration that is, the loading of solutes in the snowpack, the aquatic systems would then become acidified regionally. However, I do not see how it is going to happen now. The rain events would be brief. The more important question is, do we expect chronic changes. Based on the existing data, there is no trend. We have sampled a series of lakes every autumn for 12 years. They jumped around a lot in ANC and pH, but there was no trend of increasing or decreasing ANC or pH. So at least on the time frame of a decade, the lakes are not showing any danger signals. On the other hand, the systems are so dilute, that they are potentially very responsive.

Figure 1

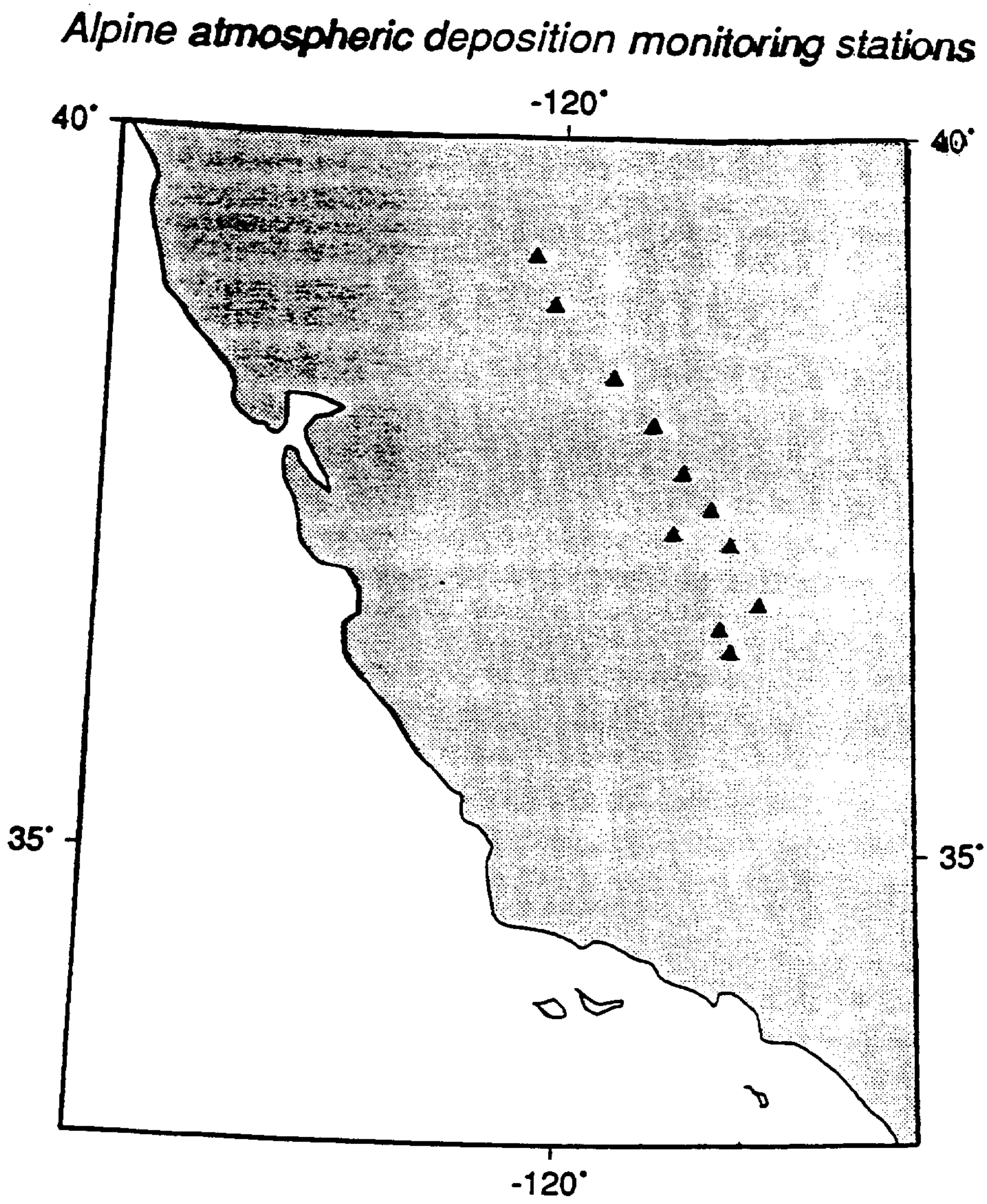

Alpine atmospheric deposition monitoring stations
40°
-120°
40°
35°
35°
-120°

Figure 2

The quantity and chemical composition of precipitation in the Sierra Nevada were measured at eleven high elevation stations during the period of 1990 through 1993.

Wet atmospheric deposition of solutes was measured by event collections of spring, summer and autumn precipitation and by sampling the aggregate of winter precipitation in the snowpack on or near April 1.

All major solutes in wet deposition were measured and a rigorous quality assurance-quality control protocol was followed.

The network spanned nearly the entire north-south extent of the Sierra Nevada and stations were located on both the western and eastern flanks of the range.

Figure 3

The amount of winter precipitation during the study was variable.

The winters of 1989-90 and 1991-92 were relatively dry (snow-water equivalence range, ca. 300 to 1000 mm).

The winter of 1990-91 had nearly normal precipitation (snow-water equivalence range, ca. 500 to 1500 mm) and the winter of 1992-93 was wetter than normal (snow-water equivalence range, ca. 1000 to 2500 mm).

Figure 4

Snow chemistry was similar among the four years of study and among the sampling stations.

Samples from the April 1 snowpack had pH levels typically between 5.3 and 5.5 (hydrogen concentration usually 3 to 4 µEq L^{-1}).

After hydrogen, the most abundant ions in solution were ammonium and nitrate with concentrations usually 1.5 to 4.5 µEq L^{-1}.

Sulfate concentrations ranged from ca. 1.0 to 3.0 µEq L^{-1}. Organic anions (acetate and formate) were found in low concentrations (ca. < 1.0 µEq L^{-1}).

Figure 5

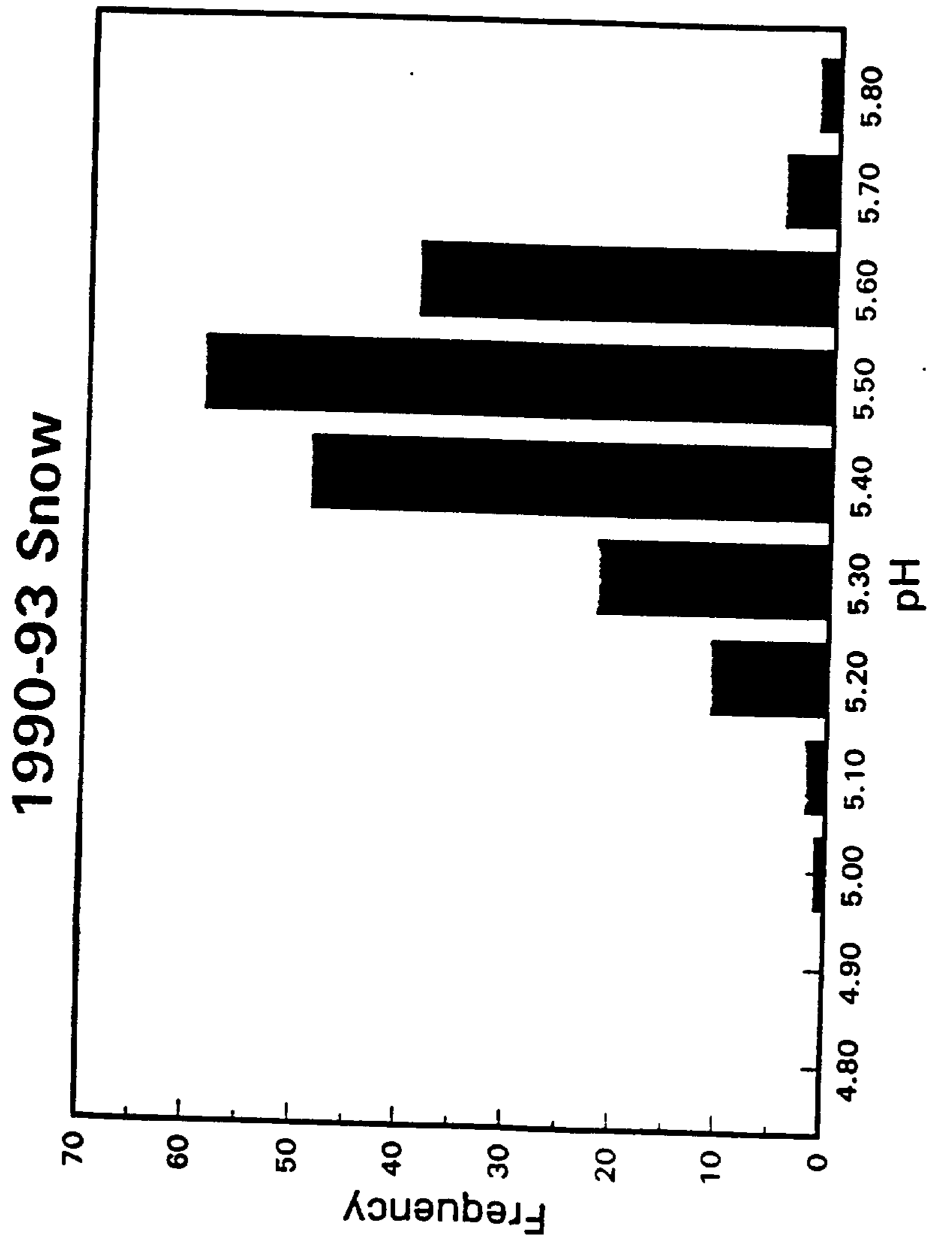

1990-93 Snow
Frequency
0
10
20
30
40
50
60
70
pH
4.80
4.90
5.00
5.10
5.20
5.30
5.40
5.50
5.60
5.70
5.80

Figure 6

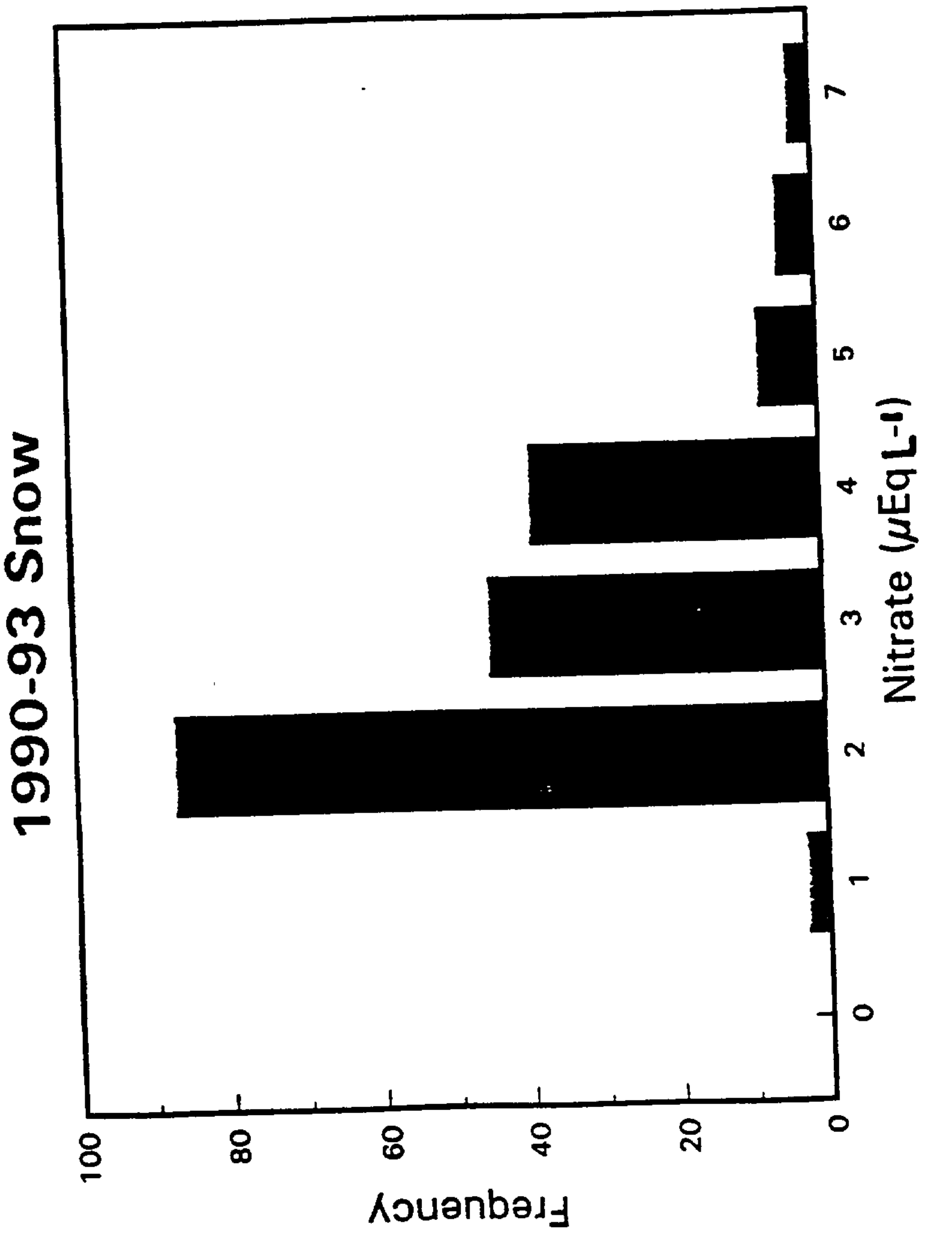

1990-93 Snow
Frequency
0
20
40
60
80
100
Nitrate (μEq L^{-1})
0
1
2
3
4
5
6
7

Figure 7

3. Deposition Monitoring (April - October):

- Tipping bucket rain-gauges
- Aerochemetrics rain-collectors
- Snowboards and buckets (during early spring and late autumn)

The above measurements are used to estimate water and solute deposition to the watersheds during spring, summer and autumn.

Figure 8

Non-winter precipitation chemistry was variable and most of the variability was due to the timing of the precipitation; spring and autumn storms being most dilute and summer rains being enriched with solutes.

Small storms more commonly had high solute concentrations and large storms had relatively dilute chemistry.

The annual amount of non-winter precipitation in the Sierra Nevada varied widely: 1992 was the wettest (precipitation ca. 90 to 200 mm) and 1993 the driest (precipitation ca. 13 to 100 mm).

Figure 9

The mean pH of summer rain in the Sierra Nevada measured during the study period was 4.66.

The lowest pH measured during the study period was 3.86.

The range of pH of spring and autumn storms was 4.4 to 6.0 with mean values of 4.99 for spring storms and 4.97 in autumn storms.

Figure 10

The northern Sierra Nevada generally receives more loading of solutes than the southern Sierra.

Loading of solutes per unit of precipitation is greater in the southern Sierra because of higher solute concentrations in winter and non-winter precipitation.

Figure 11

The average annual hydrogen deposition at the 11 study sites ranged from 26.9 Eq ha^{-1} to 63.1 Eq ha^{-1}.

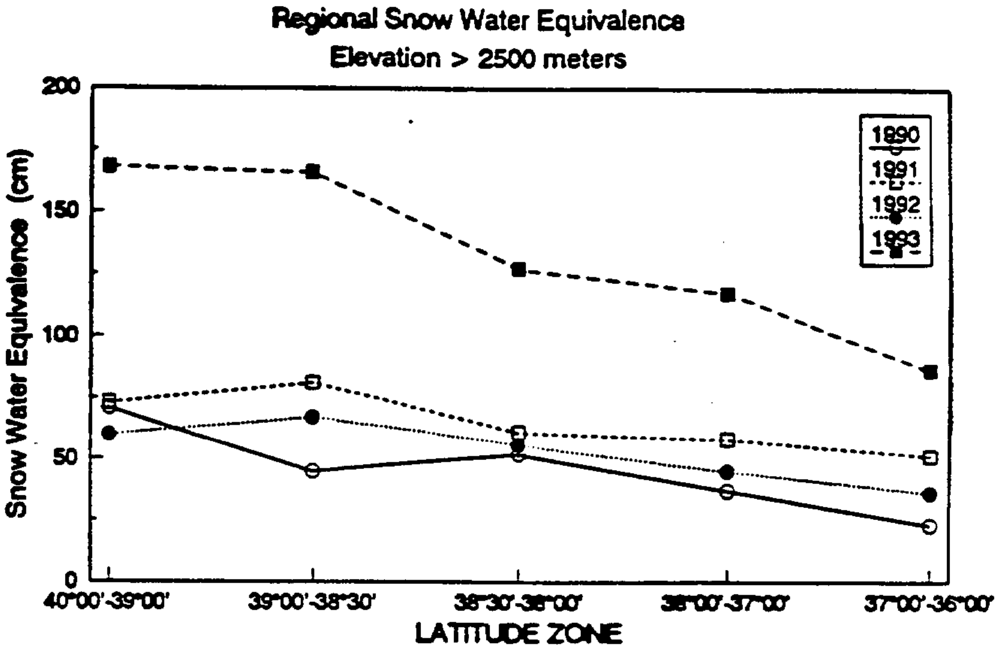
At the majority of stations, deposition of hydrogen was greater in winter than in non-winter seasons.

For ammonium, average annual loading varied from 24.3 Eq ha^{-1} to nearly 60 Eq ha^{-1}.

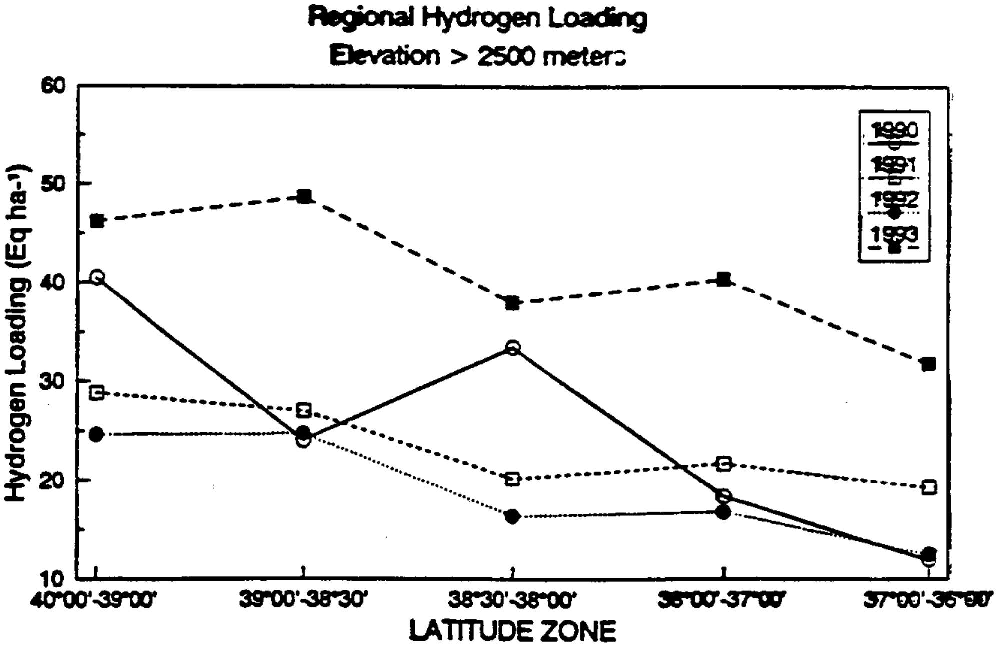
Mean nitrate deposition ranged from 24.1 Eq ha^{-1} to 54.0 Eq ha^{-1}.

For sulfate, average annual deposition ranged from 18.2 Eq ha^{-1} to 44.7 Eq ha^{-1}.

Figure 12



Regional Snow Water Equivalence
Elevation > 2500 meters



Regional Hydrogen Loading
Elevation > 2500 meters

Figure 13

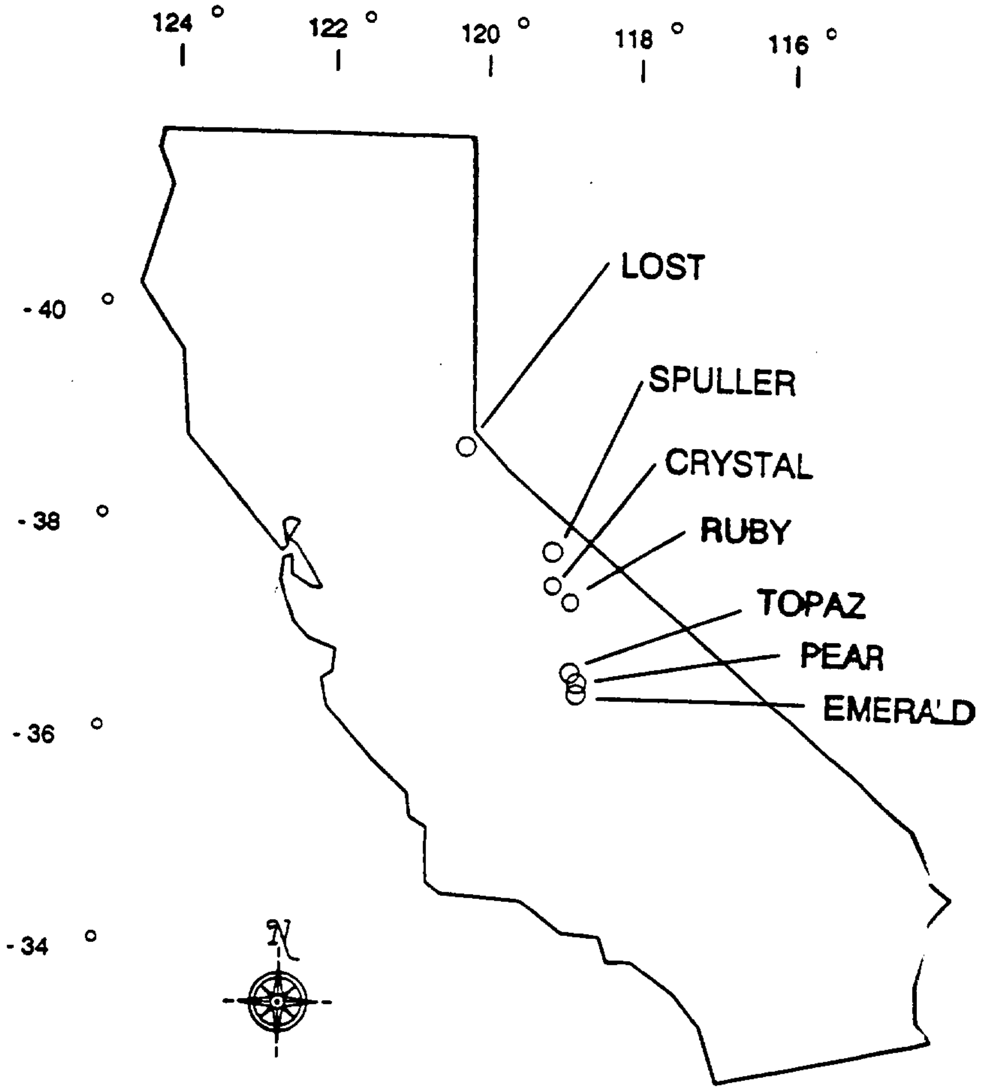

124 °
122 °
120 °
118 °
116 °
- 40 °
- 38 °
- 36 °
- 34 °
LOST
SPULLER
CRYSTAL
RUBY
TOPAZ
PEAR
EMERALD
N

Figure 14

Watershed Characteristics

Watershed	Area (ha)	Relief (m)	Lake Elevation (m)
Emerald	120	616	2,80
Pear	136	471	2,90
Topaz	142	244	3,21
Ruby	424	754	3,42
Crystal	129	293	2,95
Spuller	43	525	3,13
Lost	23	166	2,46

Figure 15

2. Stream Hydrology:

- Continuous monitoring of outflow discharge
- Continuous monitoring of outflow temperature
- Bimonthly samples of outflow chemistry (July - March)
- Weekly samples of outflow chemistry (April - June)
- Samples of major inflow chemistry when streams are clear of snow

The above measurements are used to estimate water and solute flux from the watersheds.

Figure 16

4. Meteorology:

- Solar radiation (Eppley PSP and PIR)
- Wind speed and direction (RM Young Wind Monitor, Wind Sentry)
- Relative humidity (Vaisala HMP 35 or HMP 111)
- Air temperature (Omnidata **TP10 with** vane aspirated shield)

The above measurements are used to estimate snow sublimation and evapotranspiration. These estimates will improve the accuracy of water and mass balances for the watersheds.

Figure 17

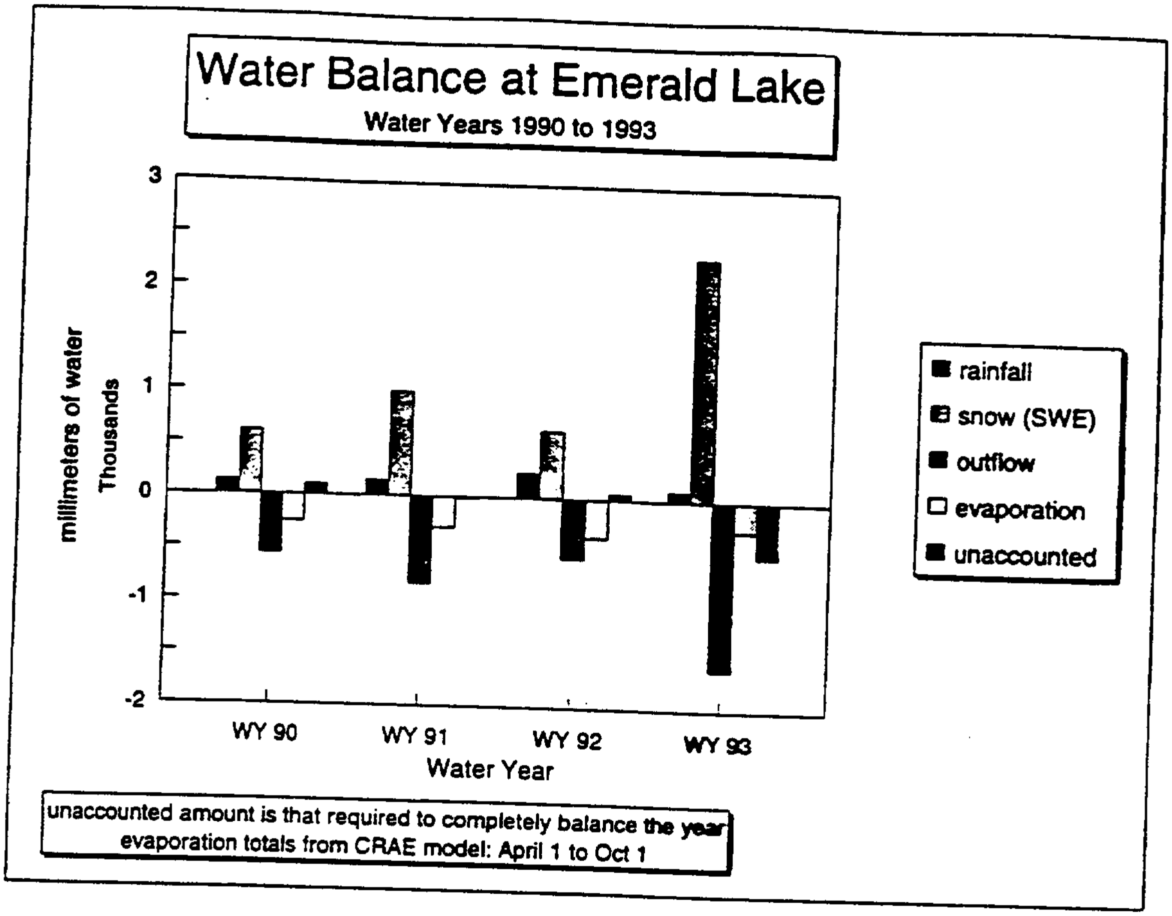
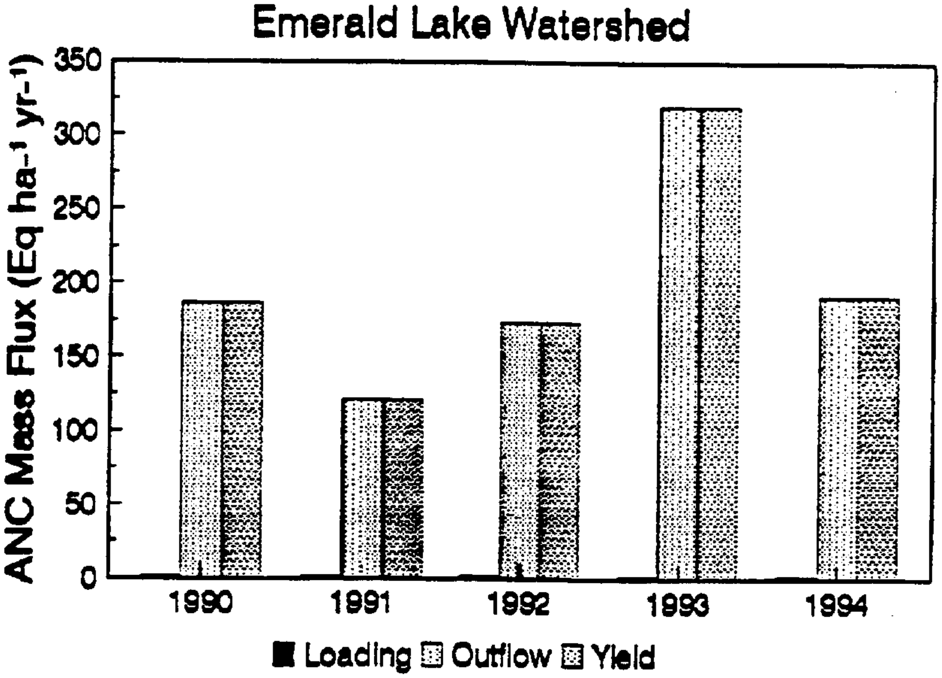


FIGURE 6: Water balances for Emerald Lake basin for water years 1990 through 1993. The unaccounted amount is that addition or subtraction required to balance the account for the year; expressed as a percentage of total input this amount is respectively, -13%, +1%, -6%, and +22% for these years. All inputs and losses are expressed in millimeters of water. 1991 and 1992 were both drought years and outflow from the lake had ceased prior to the end of the water year. If storage in the basin is considered limited or balanced for these years the close agreement could be considered at least a partial validation of the evaporation estimates as calculated by the CRAE model. 1993 was a high water year with the outlet still flowing at the end; in light of the amount of water still retained as soil moisture, with snow still in the basin during September, and whatever replenishment of storage took place, a net surplus is not unexpected. An explanation for 1990 is not as readily available; one possibility is the release of water from basin storage, given that 1989 was a respectable water year that offered a respite from previous drought conditions; another possibility is an error in measuring outflow before the installation of the weir.

Figure 18



Emerald Lake Watershed
ANC Mass Flux (Eq ha-1 yr-1)
350
300
250
200
150
100
50
0
1990
1991
1992
1993
1994
Loading
Outflow
Yield

Figure 19

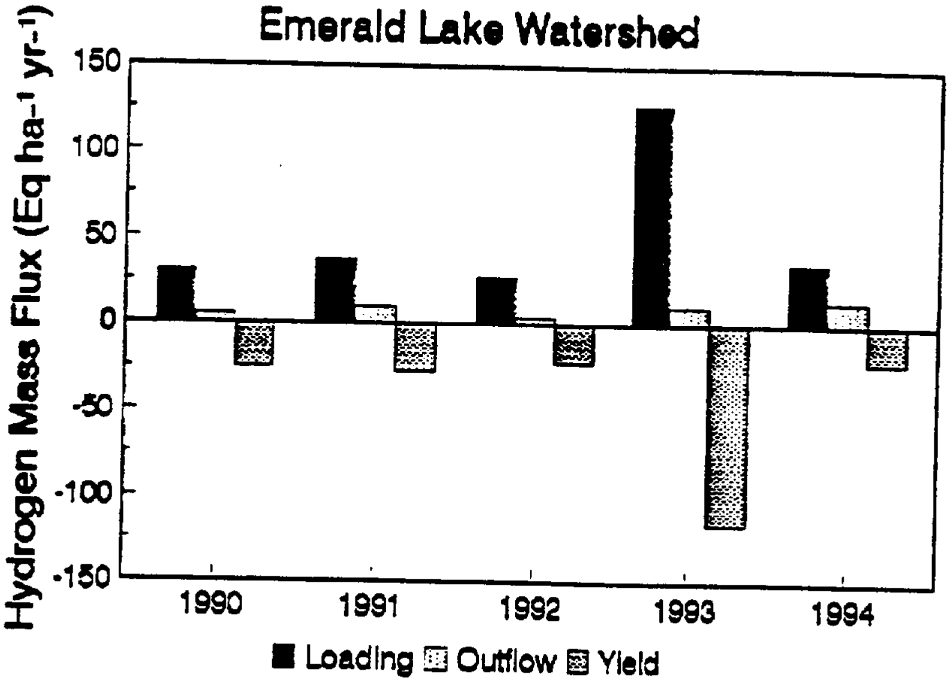
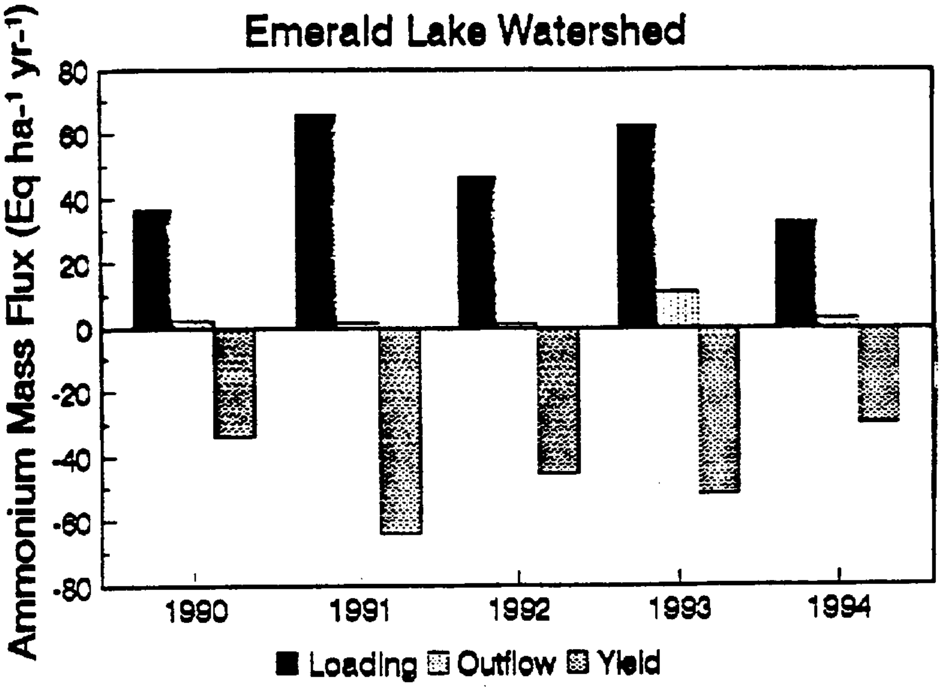

Emerald Lake Watershed
Hydrogen Mass Flux (Eq ha-1 yr-1)
150
100
50
0
-50
-100
-150
1990
1991
1992
1993
1994
Loading
Outflow
Yield

Figure 20



Emerald Lake Watershed
Ammonium Mass Flux (Eq ha-1 yr-1)
80
60
40
20
0
-20
-40
-60
-80
1990
1991
1992
1993
1994
Loading
Outflow
Yield

DR. STEPHEN BROWN, Moderator

Our next presentation will be given by Dr. Aaron Brown of UC Santa Barbara.

2. Rock, Water, and Soil Interactions at Sierra Nevada High Elevations. Dr. Aaron Brown, UC Santa Barbara.

DR. AARON BROWN, UC Santa Barbara

I got started on this project by looking at soils in the Emerald Lake watershed. As a result of my studies of the Emerald Lake and of Eastern Brook Lake watersheds on the eastern side the Sierra Nevada, it became obvious to me that the soils were a tremendous, almost inexhaustible source of neutralization for any acidity that could be added to our watersheds. From the start, I was highly skeptical that there could be any effect of acidification by rain or snow or anything else. However, through the course of that study, after quantifying the amount of soil present, after quantifying the neutralization capacity of the soil, and after looking at the rocks that were present, we concluded that, during the spring snow melts, the soil was unable to provide the neutralizing materials to counteract the effect of the big flush of melt water (Brown et al. 1990, ARB Contract Number A5-204-32). With this lead-in, I will describe how the work that I am doing now got started.

For the last few years I have studied the chemical response of the watershed to acidification or to acidifying materials. I have had two opportunities. The first opportunity was with two small watersheds in Sequoia Park: again, near the Emerald Lake watershed where we could use many of the same data. Those watersheds are very small, very tightly monitored, and we produced a tremendous amount of data. The second opportunity came when some other scientists in our group noticed that there were a series of naturally acidified lakes in the eastern Sierra Nevada. That gave us an opportunity to look at the effects of an addition of acid, of sulfuric acid in particular, and what effect that might have on watersheds on a larger scale.

I will discuss the acidified watersheds. It was not initially clear why they were acidified, but it soon was obvious that pyrite, a sulfur-containing mineral was present. We divided the lakes up into two rough groups, one acidified with pH less than 6 and one unacidified with the pH greater than 6 (Table 1). There is a difference in sulfate on the average of only about a factor of 2, but the range is much greater, and this works out to be a statistically significant difference. The standard deviation indicates that above pH 6 the sulfate concentrations are significantly greater than zero (Table 1). When the sulfate was extremely high, it was all due to pyrite. We measured aluminum and a whole suite of major elements. All of these lakes were in the neighborhood of about 2500-3000 meters in elevation.

I looked for two things there. One was for relations that would help indicate which minerals were weathering in the area, because it has been a little mystifying exactly why there was so much calcium in the runoff from these watersheds relative to other minerals. One of the major theories is that there is calcite (calcium carbonate) present in granite. Although it is difficult to see in the field, it may be present in very small particles. The one interesting relationship I was able to find was that below pH 6, which I called our acidic boundary, there was a very regular relationship between calcium and silica (Fig. 1). This makes me think that maybe a single mineral is responsible. The calcium to silicate ratio is fairly high for what one would expect in the Sierra Nevada. In anorthite, which is plagioclase and a very common mineral in the Sierra Nevada, the ratio of calcium to silica that one might expect (0.28) is much lower than the 2-4 ratio we found. One would expect a lot less calcium than was found or a lot more silica in the lake waters. However, the silica concentrations we found are pretty normal; it is the calcium that is a lot lower in concentration than one would expect. The mineral hornblende (Ca/Si=0.35) and Emerald Lake watershed soils (Ca/Si=0.1-1.0) also do not fit this model since the ratio observed was between 2 and 4 for the lakes with $pH < 6$.

Another curiosity, and I can only call it that, because I do not have an explanation for it at this point, is that the relationship of the ratio of magnesium to calcium versus pH increases dramatically as pH decreases. This indicates that there is a mineral rich in magnesium weathering with higher rates at lower pH. I would project that this magnesium bearing mineral would be the one that is weathering most rapidly in these watersheds and that would provide neutralization for acidification in the Sierra Nevada. I do not know what the mineral is; perhaps we will find out through ongoing research. One of my theories is that it may be a volcanic glass which is widely disseminated over the Sierra Nevada on a fairly regular basis. In somewhat less than a thousand years there may be deposition of as much of a centimeter of volcanic ash over the Sierra Nevada that could be sufficient to neutralize quite a few hundred years of acidity.

Q (AUDIENCE) Does each point on Figure 1 represent a lake?

A (DR. BROWN) Each point represents a lake in this graph.

Q (AUDIENCE) Then you have a whole bunch of the acid lakes there; is that right?

A (DR. BROWN) They are more acidic, yes. Now this is an arbitrary measure of acidity of course. I am arbitrarily saying that something less than pH 6 is acidic. In fact, a lake that has pH about 5.6 and above would be expected to have a positive alkalinity or acid-neutralizing capacity, but below about 5.5, you run into lakes that would have a 0 or negative alkalinity. In fact, this was the case in this area. There are perpetually acidic lakes in the eastern Sierra. It is a situation like acid mine drainage but without the acid mines.

Q (AUDIENCE) Is this a small concentrated area?

A (DR. BROWN) I do not know the exact breadth in miles. It is within about 10 miles radius.

The other interesting question is exactly what happens with amorphous aluminum. What brings aluminum into solution, and what is controlling the concentrations of aluminum in surface waters? Another set of information is available in this natural acidification experiment, because we could measure the aluminum concentration in nature. There is a very regular increase in aluminum concentration as the pH decreases (Fig. 2). That is expected because of the pH solubility relationship for Al-bearing minerals. One can try to match that regular increase by manipulating aluminum term, turning it into aluminum activities and trying to match that with the solubility of several minerals (Fig. 3). It appears that the reacting mineral is the same you find most everywhere else, and it is something releasing a ratio of 3 hydroxyls to 1 aluminum. In this case, it is most like amorphous aluminum hydroxide. For modeling purposes, I would say that this kind of a mineral has to be our choice for explaining the response of aluminum to acidification in the Sierra Nevada.

The second project I have worked on is a small watershed project, and I was interested in the geochemistry of the weathering reactions. I do not have data developed to the point where I can show you the same kind of information that John Melack just showed you. Our mass balances are not complete at this point, but I do have information that will show you a couple of the other effects that I was very pleased to see. One is the salt effect.

The salt effect is the response of the watershed output to the addition salt. When you add a neutral salt with a cation which can be absorbed by the soil, that cation will exchange for hydrogen and put hydrogen in the solution. There have been studies published on salt effect. One is in Acadia National Park in Maine in which sea salt raining in on the bogs in Acadia Park caused the pH of the streams to drop. The relationship there was very clear, and we can see the same thing in these little watersheds in Sequoia Park.

The third thing that I am working on is the hydrodynamic or kinetic effect, in which I know the watershed has enough neutralizing capacity to neutralize acidic deposition, but it is clear that there is not enough time for the watershed to interact with the water as it passes through. We did a neutral tracer experiment with lithium bromide. We added lithium bromide on a wide area over these watersheds at the base of the snowpack and allowed the snow melt to carry the lithium bromide across the watershed. Figure 4 shows the release of lithium and bromide from the watershed. The bromide was intended to trace the path of water. These data show that it took almost 6 or 7 days for the watershed to release bromide. That was completely contradictory to what I thought was going to happen. My thought was based on our earlier lithium bromide addition to the Emerald Lake watershed. There, it took on the order of 24 hours for all the lithium bromide to leave the watershed. Instead, here it took 6 days to travel 100 meters. There was a lot of retention in these watersheds even though they are very small and very high and very steep. The other thing this figure shows is that the lithium is preferentially retained. If lithium or bromide came out together, the two lines would overlap, however the lithium stayed behind. This is what I wanted to see. I wanted to see the lithium retained by soil to show that there was a strong effect of soil on the surface water. Ironically this (Fig. 4) is the watershed we predicted would have the least interaction between the soil and the snow. This was our rock watershed; just about a half hectare in size. At the same time, to test for the salt effect, we added bromide. Figure 5 shows the specific conductance of the runoff water with a nice spike just like for lithium and bromide. The hydrogen ion concentrations also rise, indicating that even though this watershed has a minute amount of soil, there was a release of hydrogen ion from some site in that watershed. There was a lot more interaction between the soil and the snow than I had expected.

The other thing that I am studying in greater detail is this lag between the release of lithium and the release of bromide (Figs. 4 and 6). I expect to develop figures for the 18 different additions that were made to demonstrate that there is a unit hydrograph and that there is some kind of consistency among all of the applications in both of the watersheds that were used. I would like to be able to develop some dimensionless hydrograph like figure 7 in order to allow some of these data and the mass balance data that are resulting to be projected over larger areas.

Q (AUDIENCE) If you have some clay with exchange of a cation, why are you surprised at the lithium life? It would seem to me that it would be the natural to have that?

A (DR. BROWN) That is right. The problem is that in the other watershed we studied, Emerald Lake, there was a lot of clay present. We knew there was more than enough to absorb lithium, but it appeared in surface water anyway, and that is all the information we had. We had information that was collected as part of a monitoring program. At this point, I wanted to prove unequivocally that cation exchange was going on, and I also wanted to determine whether or not it was on a large scale. I was astounded that so much retention took place over so small a distance with so little soil. The soil in this area was only a few centimeters deep. I had projected, based on the Emerald Lake data, that we would see acidification of the soil rather than acidification in surface water, that we would see a much more drastic effect in the soil. It did not happen that way.

Q (AUDIENCE) More of a comment. You know people, including the ARB supported researchers, who have built models and assume that the Sierra Nevada are like a Teflon basin. It is a nice way to look at the world, but I think it is worth their demonstrating conclusively in a situation where there is minimal amount of soil.

Q (AUDIENCE) Spatially, do you get much variation in the clay mineralogy?

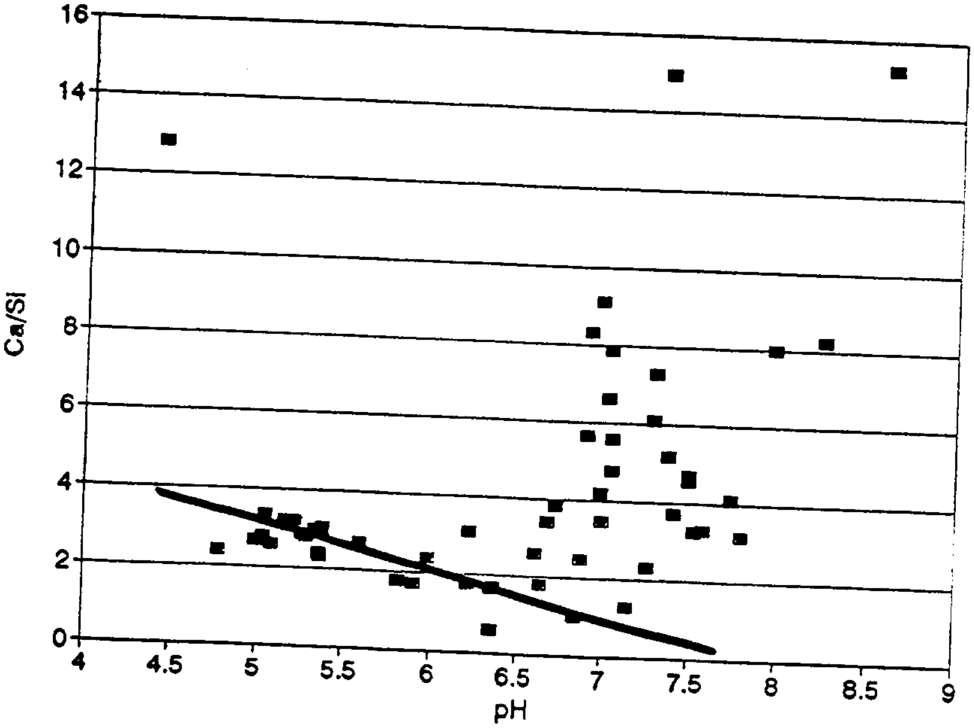
A (DR. BROWN) I cannot provide you that information at this time. In my experience, there is not a lot of difference. It is dramatic that not all of the clay mineralogy is based on the rocks that are in place. Some of the clay mineralogy is definitely volcanic deposition, so there are some bizarre mixtures.

Table 1

	Sp. Cond.		pH						
	Lab	Field	Lab	Field	Al(T)	Cl	NO3	SO4	NH4
	---uS/cm---				----------uEq/L----------				
pH > 6 Group									
Mean	39.7	37.0	6.85	7.15	3.2	5.3	4.5	217.1	0.6
Std	37.0	34.6	0.45	0.53	2.4	3.8	6.2	237.2	0.7
n	35	35	35	35	35	35	35	35	34
Median	29.8	26.6	6.82	7.04	2.7	4.2	1.6	159.0	0.5
Low	5.3	3.1	5.87	6.22	0.5	1.6	0.0	12.7	0.0
High	159.3	156.6	8.23	8.61	10.3	23.5	26.0	920.0	3.2
pH < 6 Group									
Mean	57.3	52.1	5.17	5.38	58.2	5.1	13.1	443.9	0.6
Std	15.2	13.5	0.41	0.37	43.7	1.8	6.0	126.8	0.3
n	19	19	19	19	19	19	19	19	19
Median	51.0	46.0	4.94	5.29	53.6	4.6	10.8	406.0	0.6
Low	31.8	23.2	4.72	4.78	0.2	3.4	6.9	250.0	0.2
High	83.3	78.4	6.05	6.23	130.3	11.1	26.2	708.0	1.2

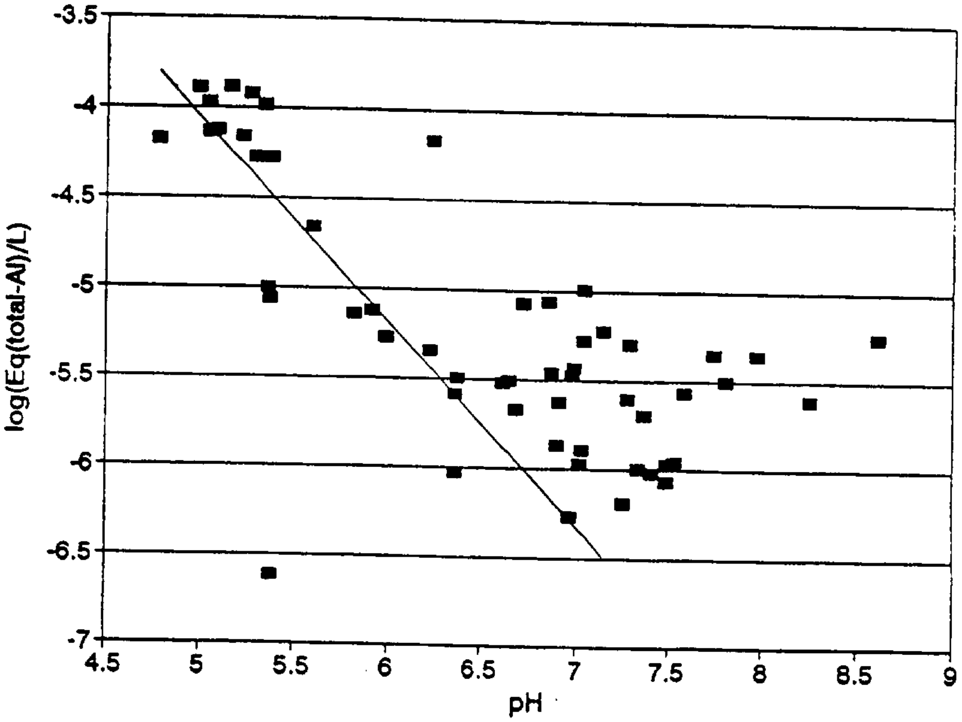
Variations in concentrations of several dissolved chemical species found in 56 eastern Sierra Nevada lake samples. Lakes with pH < 6 were naturally acidified by sulfuric acid, a product of pyrite oxidation.

Figure 1



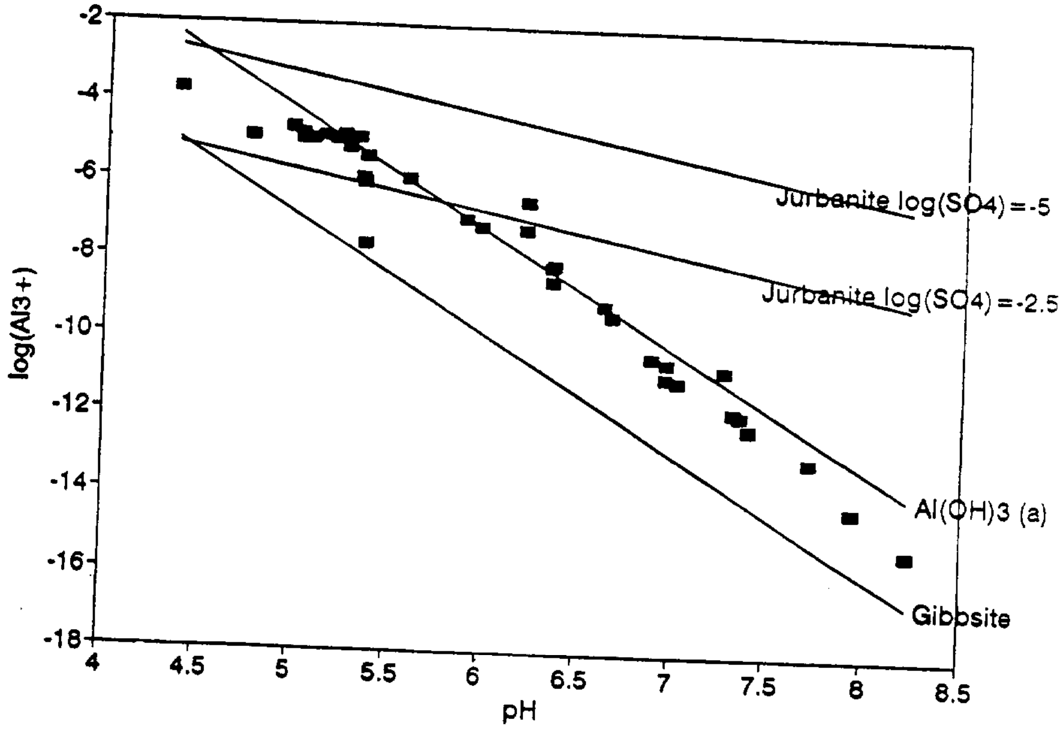
Relationship between the ratio of Ca to Si concentrations and pH in 56 eastern Sierra Nevada lake samples

Figure 2



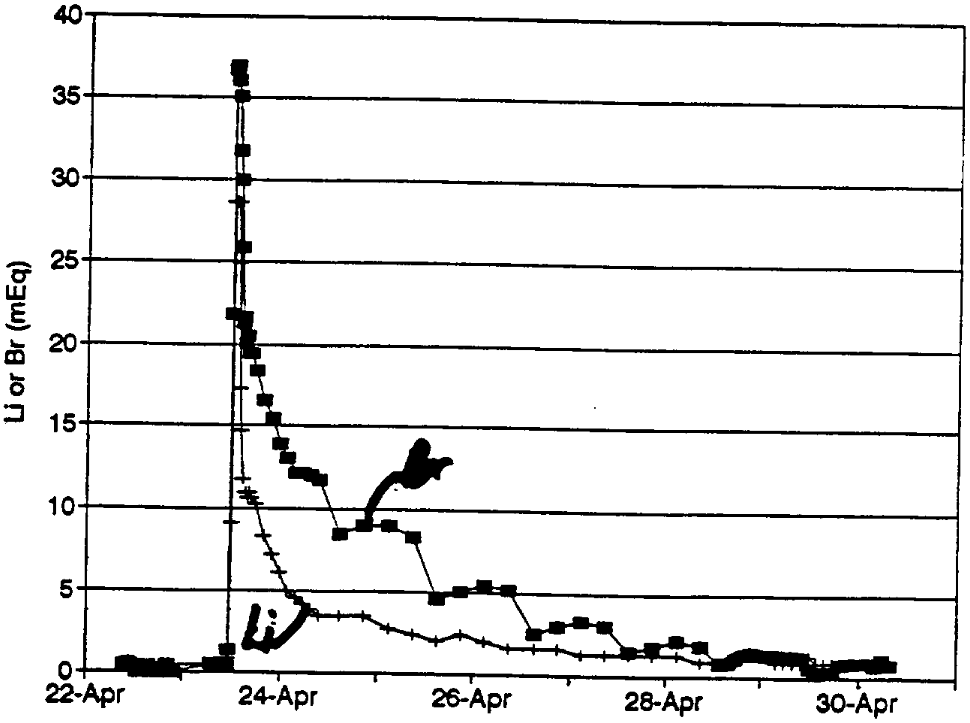
Relationship between total aluminum (Al) concentration and pH in 56 eastern Sierra Nevada lake samples.

Figure 3



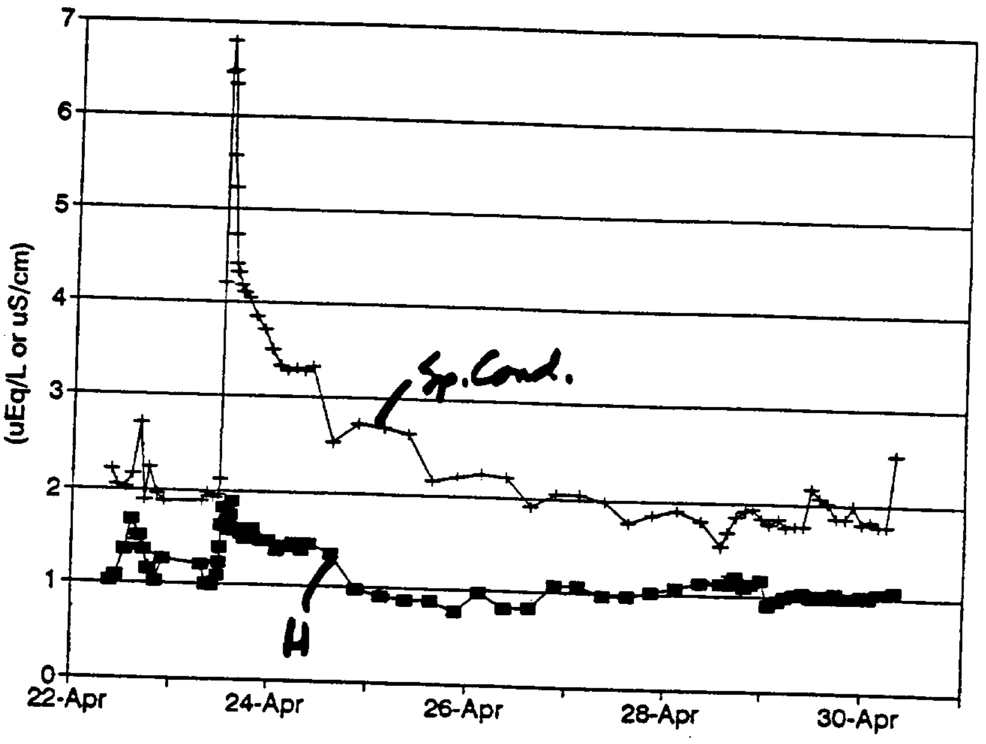
Comparsion of (Al^{3+}) calculated for 56 eastern Sierra Nevada lake samples with known solubilities of the minerals jurbanite, amorphous aluminum hydroxide ($Al(OH)_3$) and gibbsite.

Figure 4



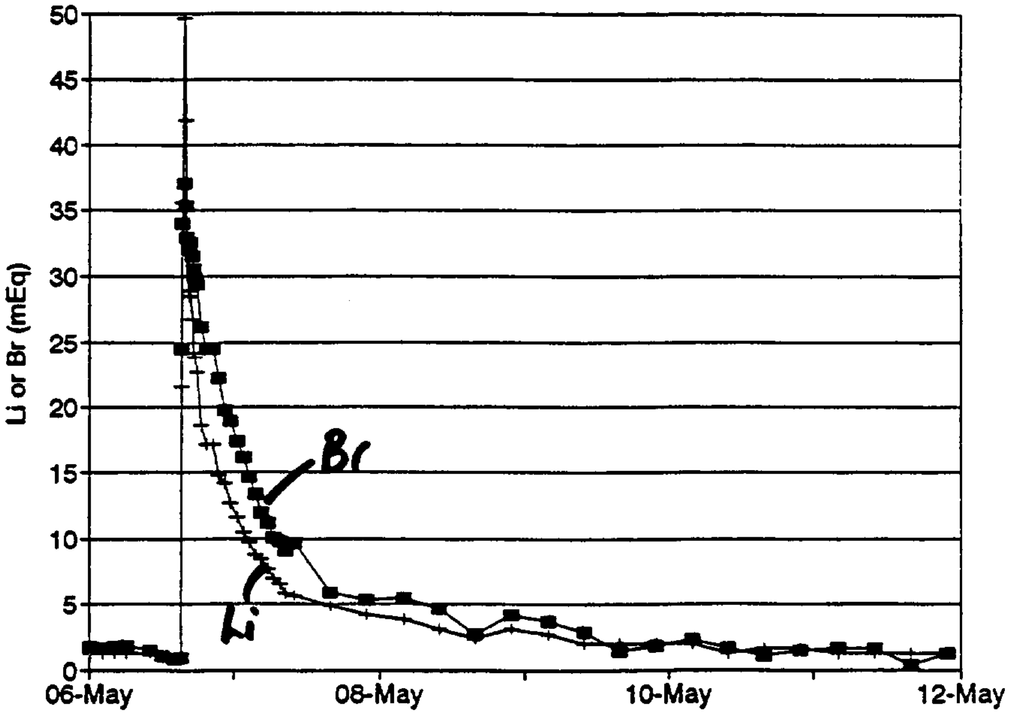
Bromide (Br) and lithium (Li) in snowmelt runoff from a very small watershed in Sequoia Park during April 1992.

Figure 5



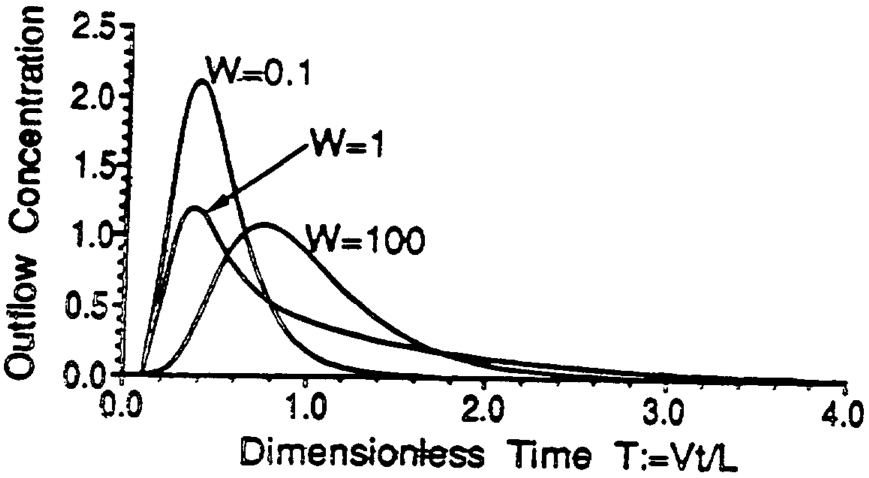
Generation of acidity (H) in response to addition of a salt (measured as specific conductance) in runoff from a very small watershed in Sequoia Park during April 1995.

Figure 6



Bromide and lithium in snowmelt runoff from a very small watershed in Sequoia Park in May 1992.

Figure 7



3.2: Flux concentration pdfs of the mobile-immobile water model

(From Jury and Roth: Transfer Functions and Solute Movement through Soil, Birkhauser Verlag, 1990).

DR. STEPHEN BROWN, Moderator

Our next presentation will be given by Dr. John Stoddard entitled "Episodic Acidification During Snowmelt in High Elevation Sierra Nevada Lakes".

3. Episodic Acidification During Snowmelt in High Elevation Sierra Nevada Lakes. Dr. John Stoddard, U.S. EPA.

DR. JOHN STODDARD, US EPA

I want to discuss the rationale behind this particular project and how we went about answering what we regarded as the last remaining big policy question in the Sierra Nevada relative to acid deposition. Figure 1 is the result of the National Surface Water Survey conducted by the EPA in the mid 1980s. Random samples of streams or lakes were taken. In each region, waters were sampled synoptically and the results presented in terms of the regional population of sites. In the Sierra Nevada and in terms of California in general, this random survey of lakes found no lakes that had Acid Neutralizing Capacity (ANC) below 0, which was used as the definition of acidity in this case.

We started from situation where we knew that on a chronic basis there were no acidic or anthropogenically acidified lakes in the Sierra Nevada. Nonetheless, at the same time that those surveys were being conducted in the Sierra Nevada, there was intensive work going on at Emerald Lake. As John Melack showed you earlier, there is indication that on a very episodic basis, the ANC in that lake can drop to 0, although it is never gone below 0. We are still left with the question: what happens during snowmelt and what happens during big rainstorms at more sensitive lakes? Is there a potential for these very dilute waters to go acidic during these events? One of the points of concern is that Emerald Lake is not an end member, this is, it is not an extreme case in the way of Sierra Nevada lakes. Figure 2 is cumulative frequency distribution of ANC for lakes from the Western Lake Survey. This includes only Sierra Nevada lakes. Figure 2 shows simply the cumulative percent, or number, of lakes that have a certain characteristic shown on the x-axis. For any given value one can read the percentage of lakes or how common that particular characteristic is in a group of lakes. In the case of Emerald Lake, the median summertime ANC is about 27. Based on the data from this survey, we would conclude that roughly 15% of the lakes in the Sierra Nevada are actually more acid sensitive than that. While the ANC gives us a good idea of the steady state capacity of a watershed to buffer acid inputs, we also have to know something about what happens when you run water through one of these watersheds very quickly, as happens during the snowmelt. That is not a steady state phenomenon.

Q (AUDIENCE) Is that Figure 2 plot just for the Sierra Nevada?

A (DR. STODDARD) It is just for the Sierra Nevada.

We have to develop an index of how "flashy" these watersheds are. Figure 3 is fairly diagnostic.

It is simply the ratio of the watershed area to the lake area. How much capacity does the watershed have to flush the lake during snowmelt? If you plot Emerald Lake, you find out that roughly 30% of Sierra Nevada Lakes are more flashy than Emerald Lake.

The conclusion from all of this is that 1) Emerald Lake has the capacity to become nearly acidic during these big events, and 2) Emerald Lake is not extreme. This raises the specter that there may be a lot of lakes in the Sierra Nevada that have a greater potential for episodic acidification. With that information, we built a very simple empirical model of sensitivity to episodic acidifications based largely on ANC and this ratio of watershed to lake area. We ranked data from all of the lakes that we know about in the Sierra Nevada, which is at this point I think, roughly 400 lakes. We ranked them all in terms of their sensitivity to episodes, and then choose 9 of those lakes for inclusion in this project. The lakes in figure 4 in bold are the ones we chose for monitoring in this project. Emerald Lake is at the end of the list. That is where it stands relative to the rest in terms of sensitivity; thus all of the lakes we chose are more sensitive than Emerald Lake.

There is one lake near Parsons Pond, which is at the top of the list, that was never monitored in the project. It turned out to be a very dangerous place to travel to in the springtime. In fact, all of our installations at that site were swept away by avalanches by the time we tried to sample them in the spring of 1993. We also included in this survey three of the lakes that John Melack was talking about earlier, and we collected comparable data from Emerald Lake, Ruby Lake, and Spuller Lake, at least in 1993. Two of those lakes in the list, Spuller Lake and the pond above Spuller Lake were dropped in 1994, because they turned out to be very insensitive.

The lakes we worked on extensively in 1993 and 1994 appear in two clusters. Figure 5 is the topography of a large area in the eastern Sierra Nevada known as the Rock Creek Basin, and it shows the 5 sites for which we have data. Ruby Lake is included in the work that John Melack and Jim Sickman are doing. The Ruby Lake watershed has two of the sites that we chose nested within it, Low Lake and Mills Lake. There are three nested watersheds there. High Lake is a very small and a very steep catchment, on the shoulder of the Ruby Lake. Treasure Lake is another large watershed, not unlike Ruby, which sits to the east. There is another cluster of lakes in Sequoia National Park. There is a reason why it seems as though we keep going back to the same areas over and over and over again. They are only ones that we can really get to during the crucial time period. Figure 6 is a view of the entire area of the Tokapah Valley, looking across the Marble Fork of the Kaweah River toward the south. Pear Lake is one the lakes included in the work that John Melack talked about. It was not included in this study. There were three unnamed lakes, M1, M2, and M3 that we chose for this study in smaller and higher watersheds than Emerald Lake. The watershed for M3 is nested in the watershed for M2.

At each of the nine sites on figure 4, we installed an instrument tower roughly 15 feet high. In each tower we placed a data logger hooked to a pressure transducer so that we could get continuous discharge data from each of the lake outlets. We also installed at each site an ISCO sampler which is an automated sampler that can take samples of the lake outlets on a daily basis. I will just state as an aside that we were very pleasantly surprised at how well the ISCO samplers worked. We were quite skeptical they were going to produce any useful samples. In fact, in two years of sampling, we only had one significant failure. In addition to the sampling once the snow started to melt, we also did surveys of the snowpack in each watershed at peak accumulation. One contribution we made that had not been done previously was to start using Global Positioning Systems to locate where every individual measurement of snow depth was made in each watershed (Fig. 7).

A crucial part of any work on Sierra Nevada watersheds is to estimate what the loads are, and this is far from trivial. We set up transects in each watershed where we measured the depth at a number of individual points. There were large areas of the watershed outline that were not covered by these transects. The reason was that either areas of cliffs where essentially impassable or there was no snow. We did a fairly good job of sampling the snow covered areas of these transects. We combined aerial photographs that were made at the same time. Figure 8 is an aerial photograph of the High Lake watershed as an example. We used the aerial photographs to establish the extent of the snow-free areas, and we combined the transect data with our measurements of snow free area (Fig. 9). We mapped the extent or the depth in each of the basins. Once we mapped the distribution over the basin, we summed up the volume. We also had density measurements made at pits in each watershed, so we could convert that volume of snow into a volume of water, in this case about 187,000 cubic meters of water in 1993. This corresponds to a mean depth of snow water equivalence of about 1.1 meters in this watershed in 1993. Eventually, we will use this information to conduct the same sort of analyses that John was talking about earlier. We will calculate input-output budgets and better estimates of the loads to each one of these basins.

What happens when the snow begins to melt? Figure 10 shows data from M3 which is the highest of the three new sites that we established in Sequoia. It shows the daily chemistry. The water depths have not been converted to discharges yet because we have not finalized the rating curves, but it gives you an idea of the progress of snowmelt in one of these basins. In most cases, we were able to measure the initiation of snowmelt with the pressure transducers and collect a sample with an ISCO sampler within a couple of hours of when the first snow water began to run. At the bottom is the hydrograph of the outlet stream.

This was a typical pattern. In fact, 10 out of the 11 lakes for which we have data did the same thing. ANC declined over a very long period of about two months. It reached a minimum value, which is not acidic, at the time of maximum discharge. There was a significant acid pulse or at least an ion pulse for nitrate in every watershed we looked at. In this case, there was a small pulse in sulfate, although I would have to say that is not typical. Finally, the base cation curve looks very much like what the ANC is doing. This is not news to anybody who has looked at these data; it is simply a long term dilution of the base cation concentrations.

It would appear from that site and from most of the other sites, that dilution is the major mechanism causing a decline in ANC. There is one example where that is not true. High Lake (Fig. 11) is the only site we examined where ANC ever went below 0. This was the first time that anybody has actually measured true episodic acidification in a Sierra Nevada site. It went acidic twice within the first 10 days of snowmelt. That gap in the July data is that one significant failure of an ISCO sampler that we had. It is unfortunate that it happened at this site. There was a significant pulse in nitrate, with peak concentrations just over 40 micro-equivalents nitrate. This is the highest nitrate concentration that anybody has ever measured in a Sierra Nevada lake at high elevation. There was no pulse in sulfate, although sulfate concentrations are quite high, and surprisingly, there was a very big boost in base cations. You may recall that figure 10 showed a long-term dilution of base cation. In High Lake, that was not the case; there is a pulse that corresponds very closely to what happens in nitrate. The ANC is a laboratory measure. An alternative way to get at that value is to simply take the sum of the base cations and subtract the sum of acid ion concentrations. That allows us to partition the responsibility of the various ions for producing the negative ANC's. This is called a Molot analysis after the person who first put this sort of analysis into print. It takes the change in each major ion and expresses those changes in terms of their affect on ANC. If the base cations go up, it produces an increase in ANC. Nitrate went up which caused a decline in ANC. Sulfate actually went down a little, and that caused an increase in ANC. In the case of High Lake (Fig. 12), which is the one site where we had ANC's less than 0, the major player was the nitrate pulse. Even though there was a peak in base cations, the increase in nitrate was greater than the increase in base cations and, therefore, we had an acidic event. In the case of M3 (Fig. 12), which is the more typical pattern, the time to minimum ANC was a very long time period, and it included a very large decline in base cations which was really the driving mechanism.

Figure 13 details this unusual or unpredicted big increase in base cations that occurred at High Lake. Apropos of some of the things that Aaron was just talking about, we have this conundrum in the Sierra Nevada where there seems to be too much calcium just about everywhere that anybody has ever looked. If you analyze the amount of sodium and calcium in bedrock, you come away with the idea that when the rock weathers, there should be approximately equal concentrations of sodium and calcium in the lakes because that is where all that weathered material is going. In point of fact, if you measure those lakes, you find that there is a lot more calcium than you would have predicted from the bedrock. This excess in calcium is what happens at base flow in the summer and fall in these lakes. In High Lake, where there was a big increase during snowmelt, the situation was even more extreme. Calcium was by far the biggest player in this increase in base cation. The interpretation is that, when the acid ions melt out of the snowpack and come into contact with bedrock or talus or soils, they cause a preferential movement of calcium, relative to all the other base cations, out of the watershed and into the lake.

I think there has been a very strong tendency on the part of naive biogeochemists, to look at Sierra Nevada watersheds as bedrock catchments, not necessarily Teflon catchments, but catchments that consisted of very raw geological material so that the only source of cations in the watershed was from incongruent weathering reactions. These are kinetic, they take a long time, and at steady state you can make some estimates of the quantity of cations that ought to be produced by a particular kind of geology. I have moved away from looking at things that way. I would agree with what Aaron was saying and also with John's comment on Aaron's talk that, even in this watershed, there is nothing you would identify as soil. You would not recognize anything as soil in this watershed. It consists almost entirely of a pile of talus, but underneath that talus is the stuff that has been weathered out of that bedrock over the 10,000 years since the glaciers last moved through. When granite weathers, clays are produced. That clay is going somewhere, and it goes underneath all the talus, and it is sitting there even though we cannot see it, and we would not identify it as soil. This watershed, which is almost entirely devoid of obvious soil, nonetheless acts just like the watershed that is covered with soil.

The initial rationale behind this project was to look at acidification, and clearly, one of the things we are most interested in is what happens to the aluminum concentrations (Fig. 14). Aluminum is toxic, and the primary concern when a lake or stream goes acidic is how high the aluminum goes and what the effect is on the fish. There are indications of the weathering response at these watersheds. I will point out for Aaron and John's benefit, that even though there is a big increase in calcium, silica is absolutely flat during that period. Over the long term, there is a very gradual increase in the ratio of sodium to calcium which is caused largely by the fact that calcium was very high and declined over time. Focusing on the aluminum concentrations, I will first point out that the aluminum in figure 14 is micrograms of dissolved aluminum, not milligrams of aluminum per liter. These concentrations are extremely small. Even though this lake went acidic twice, the concentrations of aluminum are extremely low. If you sampled a lake in the Adirondacks or the Catskills where episodic acidification is a real issue, these concentrations would be on the order of 500 to 1000 micrograms per liter, so these Sierra Nevada concentrations are infinitesimally small compared to Northeastern lakes.

One of the big differences between the sites we monitored in the eastern Sierra Nevada and those in the western Sierra Nevada is that the aluminum concentrations in the west are significantly higher (Fig. 15), although still quite low. The other really interesting thing about the western Sierra Nevada, at least in all the Sequoia area, is that aluminum followed the same pattern of concentrations that these cations do. While we expected at low pH, a lot of aluminum mobilization, in fact, the reverse happened. The minimum ANC's and therefore the minimum pH's are occurring at the same time that the aluminum concentrations were minimal. To look at that in a little more detail, figure 15 is simply two plots of the pH measured in each of these samples versus dissolved aluminum and divided into the eastern and western Sierra Nevada. If you look first at the bottom panel which is the Rock Creek sites, you will see a slight tendency, for the aluminum to increase at low pH, which is what we would expect based on experience everywhere else in the world. If you go to the western Sierra Nevada, however, that pattern falls apart. The peak aluminums concentrations occur in the range of pH of above 6. These are not acidic samples by anybody's definition.

The important point from all of this is that, in the current situation in the Sierra Nevada, aluminum is simply a weathering product even on an episodic basis. It is produced when base cations are produced. It acts just like every other weathering product that is produced, in that it occurs in highest concentrations when base cations are being produced out of a watershed. I want to touch on one other idiosyncrasy that turns up in looking at these lakes. It is something that John showed very early at Emerald Lake. When frequent samples during snowmelt were first collected, they measured a strong pulse in nitrate concentration early in snowmelt but no corresponding pulse in sulfate. That is largely true in all the sites that we looked at. There are a few sites, however, where we have what looks like preferential elution of sulfate out the snowpack, and a peak in sulfate that occurred more or less corresponding to the time when nitrate went up (Fig. 16). One the nice things about having had these nested watersheds, particularly in the Ruby Lake watershed, is that we can look at the mechanism for peak in sulfate. Figure 17 shows data from Mills Lake, the highest of those three nested watersheds. It has, for the Sierra Nevada, atypical geology high in the watershed. It produced a lot of sulfate almost certainly due to the presence of pyrite. In the winter time, sulfate concentrations are roughly 10 times what you would expect to see based on deposition. Over the course of the melting of the snow, this is essentially diluted because the water is moving through too fast to pick up any more of that sulfate. When sulfate began to decline in Mills Lake, the next lake downstream, Low Lake (Fig. 17) showed a peak. That previous panel showed a peak in sulfate which can be attributed almost entirely to a watershed source of sulfate. It is not a snow melt effect at all. If we sampled downstream to Ruby Lake (Fig. 17), which is a much bigger watershed, the effect of the Mills Lake water eventually reaching Ruby Lake can be seen. If you had just been looking at Ruby Lake, and observed that sulfate, you probably would not have any idea that there was a watershed source involved.

I conclude (Fig. 18) with some sweeping generalizations made on some quite preliminary data. Unfortunately, I have been talking almost entirely about 1993 data so far. We do have another year of data to analyze, however we do have the ANC data from 1994. Acidification during snowmelt is likely to be a rare event in the Sierra Nevada, so the fact that it happened at Emerald Lake, as John pointed out, was the result of a rare, very large rainstorm. We picked the most sensitive lakes we could find. We could find only one that went acidic, and it went acidic in 1993 and not in 1994. From that, we draw the conclusion that this event is probably very rare. It does not happen every year in the most sensitive lake we could find. The major mechanism causing the long term decline in ANC over the course of snowmelt in almost all the lakes was base cation dilution. It is simply taking the weathering products and diluting them with a lot of very dilute snow melt. In the case of most sites, about 75% of the decline in ANC can be attributed simply to dilution of base cations. There are pulses of acid ions that happen everywhere, particularly for nitrate and in some cases for sulfate. Only in rare cases are those pulses high enough to overcome the increases that also occur in base cations. When acidification does occur, it occurs very early in the snowmelt. If you have a watershed that takes a long time for the snow to melt, you are not going to see the kind of events that we saw at High Lake. It is a very steep watershed. It melts very late, but very quickly when it does melt. If acidification is going to happen, it is going to happen early in snowmelt. Finally, toxic effects attributable to aluminum and pH are likely to be minimal and may be nonexistent. We were unable to measure anything approaching a toxic concentration of aluminum in any of these sites including the one that went acidic in 1993.

Q (AUDIENCE) This is a comment rather than a question. You expressed some surprise about the calcium being higher than the sodium, although from the bedrock, one might have suspected they would have been equivalent. It does not surprise me at all because calcium rich minerals will almost invariably weather faster and sooner than those that are lower in calcium. I do not understand why there is a surprise. It is a natural phenomenon.

A (DR. STODDARD) It is a natural phenomenon everywhere that we know that those calcium rich minerals occur. The surprise was that when we began this research, there was no idea that those things existed in a glaciated, granitic batholith like the Sierra Nevada.

Q (AUDIENCE) But that is not a uniform batholith by any means. Let me suggest that if the opportunity presents itself, it may be well worthwhile to do some mineralogical prospecting.

A (DR. STODDARD) There are least two different mechanisms that can produce a lot of calcium like this. One of them is simply that you have something like calcite in the watershed. That is the most commonly theorized solution to this problem. The other is that the bedrock is actually granite. If you take a piece of granite into the laboratory and grind it and expose it to water, you will get a lot of calcium off. There will be much more calcium than you predict from the ratios in the bedrock, and that is because calcium weathers very fast if you have a raw surface. The theory is that every winter, fresh rock surfaces are exposed just by freeze-thaw cycles. Those fresh surfaces, when exposed to water, lose their calcium much faster than they lose anything else. That is consistent with the pattern that we saw in all of these sites, and it is indistinguishable from a calcite source.

Q (AUDIENCE) Would you remind us of the way that ANC is actually determined experimentally?

A (DR. STODDARD) Take a sample of water, add measured amounts of an acid, usually sulfuric acid, and measure the pH change. The pH undergoes a predictable curvilinear response to the addition of acid, and the location of inflection points along that curve determines how much alkalinity you started with. The quantity of acid you have to add in order to get to those inflection points determines the alkalinity or the ANC.

Q (AUDIENCE) Two minor questions. Are any of these waters influenced to any degree by other cations and bicarbonates in the actual titration? That is to say, is there any evidence for any significant concentration of organic acid ions?

A (DR. STODDARD) It is a good question and one that is almost impossible to answer because of the dilute nature of the waters. Analytically, we are pressed right up to the edge of being able to measure the inorganic ions in the samples. The technology for doing the organic analyses lags behind the inorganic chemistry. As a result, all we can say is that we know that the amounts of dissolved organic carbon in these samples are very low. That is not a completely satisfactory answer, because the concentrations of everything else are also very low, and what we are trying to do is compare the relative importance of two very small numbers. It appears from the charge balances, the balances between cations and anions, for the inorganic chemistry that there cannot be a large influence of organic acids, but we do not really know.

Q (AUDIENCE) The reason I asked that question is that there seems to be an almost magical resistance to penetrating the ANC equals 0 barrier. From a chemical point of view, I would imagine that should not be a rare crossing, because the hydration curve is relatively steep in that region and should be about as likely to have plus or minus 2 or 3 or 4 units of ANC. I follow your logic that you are looking at a titration, and the water you are titrating has almost no buffering at that point, that is the reason the titration is possible. That is why I was curious if, unbeknownst to us, there was some hidden variable that was appearing in these titrations. The first thing I could think of would be organic acid ions. The only other thing I could think of is fine particles, fine particles that are serving as proton donors.

You have brought up a curious point. I think the first thing we have done over the last 10 years is to destroy the idea that pH is really a consequential variable. Now I think the second thing might be that we look more critically at ANC. It appears to me like the Sierra Nevada research and policy analysis is going to demand better science on acid-base chemistry than in just about any other place in the world.

(DR. STODDARD) I would agree with that. The other thing to remember is that when you perform an ANC titration, organic acids are included in that. What you actually measure when you measure ANC is the sum of the cations minus some of the anions.

(AUDIENCE) But not all of them.

(DR. STODDARD) Well, it depends on the pH, but in fact, some of these organic acids are actually contributing ANC; they are not acidic at all. ANC is a composite measure of something we do not really have a perfect handle on. but it is the best one we presently have.

Q (AUDIENCE) You mentioned that pH is relevant to toxic effect, but you did not show any pH values. I am wondering what you saw relative to those ANC valleys you got at snowmelt. You seem to have some with summer rains as well.

A (DR. STODDARD) I did not show any pH plots, because, contrary to what is commonly thought, pH is probably the most difficult of all of those measurements to make well. We can on any given day go out and measure the pH on the same sample with different machines and different technicians and come up with an answer that is, in some cases, plus or minus half a pH unit. The lowest pH values we measured at High Lake were around 5.4. You can debate a lot about what is a threshold value for significant biological effects, but 5.5 is in the upper range of what is commonly used, and 5.0 is in the lower range. We are verging on the boundary of where biological pH effects might start to occur. That happened in only one sample out of thousands.

(AUDIENCE) With the nitrate peaks at their various points in snowmelt, where do you think our nitrate is coming from?

(DR. STODDARD) It is very easy to conclude that nitrate comes from the snow. In the lakes where we know there is a sulfur source in the watershed, the peak in sulfate occurs at the same time as the peak in nitrate. This certainly leads you to start thinking about whether this is nitrate that is stored in the watershed, and we are seeing it come out. I am gradually beginning to think there may be a pool of nitrate that sits at the bottom of these talus piles over the course of the winter. It sits there and mineralizes in the watershed. The ultimate source of that nitrogen is probably deposition, but as it falls and melts, it gets incorporated into organic matter in some fashion. In the wintertime that organic matter mineralizes and creates that pool of nitrate that is waiting to flush out. That is what happens everywhere else in the world. I do not know why we would expect it not to happen in the Sierra Nevada, except that we have this sort of naive view that Sierra Nevada watersheds are made of bedrock and not soil.

(AUDIENCE) We made a snowmelt collector that is essentially a bottle with the top cut off, halfway buried in the soil. Under that is a collection bottle buried deeper and the lines are run up to the top on a pole. When we collected snowmelt last winter, the nitrate was coming straight out the of the snowpack, not out of the soil.

(DR. STODDARD) It undoubtedly does come out the snowpack. The question is, what happens when it reaches the base of the snowpack? It is still a long way from the lake, and does it ever get to it? Without using isotope tracers, that is not a question we are going to answer right now. The jury is still out.

(AUDIENCE) At least from my observation, I do not see that it is coming out of the soil. It is going through the soil, but it seems to be coming out of the snowpack.

(DR. STODDARD) Ultimately, it has to come from the snowpack. That is really the only significant source of nitrogen in these watersheds, but the question is whether it goes through some nitrogen cycle one or two times before we see it coming out during snowmelt. It could be enriched in such a way that it is clear that it has gone through a cycle maybe once, or twice. It may cycle its way down to a stream over a short time in a geologic time frame. Nonetheless, it could be significant enough to cause some difference in the isotopes.

(AUDIENCE) So there is a nitrogen cycle for sure, but the fact that the snowmelt nitrate and this stream nitrate occur coincidentally would suggest that at least some of the nitrate goes straight through the system, without any contribution from flow through the soil.

(DR. STODDARD) Dale, I do not have an answer for that. I can tell you that in the Rockies, which are not necessarily equivalent to the Sierra Nevada, you cannot balance the nitrate budget without coming up with some watershed storage of nitrate. No, not a sink, a source. The nitrate concentrations in the Loch Vale watershed during snowmelt are up around 50 micro equivalents. There is not enough nitrate in the snowpack to account for that. You have got to have a watershed source at least over the short-term. On an annual basis, they balance pretty well, but if you start looking at the snowmelt period, they do not.

(AUDIENCE) I do not want to delay any of this too long, but you're saying there is too much nitrate coming out of snowmelt; you cannot find it in the snowpack itself?

(DR. STODDARD) That is right, it's coming out of runoff, but not necessarily snowmelt.

Figure 1

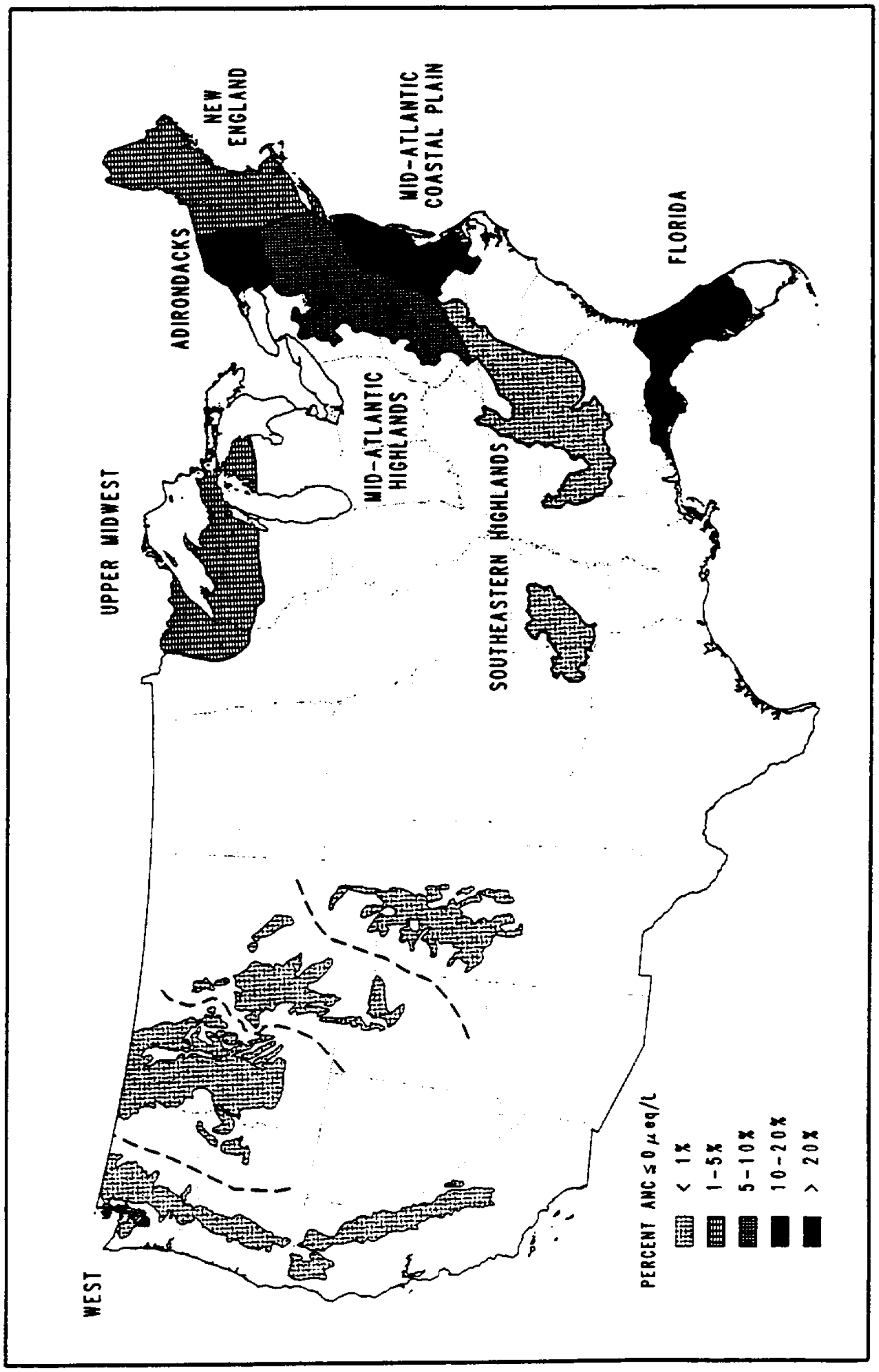

WEST
UPPER MIDWEST
ADIRONDACKS
NEW ENGLAND
MID-ATLANTIC COASTAL PLAIN
MID-ATLANTIC HIGHLANDS
SOUTHEASTERN HIGHLANDS
FLORIDA
PERCENT ANC ≤ 0 μeq/L
< 1%
1-5%
5-10%
10-20%
> 20%

Figure 2

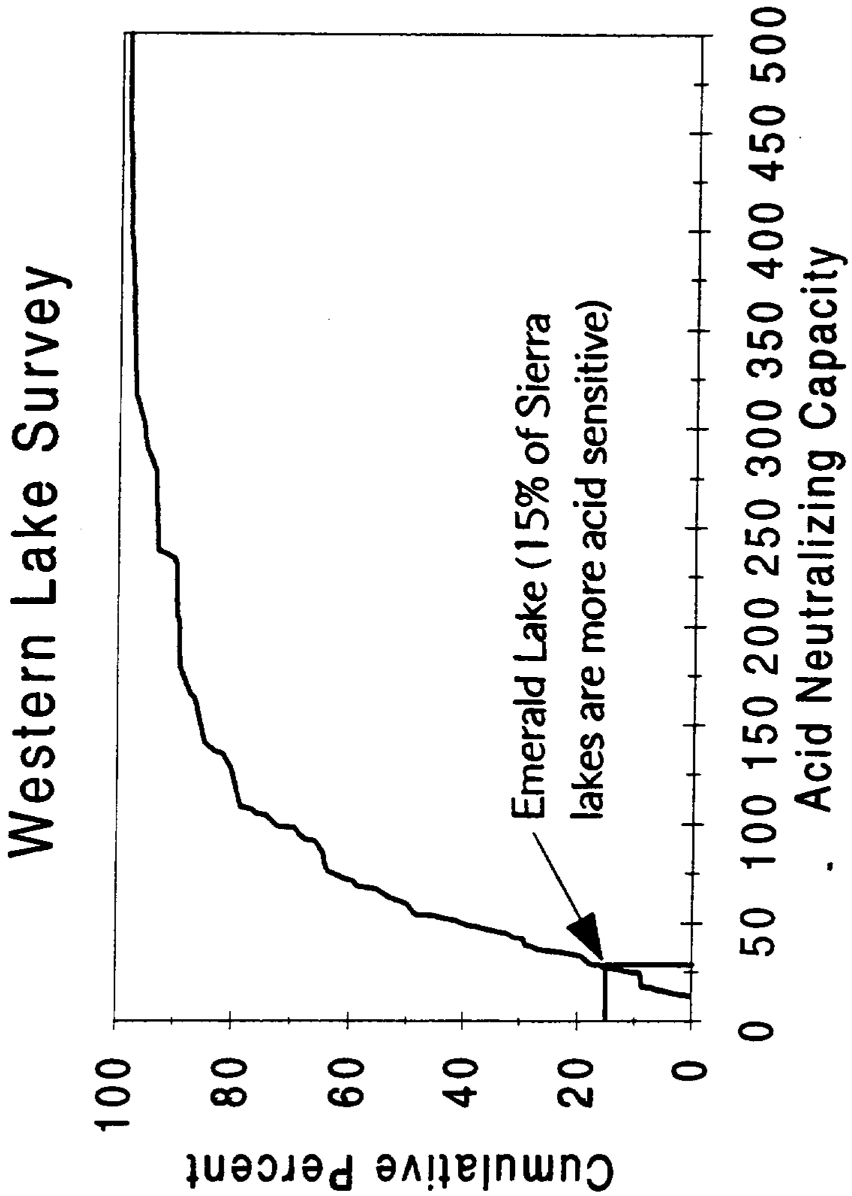

Western Lake Survey
Cumulative Percent
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Acid Neutralizing Capacity
Emerald Lake (15% of Sierra lakes are more acid sensitive)

Figure 3

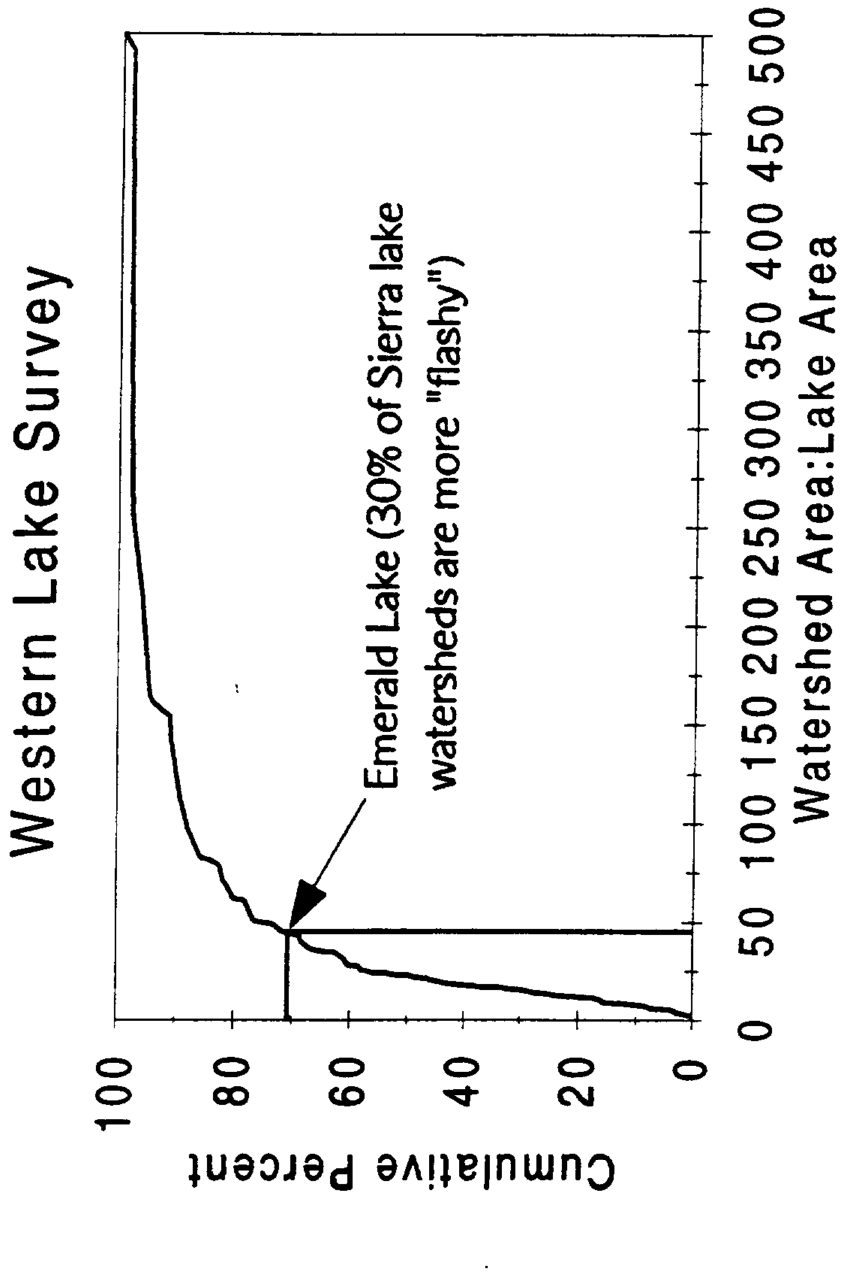

Western Lake Survey
Emerald Lake (30% of Sierra lake watersheds are more "flashy")
Cumulative Percent
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Watershed Area:Lake Area

Figure 4

	ANC $(\mu eq \cdot L^{-1})$	Latitude	Longitude	Watershed Area (ha)	Lake Area (ha)	Location
POND ABOVE RUBY	**27.2**	**37-24'30"**	**118-46'16"**	**224.7**	**0.16**	**John Muir**
ROCK CREEK #3	**1.0**			**16.9**	**1.00**	**John Muir**
ABOVE SAM MACK	19.0	37-06'34"	118-31'12"	145.8	1.04	
COW MEADOW LAKE	52.4	38-08'35"	119-44'10"	3965.5	10.28	
WLS NONAME #16	25.1	37-42'15"	119-17'15"	1020.0	6.30	
PARKER PASS	5.2	37-50'08"	119-12'35"	72.6	2.78	Yosemite
MARBLE FORK #2	**26.4**			**74.4**	**0.50**	**Sequoia**
MOSQUITO #3	37.0	36-25'09"	118-37'16"	132.3	0.78	Mineral King
PARSONS POND	**19.3**	**36-35'01"**	**118-40'00"**	**38.3**	**0.48**	**Sequoia**
ARCTIC #6	40.0	36-35'14"	118-17'44"	84.4	0.52	
ROPI LAKE	17.9	38-50'22"	120-07'49"	603.0	8.50	
MARBLE FORK #3	**24.6**			**46.5**	**0.50**	**Sequoia**
POND ABOVE GEM	25.3	37-23'03"	118-45'17"	86.5	1.06	John Muir
TREASURE LAKE #2	**20.4**			**177.6**	**2.70**	**John Muir**
DANA	12.4	37-54'35"	119-13'07"	189.1	5.18	Yosemite
GROUSE LAKE	28.8	38-51'28"	120-11'54"	127.0	1.60	
SUMMIT	17.1	37-26'00"	118-46'11"	82.9	1.81	John Muir
TABLE MEADOWS #2	**40.8**	**36-36'25"**	**118-39'30"**	**58.5**	**0.55**	**Sequoia**
MILLS	**29.7**	**37-24'07"**	**118-46'01"**	**177.2**	**2.38**	**John Muir**
POND ABOVE SPULLER	**43.6**	**37-56'42"**	**119-17'06"**	**37.6**	**0.35**	**Hall RNA**
SUMMIT LAKE CAFG	41.3	37-14'00"	118-41'00"	109.2	3.14	
ROCKBOUND LAKE	71.8	38-59'53"	120-14'15"	8094.0	48.90	
SMEDBURG	31.5	38-00'49"	119-28'58"	1189.4	17.15	
EDIZA	43.0	37-41'04"	119-09'55"	944.8	10.10	
UPPER TREASURE	29.3	37-23'13"	118-46'00"	174.4	2.95	John Muir
LAKE VERNON	53.6	38-00'50"	119-43'22"	2960.0	26.10	
ISLAND	44.0	37-42'31"	119-10'00"	1195.5	12.95	
KEARSARGE E11040	98.0	36-46'10"	118-23'04"	211.1	1.04	
NELSON	35.1	37-47'03"	119-22'31"	354.1	5.63	John Muir
DADE	23.6	37-22'47"	118-45'42"	129.5	3.11	John Muir
GRANITE (FAR NORTH)	19.5	38-39'00"	120-05'00"	182.1	5.30	
TABLELAND	17.0			41.1	1.38	Sequoia
EMERALD	25.6	36-35'49"	118-40'30"	120.0	2.72	Sequoia

Figure 5

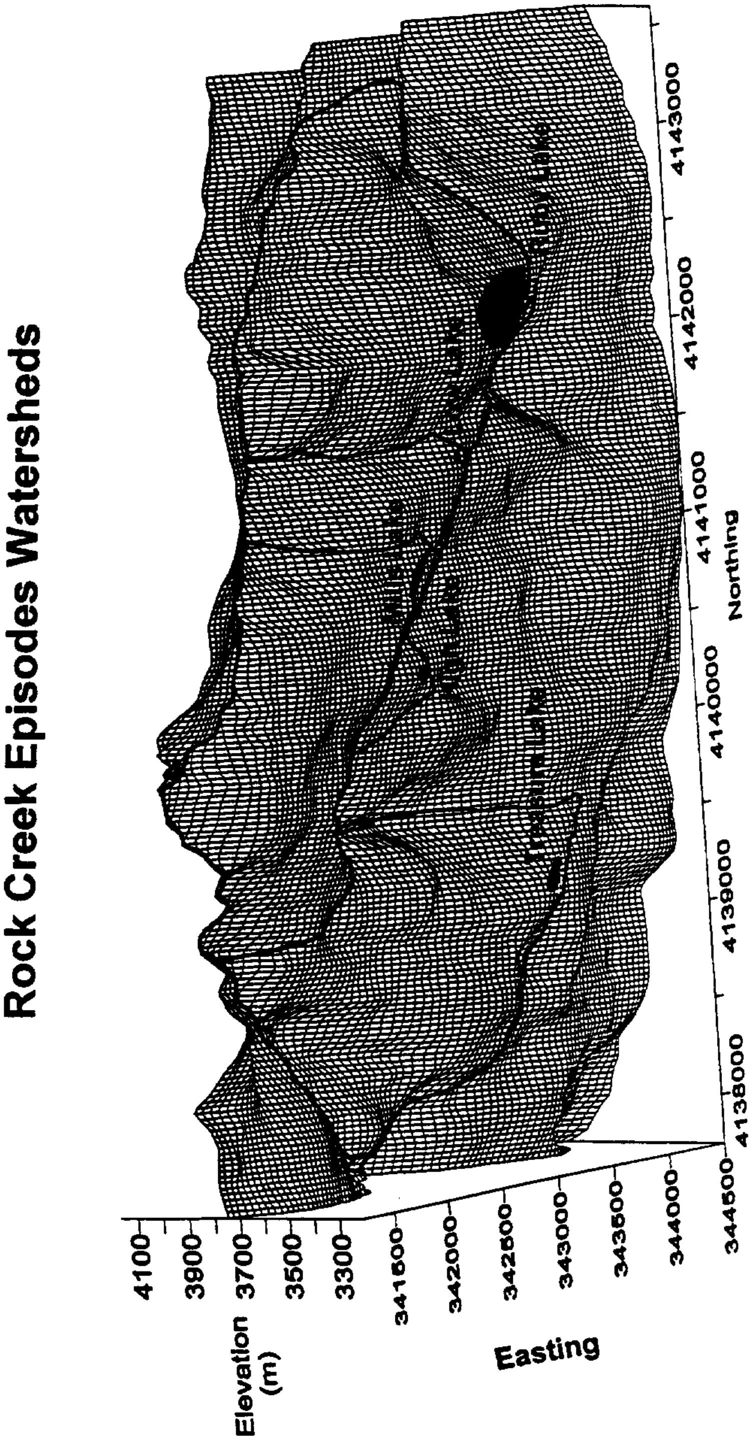
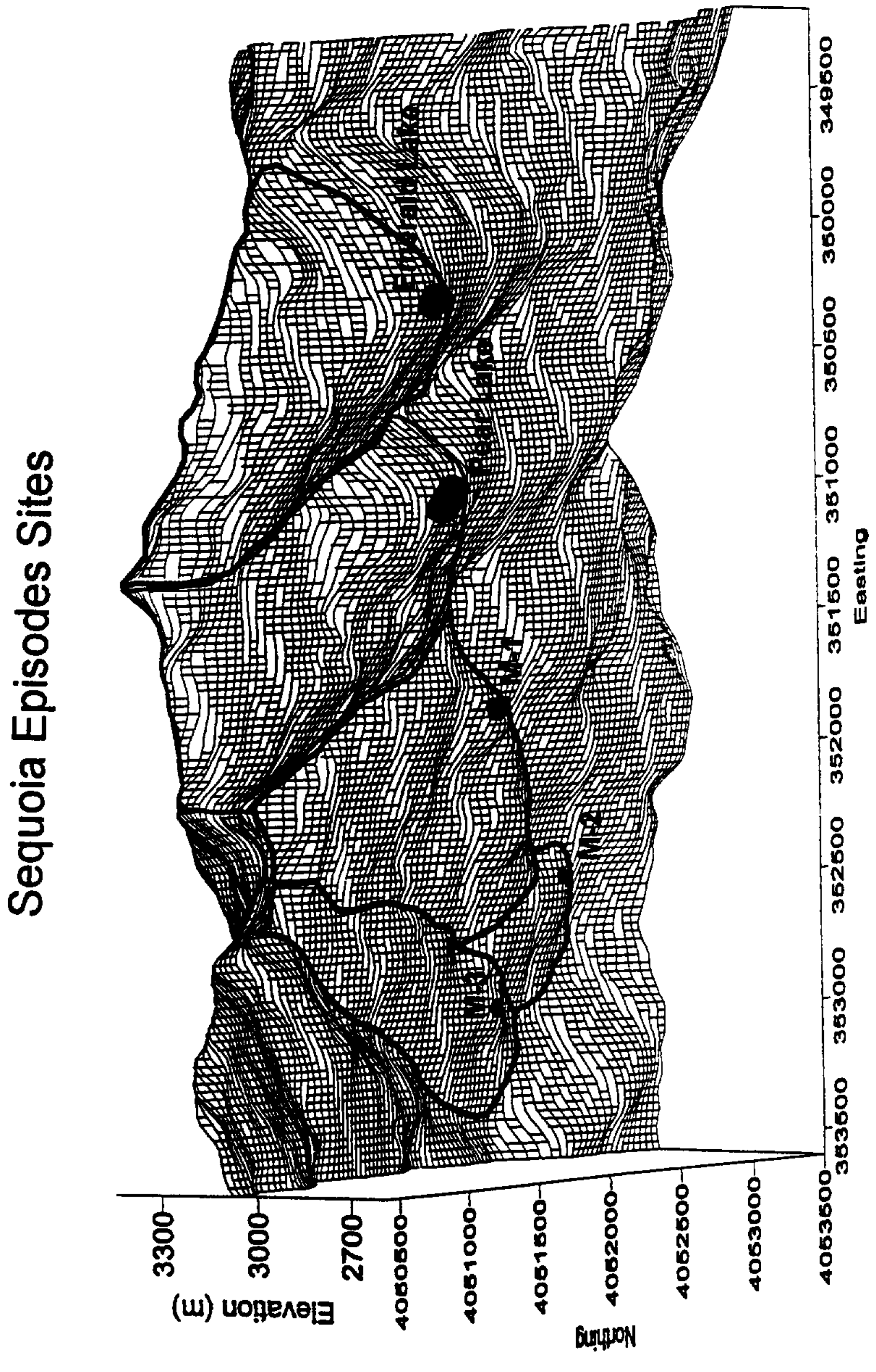

Rock Creek Episodes Watersheds
Elevation (m)
4100
3900
3700
3500
3300
Easting
341500
342000
342500
343000
343500
344000
344500
Northing
4138000
4139000
4140000
4141000
4142000
4143000

Figure 6



Sequoia Episodes Sites
Emerald Lake
Pear Lake
M-1
M-2
M-3
Elevation (m)
3300
3000
2700
Northing
4050500
4051000
4051500
4052000
4052500
4053000
4053500
Easting
349500
350000
350500
351000
351500
352000
352500
353000
353500

Figure 7

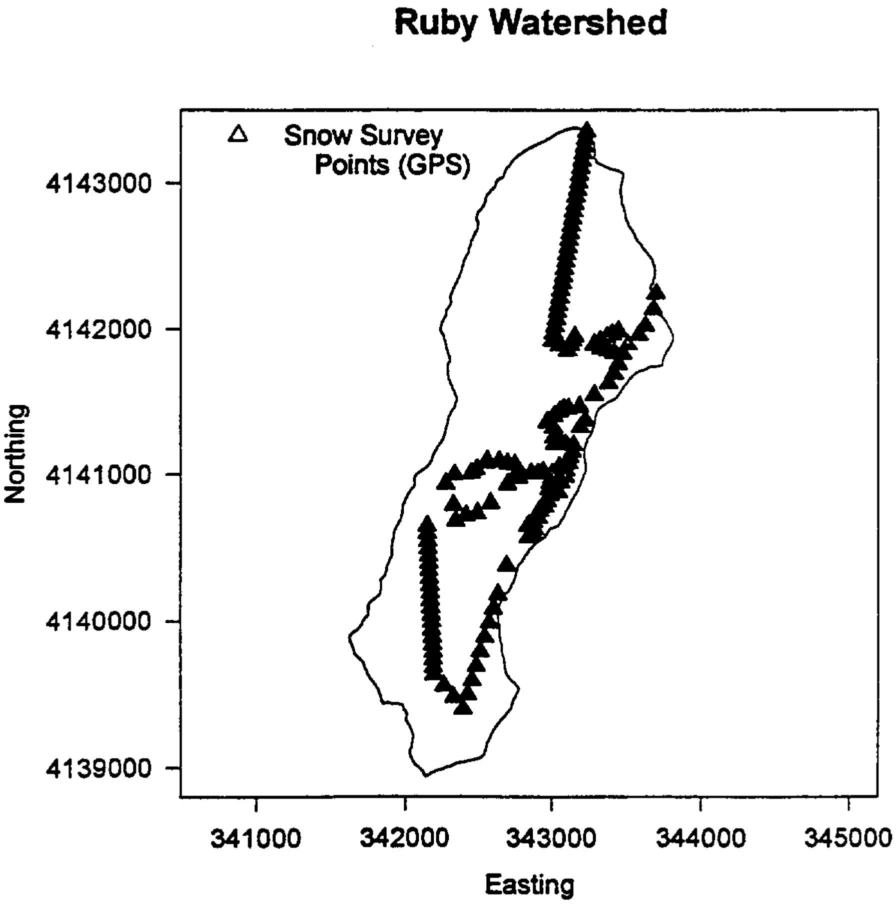
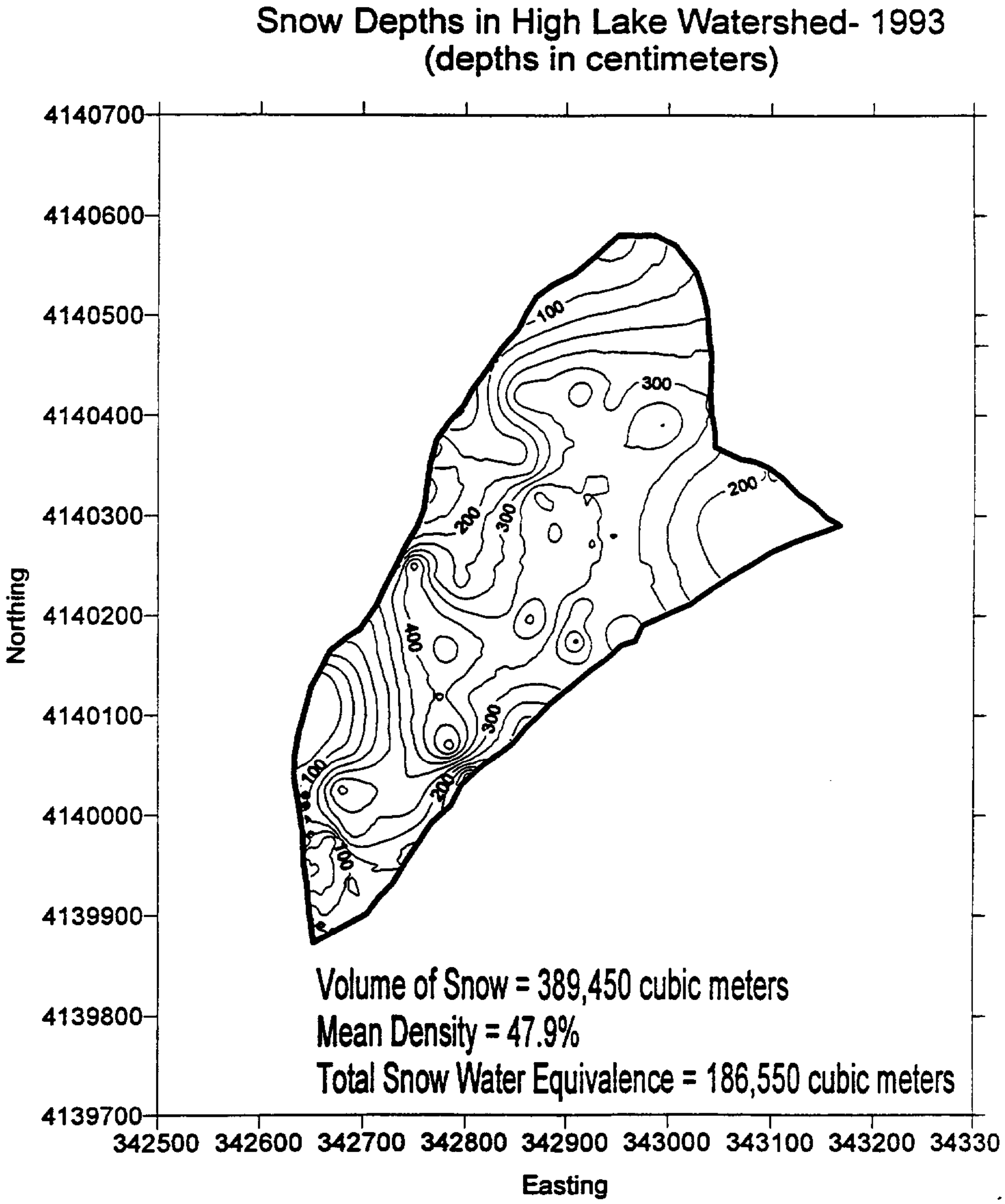

Ruby Watershed
△ Snow Survey Points (GPS)
4143000
4142000
4141000
4140000
4139000
Northing
341000
342000
343000
344000
345000
Easting

Figure 8

Figure 9


Snow Depths in High Lake Watershed- 1993
(depths in centimeters)

Volume of Snow = 389,450 cubic meters
Mean Density = 47.9%
Total Snow Water Equivalence = 186,550 cubic meters

Figure 10

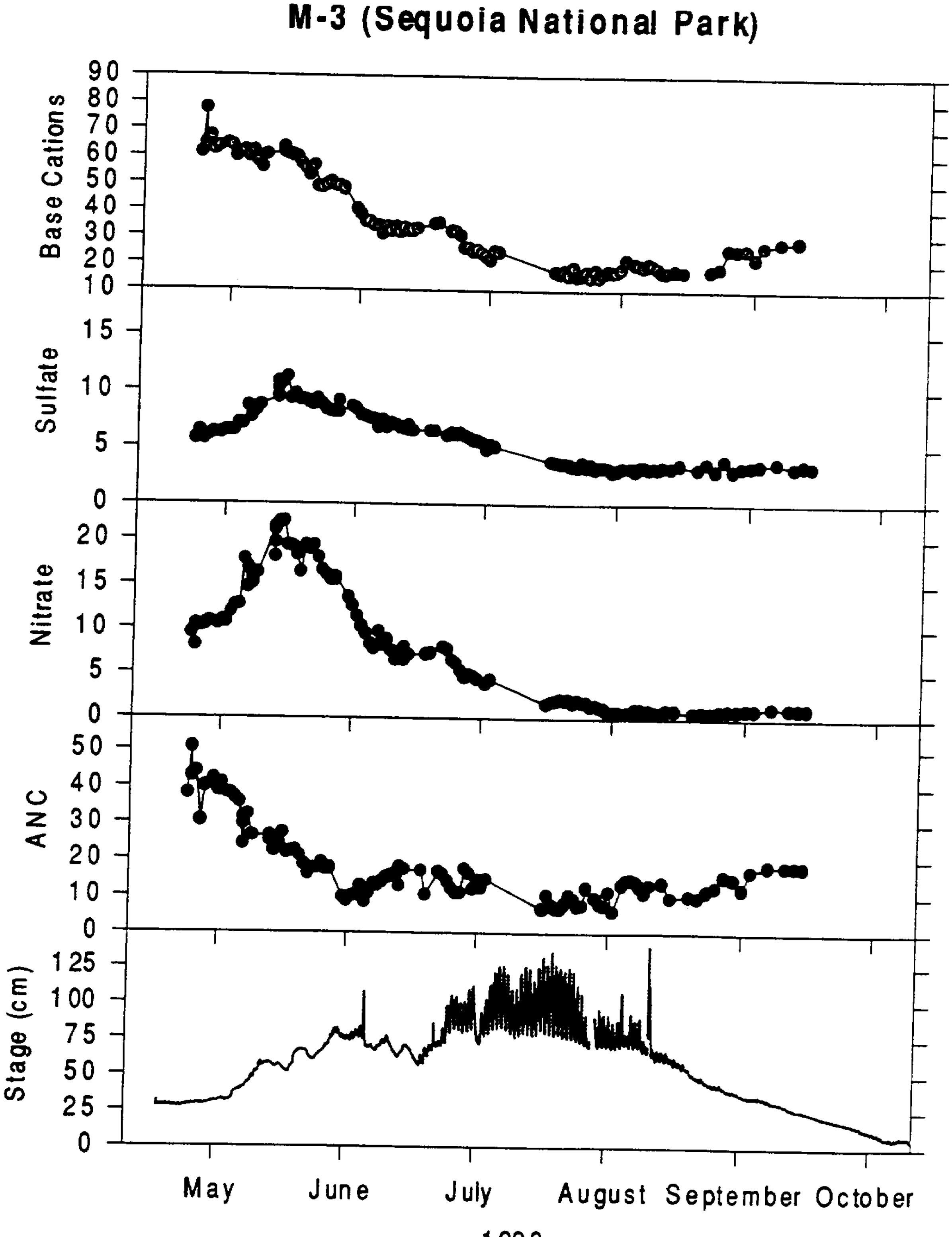

M-3 (Sequoia National Park)
Base Cations
90
80
70
60
50
40
30
20
10
Sulfate
15
10
5
0
Nitrate
20
15
10
5
0
ANC
50
40
30
20
10
0
Stage (cm)
125
100
75
50
25
0
May
June
July
August
September
October
1993

Figure 11

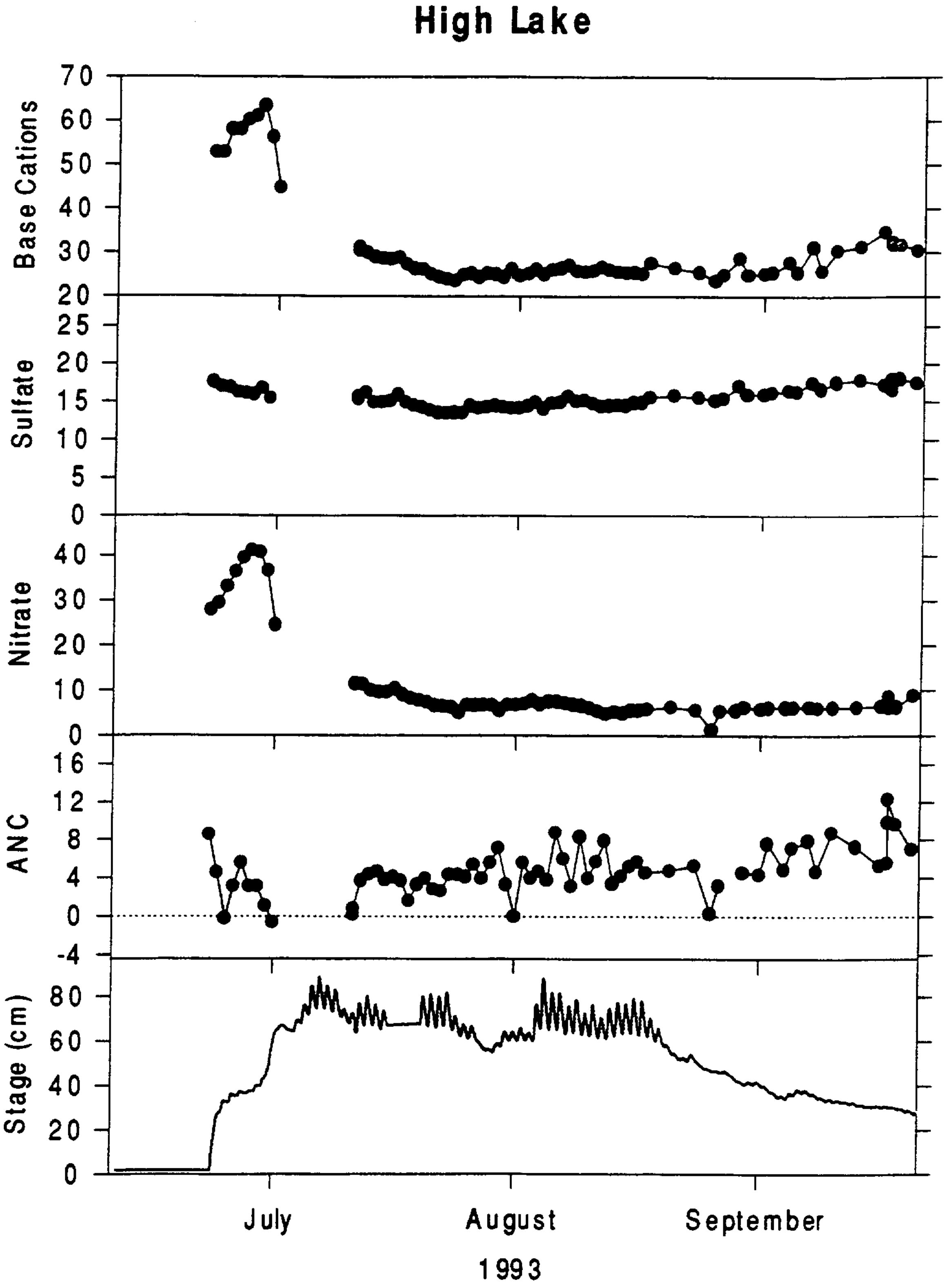

High Lake
Base Cations
70
60
50
40
30
20
Sulfate
25
20
15
10
5
0
Nitrate
40
30
20
10
0
ANC
16
12
8
4
0
-4
Stage (cm)
80
60
40
20
0
July
August
September
1993

Figure 12

High Lake

Change in ANC Attributable to:			Calculated Change	Measured Change
Base Cations	Nitrate	Sulfate	in ANC	in ANC
+ 7	-12	+ 1	- 4	- 5
(35%)	(60%)	(5%)		

M- 3

Change in ANC Attributable to:			Calculated Change	Measured Change
Base Cations	Nitrate	Sulfate	in ANC	in ANC
- 47	+ 9	+ 7	- 31	- 33
(75%)	(14%)	(11%)		

Figure 13

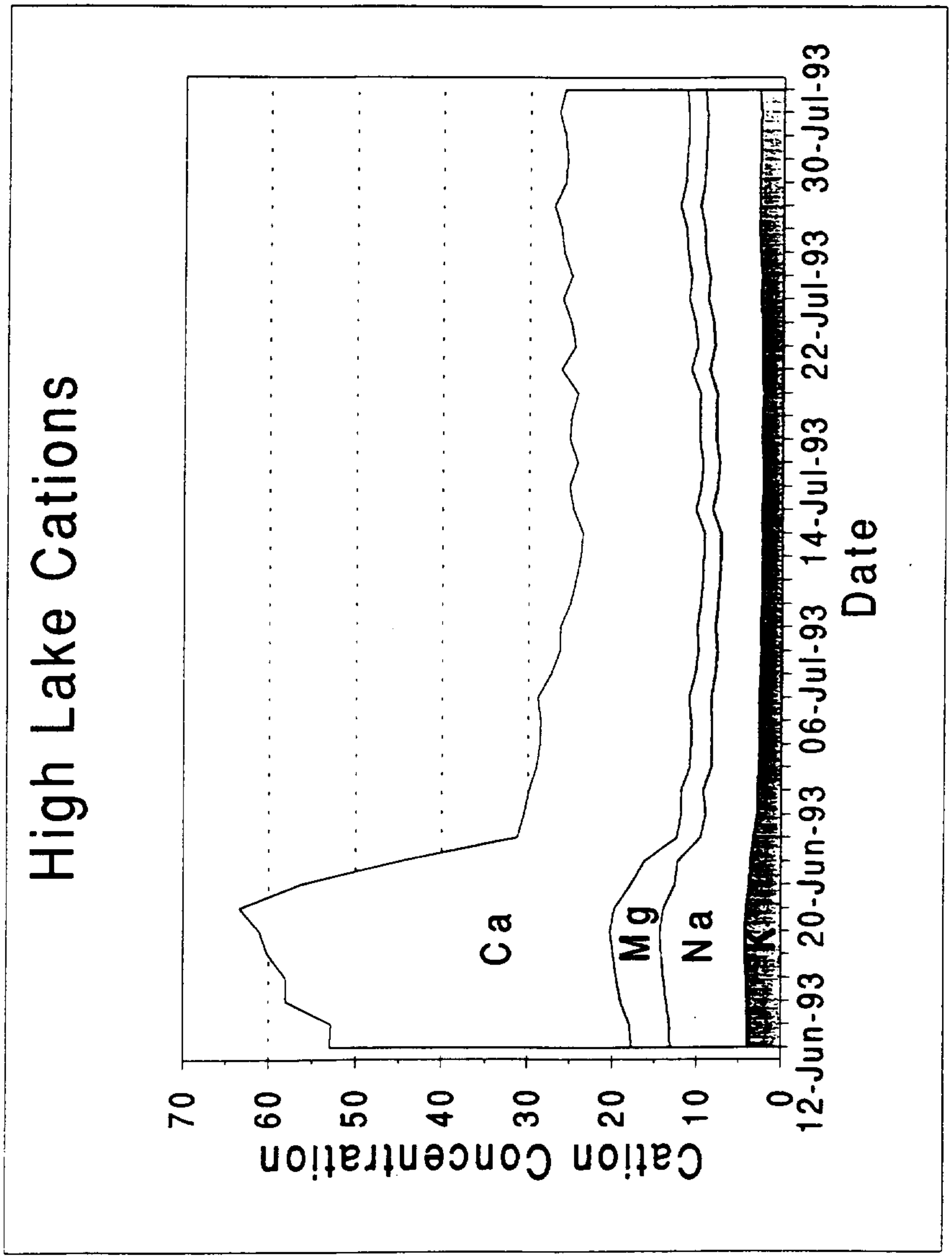

High Lake Cations
Cation Concentration
70
60
50
40
30
20
10
0
12-Jun-93
20-Jun-93
06-Jul-93
14-Jul-93
22-Jul-93
30-Jul-93
Date
Ca
Mg
Na
K

Figure 14

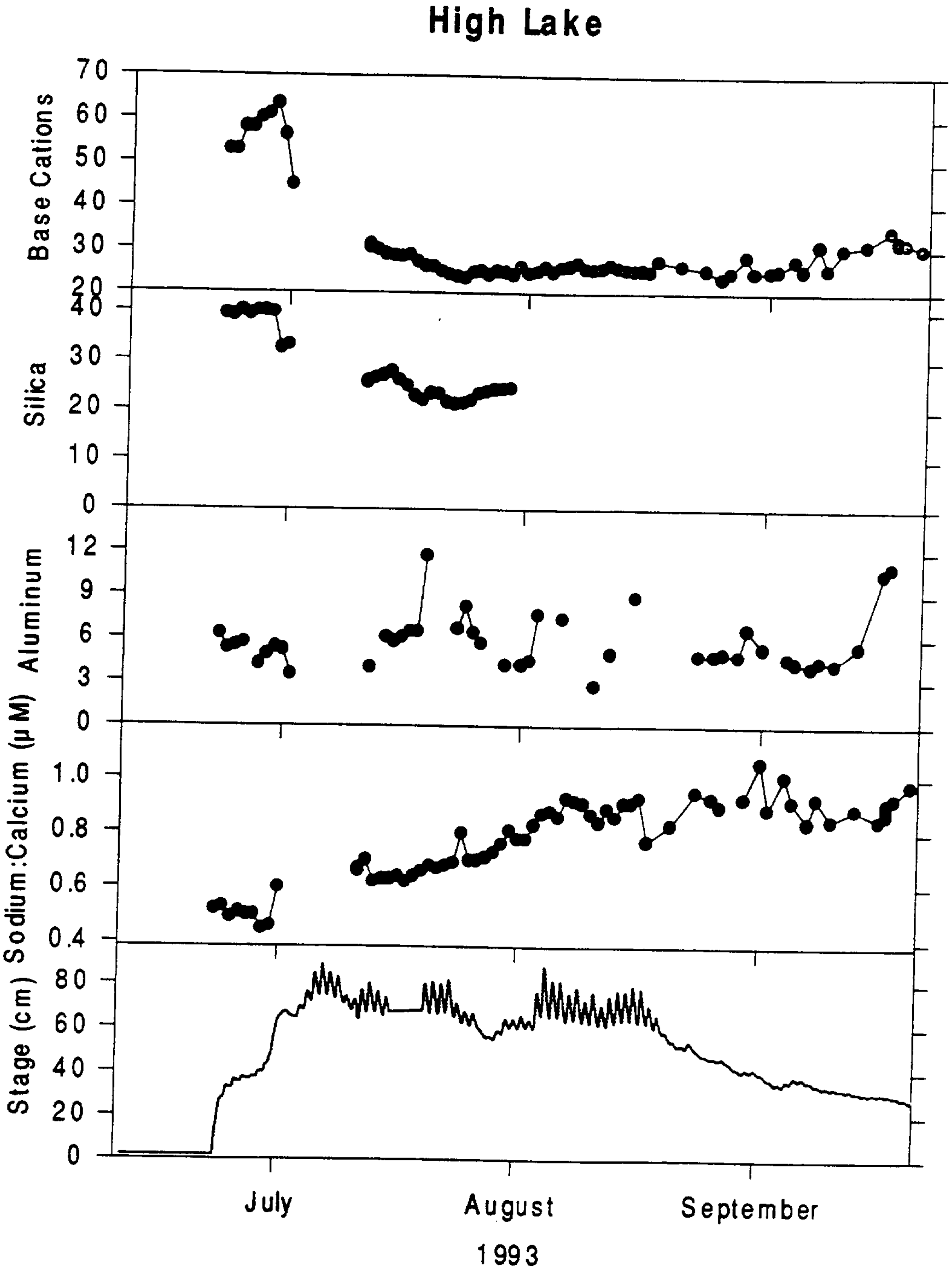
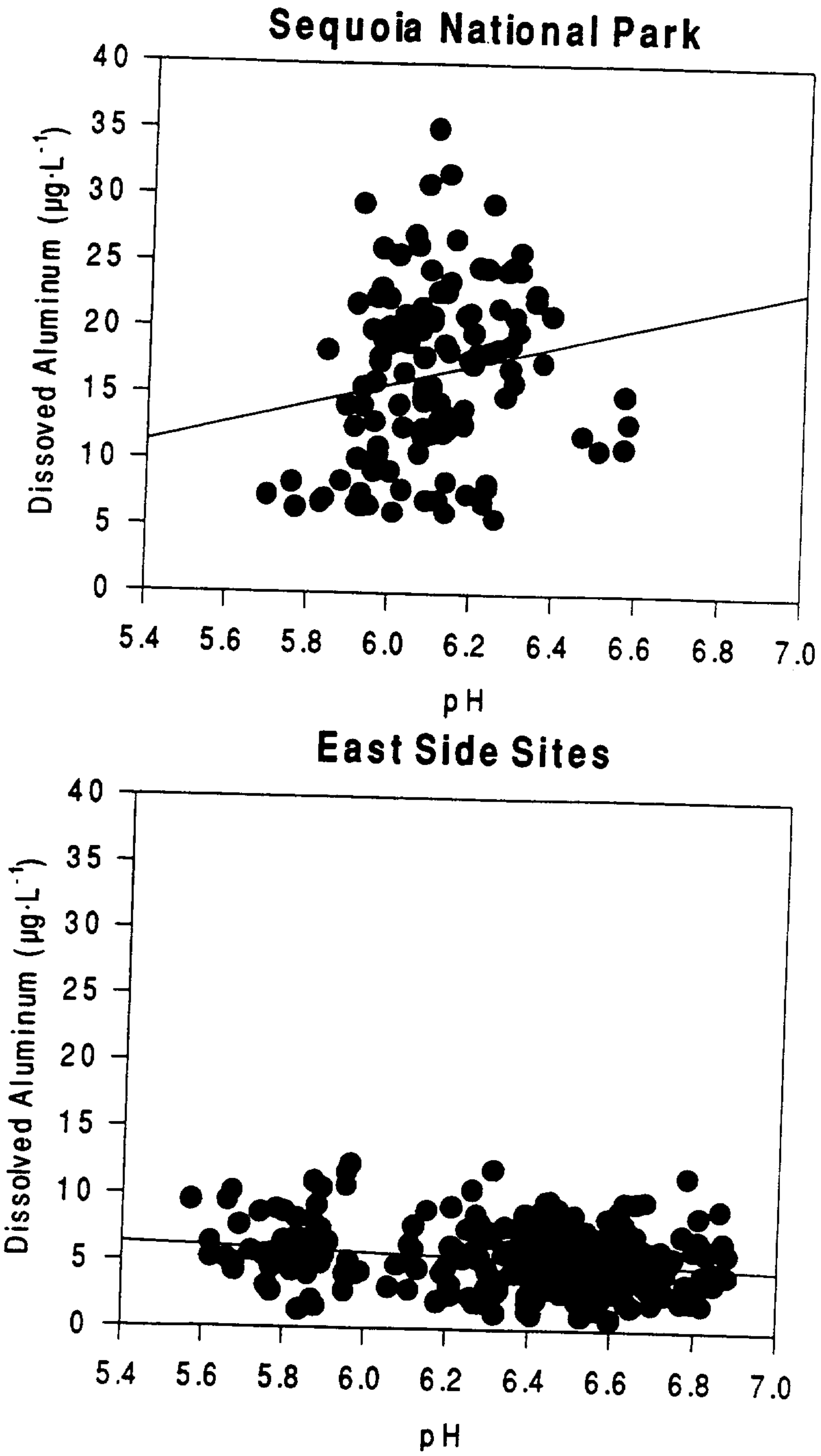

High Lake
Base Cations
70
60
50
40
30
20
Silica
40
30
20
10
0
Aluminum
12
9
6
3
0
Sodium:Calcium (µM)
1.0
0.8
0.6
0.4
Stage (cm)
80
60
40
20
0
July
August
September
1993

Figure 15



Sequoia National Park
Dissoved Aluminum (μg·L^{-1})
0
5
10
15
20
25
30
35
40
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
pH
East Side Sites
Dissolved Aluminum (μg·L^{-1})
0
5
10
15
20
25
30
35
40
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
pH

Figure 16

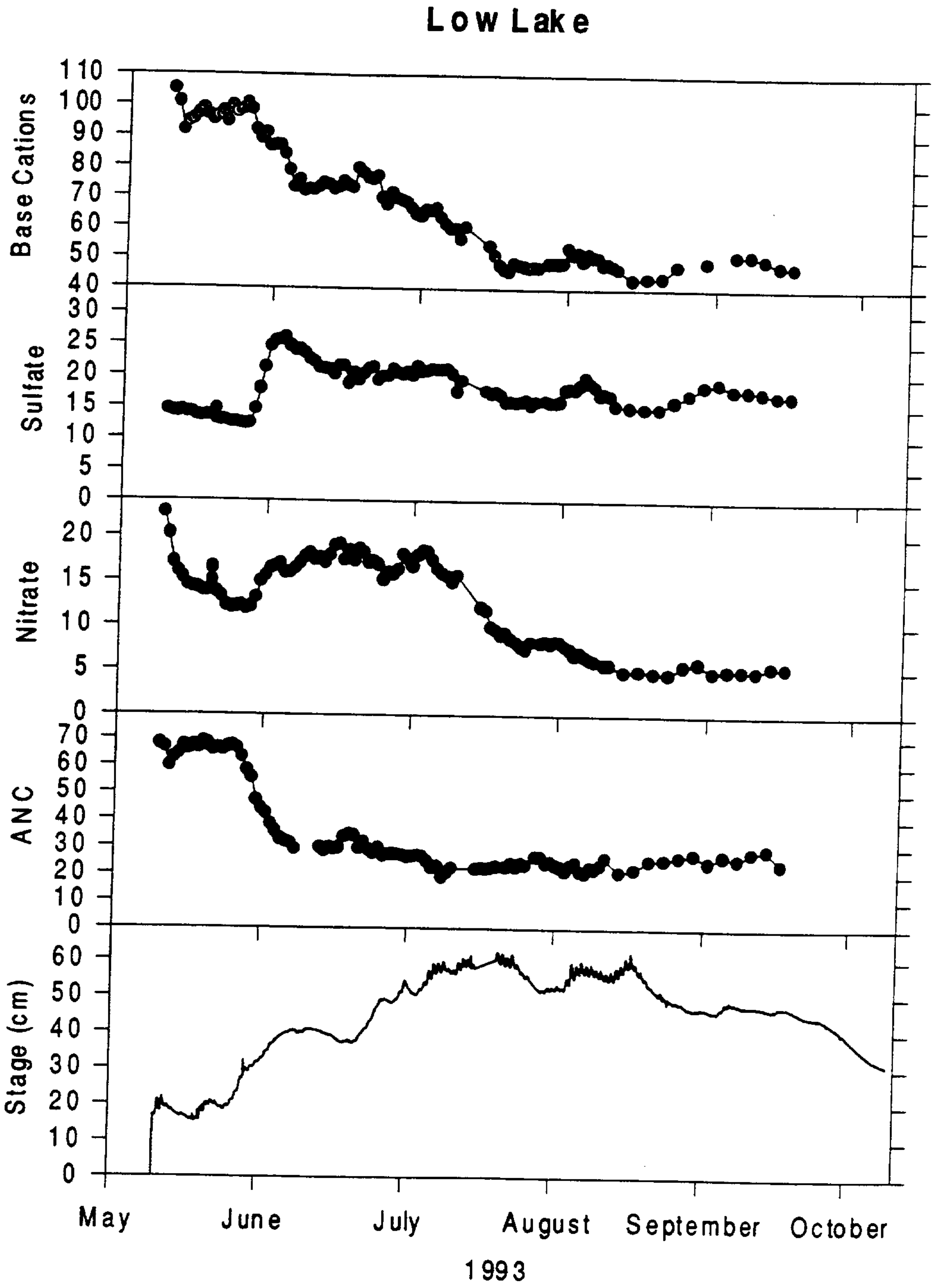

Low Lake
Base Cations
110
100
90
80
70
60
50
40
Sulfate
30
25
20
15
10
5
0
Nitrate
20
15
10
5
0
ANC
70
60
50
40
30
20
10
0
Stage (cm)
60
50
40
30
20
10
0
May
June
July
August
September
October
1993

Figure 17

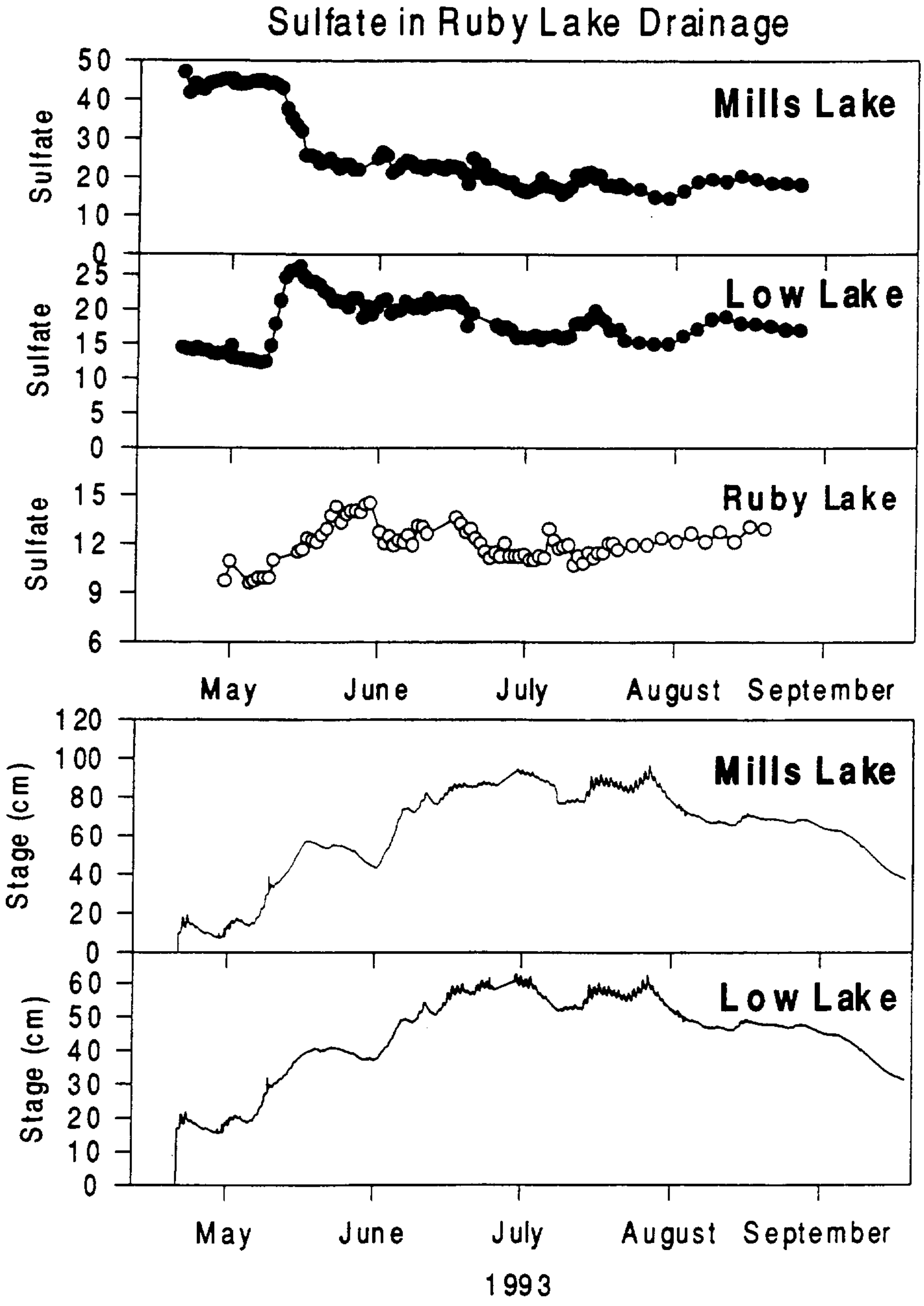

Sulfate in Ruby Lake Drainage
Mills Lake
Low Lake
Ruby Lake
Sulfate
50
40
30
20
10
0
25
20
15
10
5
0
15
12
9
6
May
June
July
August
September
Mills Lake
Low Lake
Stage (cm)
120
100
80
60
40
20
0
60
50
40
30
20
10
0
May
June
July
August
September
1993

Figure 18

Conclusions

- Acidification during snowmelt is likely to be a rare event in the Sierra
- Most lakes undergo a large decrease in ANC during snowmelt, which is largely (75%) attributable to base cation dilution
- Pulses of acid anions, particularly nitrate, are ubiquitous, but rarely large enough to balance base cation concentrations
- When acidification does occur, it occurs during the very early phases of snowmelt, and is the result of nitrate pulses being larger than base cation pulses
- Toxic effects attributable to Aluminum and pH are likely to be very minimal. Aluminum appears to act like other weathering products (e.g., base cations and silica), and is maximal at base flow

DR. STEPHEN BROWN, Moderator

The next speaker, Dr. Roger Bales, from the University of Arizona, will be presenting "Integrated Hydrochemical Modeling Applied to the Emerald Lake Watershed".

5. Integrated Hydrochemical Modeling Applied to the Emerald Lake Watershed. Dr. Roger Bales, University of Arizona.

DR. ROGER BALES, University of Arizona

I want to give a little background on how we got started on this project and where we are now, (Fig. 1). Although I work with integrated modeling, I began under the deposition program, and we were working in the time period, 1987 through 1989. We have since continued that work under other programs, the USGS Water Resource Research Program and currently under NASA's Earth Observing System Program. It has been tied in with remote sensing and much broader global and regional studies of alpine areas now. This latter work (Fig. 2) is in cooperation with John Melack at UC Santa Barbara, Kathy Tonnessen from the National Park Service, and also Mark Williams at Colorado. We have developed the alpine hydrochemical model during the five year period, 1987 through 1992, and applications of a workable model to watersheds only began last year.

Figure 3 is taken from our NASA statement of objectives. I will focus today on the solute and biogeochemical transformation in the Emerald Lake watershed, but notice also that some of the general issues we are studying are the role of the snowpack and alpine hydrology. Using remote sensing data, we are studying to spatial distribution of snow depth and water equivalence. From the ground, we are studying chemical content, the melting of the snowpack, and run off, because in order to do chemical balances, we need water balances first. We know there are various hydrochemical laws that have been applied to watersheds. The motivation for developing the current alpine hydrochemical model (Fig. 4) was that other models would not do what we needed to do in the Emerald Lake watershed or other watersheds in the Sierra Nevada where the hydrology is driven by snow and snowmelt. We found it unworkable to modify existing models, so we then developed the current set of algorithms. The alpine hydrochemical model (Fig. 5) is serving as a research tool to identify the processes that are important, and when changes due to these processes are occurring in the watershed. It is an assist in interpreting the to identify field monitoring and process level research and then planning future research. I will show how we are starting to use it as a predictive model for scenario analysis and how a watershed responds to changing input conditions. The alpine hydrochemical model is really an integrated set of algorithms that does water balance and chemical balance. There are equations to describe the hydrologic and chemical processes in the watersheds.

Figure 6 is a schematic and lists some of the compartments that would be within the soil subunit.

We can divide the watershed into various subunits. In this case, I lumped things into soil versus stream and lake (Fig. 7). We define a soil subunit, and that can also include rock. We have processes or compartments where we track the mass balance (Fig. 8) and chemical changes (Fig. 9). We have canopy and litter interception of water and the chemicals included in it. We have the snowpack, soil, multiple horizons or single horizon, horizontal flow in the soil, surface run off, vertical flow in the soil, and the litter either beneath the snowpack or not beneath the snowpack. The stream and lake subunits are a little simpler in that we have stream, lake, and epilimnion that mixes with the stream, a lower hypolimnion that does not mix with the stream, and ice and snow on top of the lake as well. These can be defined by the user of the model in terms of the number of subunits, the number of compartments and in that way we build a flexible model. For the application to the Emerald Lake watershed, we include the all important soil properties. Figure 10 is a summary from one of Aaron Brown's and the UC Riverside group reports. We have essentially used all of the field process research and monitoring work that went on during the time period of the 80's in our integrated modeling. I will not acknowledge each person whose data we are using but just the most pertinent at Emerald Lake watershed.

For the work I will present today, all the soils are lumped together into a single soil type, and then we have talus (Fig. 11). It quickly became apparent to us when we started doing this modeling that there was soil under the talus. There had to be more soil out there in the watershed than was indicated by the field survey, so we applied the same soil depth under the talus as was not under the talus. There is also exposed rock which is the darkest area in figure 11. We considered having rock as relatively unreactive component, but that certainly is something that could bear revisiting.

Let me quickly outline how we are treated the different processes and compartment subunits in the lake. Water storage in the snow covered area was a very important prompt for driving the hydrology. At a minimum, we need changes in the snow covered area for the watershed, and fortunately these were generally available either from the photographs or from remote sensing data. We need time series of snow covered area, then field surveys for snow in which water equivalent is in the watershed. Soil depth and then evapotranspiration, for example, depended on the soil properties as did water flow through the soil, so those end up as parameters that had to be estimated. A one day time step was used for the overall material balance, although some of the processes were modeled at a smaller than daily time step in order to capture water flow through soil, for example. For some of these data, like potential evaporation and actual evapotranspiration, I have indicated the type of function we used. This model is modular. For example, John Melack mentioned that further work is being done by one of his students on the evaporation and evapotranspiration estimates. We can easily incorporate that. Routing of water in the watershed ends up being important to the result, that is, the fraction of snow melt that goes into the soil versus what runs from rock directly into the stream. I will show some results of that (Fig. 12).

The routing we used is empirical.

Moving from the hydrological to the chemical material balance, solute released from the snowpack, that is the loading of the chemicals from the snowpack to the soil and then to the stream, is quite important. Figure 13 indicates the concentration of the chemical species coming out. We used an exponential function, which is empirical, but it was backed up by a physical model and data to estimate the parameters. Aqueous reaction and equilibrium chemistry parameters end up equal to the equilibrium constant. Similarly, for ion exchange of percent based saturation, from the work with the UC Riverside group, the parameters end up as important initial conditions with regard to ions present in the soil at the beginning. Sulfate is absorbed and attenuated in the soil.

As we were going through the modeling, we found we needed a source of labile silica. Silica concentrations were sometimes varying independently of the base cations, so it was not a stoichiometric balance. The weathering stoichiometry was not apparent on a sample-to-sample basis, so we also put silica in as an absorption reaction. CO_2 partial pressure in the soil is another important parameter for influencing the ion exchange and how the soil responds to snowpack. Mineral weathering is a kinetic reaction, but one that basically replaces the ion exchange capacity in the soil. For nitrogen transformation, the important thing was how much ammonium was important for acid neutralizing capacity. There is quite a bit of ammonium in the snowpack, compared to the organic nitrogen versus nitrate. There were organic acids in the snowpack, and snowfall from John Melack's work, and we have assumed that they were removed in the soil with a 0 order reaction.

For snowmelt modeling, we put together a digital elevation model, because we need spatially distributed snowmelt. We need to know where on these different soil compartments the snowmelt occurred, whether on the rock, on the soil, or on the talus. Insolation was the amount of radiation distributed across the basin, in this case from a high radiation to low radiation, and snow water equivalent was how much water was present. As those go together, a physically based snowmelt model that uses the radiation data was an energy balance model for snowmelt distributed across the watershed. Figure 14 outlines the results of that, and it is fairly easy to model snowmelt on a whole watershed basis.

For the hydrochemical modeling, we first used a lumped parameter application to the Emerald Lake watershed (Fig. 14 and 15). It is lumped in the sense that we lumped all the soil compartments together. We spent quite a bit of time on empirical parameter estimation. We felt this empirical estimation, yielded a physically realistic parameter set when compared with the literature. The lumped parameter application provided an equally good simulation of our calibration and validation years. Figure 16 shows two water years. The water year from October 1, 1985 through the following October 1 is water year 1986, and following that is water year 1987. 1987 was our calibration year. We used these data to fine-tune the parameters that could not be estimated independently. The solid line is the model calculation, the best fit from the empirical parameter estimation. At the bottom is chloride which comes from the snowpack. Chloride showed the ionic pulse from both the data and the model. Nitrate is also from the snowpack but undergoes soil reactions. Calcium was responding to the dilution and responding to hydrogen ions coming out of the snowpack in exchange for calcium in the soil and then the ANC. We were reasonably happy with this fit, especially when it appeared that, on the validation year, we got an even better match between the data and the model, than in 1987. 1987 was the first year of a drought, and one of the worst years on record, while 1986 was very one of the higher years in the record for snow accumulation. These are extremely different years, but a common set of parameters appears to capture the change. There were some analytical problems with chloride that year, so I would not worry too much about the poor match there. The model captured reasonably well the calcium that was coming out of the soil and the acid neutralizing capacity changes. Note that the drop in acid neutralizing capacity in the model was the initiation of snowmelt and the later drop was from the larger amounts of snowmelt which diluted the hydrogen ion of the snowpack and the species that came out of the soil. We did an automatic parameter estimation, we got a slight improvement over the empirical model. It showed us the sensitivity of some of the parameters and processes that we are evaluating.

I listed the response to perturbation for the 1986 and 1987 water years. The perturbations I applied were both to the parameters and to the inputs. First, we looked at the effect of about 30% higher snowmelt rate (Fig. 17). This is a severe perturbation, but one intended to simulate a high degree of warmth. We double the chemical inputs in wet deposition and then combine the two. Coming out of the snowpack, we have the higher concentration of chloride. Nitrate is, of course, also higher but attenuated by reactions in the soil. There is higher calcium responding to the higher hydrogen ion coming out of the snowpack.

In this case, doubling chemical inputs in wet deposition but leaving dry deposition the same, we see ANC going from maybe 50 down to 15 micro equivalents per liter during the initiation of snowmelt, but only for a 3, 4, or 5 day period. There is then even more depression as the peak of snowmelt comes out. These all appear over relatively short time periods on this year-long graph. These time periods are sufficient to have aquatic effects, so we were using a one day time step rather than a weekly or a five day time step as some other models have used. It is over a period of a few days that we were interested in observing depressions of acid neutralizing capacity. At least in the simulation, we were reaching for that pH 5.5 threshold that people mentioned. The spring and summer rains during 1987 resulted in significant depressions, but they tended to be shorter in duration than the snowmelt ionic pulse (Fig. 18). This slightly increased the loading from the snowpack, and you cannot really see the difference here on species like chloride, nitrate, and calcium. We see a 2-3 μg per liter drop in ANC during the ionic pulse, similar in 1987, and a little shift of the curve downward during most of the snowmelt. When you put these two perturbations together, it is just more of the same thing. There was better discrimination of the depression in ANC during the initiation of snowmelt and during the peak of snowmelt. The soil was drying out during the end of the year. This of course was the discharge under the best fit and the perturbed case in both years. We are drying out the soil, so that it may or may not be realistic from a modeling standpoint. The concentrations go quite high because of the depletion of water in the watershed. These spring and summer rains give us 1 to 3 day depressions in ANC and pH.

I also want to illustrate importance of solute release from the snowpack (Fig. 19) and the importance of the nitrogen reactions and final routing in the watersheds. We released the ionic pulse from the snowpack ahead of most of the water, because the ions or impurities tend to be washed out of the snowpack when the first melt occurs. If we take that out of the model the pulse disappears, and it gives a higher ANC of 2 micro equivalents per liter and 0.10 or 0.20 of a pH unit. That is an indication of the magnitude of the effects of this ionic pulse.

The nitrogen reactions are shown in figure 20. The best fit is the very light dash, and there are two perturbations on this graph. There is nitrogen stimulation; all the nitrogen just passes through the watershed. The second is ammonia simulation but no nitrate. All nitrate passes directly to the watershed. There were very small effects during the period of main snowmelt on ANC and pH, although it was not inconsequential during the summer rains. It looks like it was quite important there. It was not during the episode of peak snowmelt but during the summer rains that the modeled data look like the nitrogen simulation. It is that period when we need a better understanding of the processes in order to stand behind some of these calculations.

Finally, there is the effect of routing in the watershed (Fig. 21). Initially, we were routing snowmelt from the rocks directly into the stream. This included 20% of the runoff going from the rock surfaces directly into the stream, and we have assumed the rocks were made of Teflon, which is to say they do not have ion exchange capacity. We noted several spikes (Fig. 21). The sampling programs in the field were not designed to capture these spikes because these occur on a single day, but it does reinforce the point that there must be more soil out there than had initially been estimated. The modeling of perturbations shows that Emerald Lake is sensitive to this first simulation of what could be called climate warming of pasture snowmelt and increased acid loadings. If acid loadings were decreased the effects would reverse, and there would be a higher ANC instead of a lower ANC. The response would be a greater ionic pulse, faster snowmelt, and a drier summer; these three processes respond to that.

What are the future directions (Fig. 22)? I do not have results on this, but we feel we are at the point that we can use this integrated snowmelt and hydrochemical modeling as a tool for regional analysis. We focused on the Emerald Lake watershed because that is where the more intensive data were. In using alpine basins as sensitive indicators of change and in collaboration especially with John Melack's field program, we want to go on to using Emerald Lake as the main test basin for other basins in the eastern Sierra Nevada. There is a distribution of response across different basins. In understanding perturbations, the historical record may not be sufficient. We must look at three periods, not only the recent monitoring and the instrumental record for the hydrology. We must look also at the tree ring record to give us some idea of how the hydrology and temperature change from year to year. We hope to exploit the larger perturbations there and put together scenarios in multi-year simulations. We plan to move this model not only to other catchments, but beyond the conditions on which it has been tested.

(AUDIENCE) Roger, what is the mathematical structure of the algorithm for using the nitrogen simulation? Is it a simple one?

A (DR. BALES) Yes, it is simple. It is in the model right now; it is simply a first order algorithm.

Q (AUDIENCE) I did not quite understand the part toward the end about a routing alternative for water with respect to rock. What produces that very structure?

A (DR. BALES) The rock was assumed to have no ion exchange capacity. It is granite or granodiorite, so water that melts and runs directly into the stream should have nearly the same composition as the snowpack that released it.

Q (AUDIENCE) Is the resolution of that on about a daily basis?

A (DR. BALES) Yes, we have used the daily time step, so these spikes are an indicator of what is coming out of the snowpack.

Q (AUDIENCE) And what about the 20% figure? What guides that and what are the alternatives there?

A (DR. BALES) I do not think there is a short or simple answer to that. I should acknowledge the main developer of this work was Ross Woolford, a Ph.D. student, and after two years of analyzing the data and estimating how much rock is there and where it is located relative to the soil, and he came up with this 20% number as being a maximum routing.

Q (AUDIENCE) So 20% is in somebody's good judgment an upper bound, and it might be 10% or 5%?

A (DR. BALES) It appears to be somewhat smaller than 20% unless those spikes have simply not been observed. The sampling programs were not designed to observe them either.

Q (AUDIENCE) Actually, the most recent sampling that John Stoddard analyzed on a daily time daily basis did not show that.

A (DR. BALES) Right. Also, the response time in the watershed is less than a day.

Q (AUDIENCE) Secondly, just a comment. When you increased the snowmelt 30%, you did not change the snow melt timing. You did not make it come earlier. You simply raised the melt at the same time.

A (DR. BALES) We melted it 30% faster each day.

Q (AUDIENCE) Each day. So you actually had warming. You could also surmise there could be a change in timing, a change in climate in other words. That is another perturbation that you could apply.

A (DR. BALES) That is a perturbation we will apply, but that is ahead of us in terms of the snowmelt modeling at this point.

Q (AUDIENCE) I think I saw you had input of dry deposition in the model, but I am not sure. I want you to remind me whether that was true or not and discuss that issue a little bit.

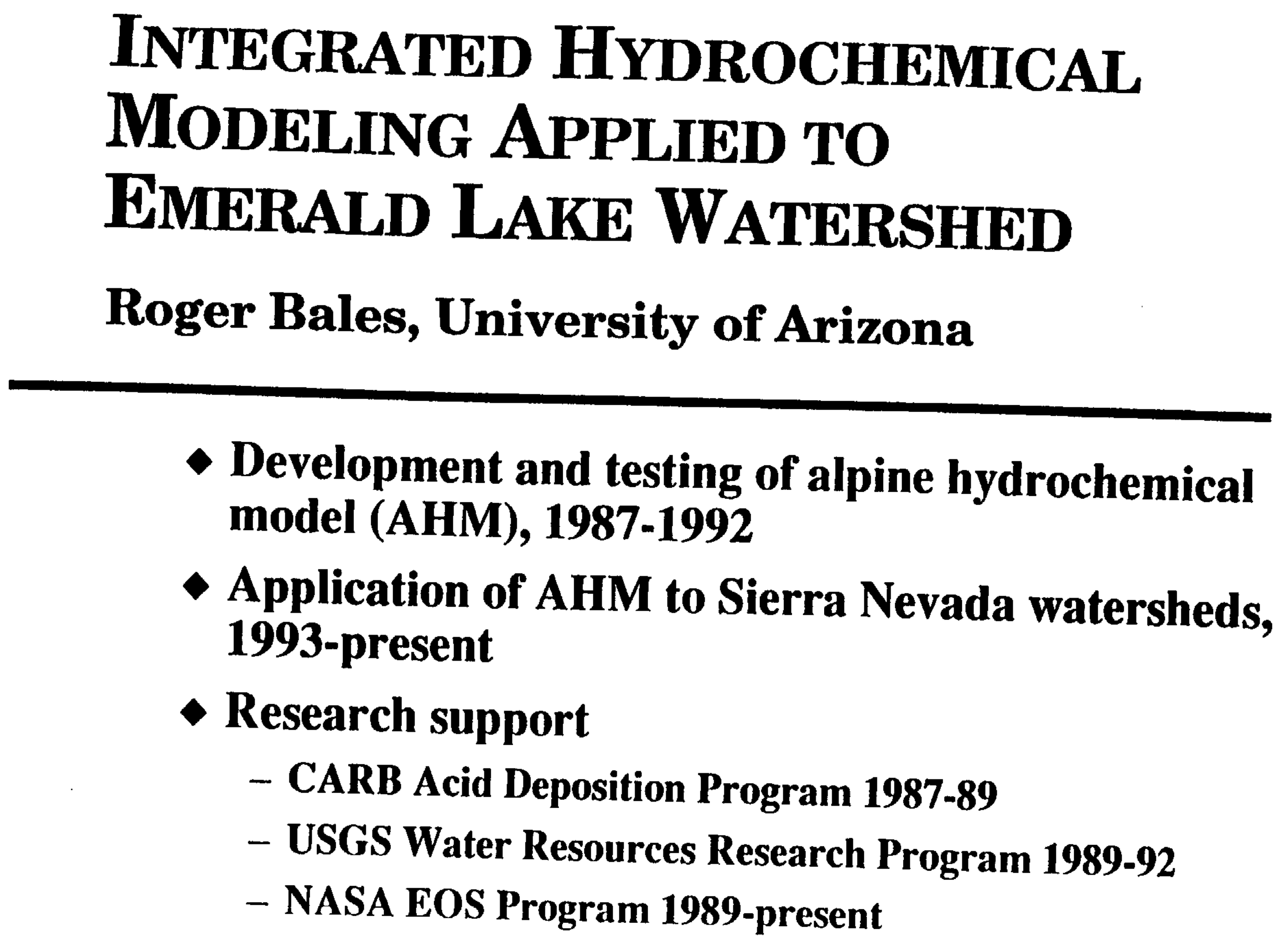
A (DR. BALES) Yes, dry deposition was included. We estimated dry deposition by using the two studies that were part of the program when Kathy was running it and included a collection on surrogate surfaces and pine needles. We used those fluxes and applied them to the periods when they had been measured. We went to the Noah Station at Wolverton to get an idea of the annual cycle that includes the month-to-month changes in dry deposition. We applied those month-to-month changes as a factor to the measured values from the studies that were done by the Carnegie-Mellon and Riverside groups. There is clearly a need for more data on dry deposition, but that was all the data I know of at this point. The dry deposition is not insignificant at least for the nitrogen budget. We did a much closer analysis with that. I do not remember if it was 30% or 50%, but it was not insignificant for the nitrogen flux into the watershed.

Q (DR. STODDARD) It was 30%, I think.

Q (AUDIENCE) Are you asking to include it in the model or is it included in the data base?

A (AUDIENCE) In the model.

Figure 1



INTEGRATED HYDROCHEMICAL MODELING APPLIED TO EMERALD LAKE WATERSHED

Roger Bales, University of Arizona

- Development and testing of alpine hydrochemical model (AHM), 1987-1992
- Application of AHM to Sierra Nevada watersheds, 1993-present
- Research support
  - CARB Acid Deposition Program 1987-89
  - USGS Water Resources Research Program 1989-92
  - NASA EOS Program 1989-present

Figure 2

Hydrology, Hydrochemical Modeling and Remote Sensing in Seasonally Snow-Covered Alpine Drainage Basins

University of Arizona EOS Team

- Roger Bales, Co-I
- Bob Harrington, Ph.D. student
- Tom Meixner, Ph.D. student
- Remigio Galarraga, Ph.D. student
- Jeff Shaw, M.S. student
- Ray Brice, programmer
- Nobu Ohte, postdoc (1993-94)
- Ross Wolford, Ph.D. student (1987-92)

CARB Project Team

- Soroosh Sorooshian, PI
- Vijai Gupta, postdoc
- Phil Noppe, M.S. student

Figure 3

Hydrology, Hydrochemical Modeling and Remote Sensing in Seasonally Snow-Covered Alpine Drainage Basins

Process Studies

- Spatial distribution of snow depth, water equivalence & chemical content
- Spatial & temporal distribution of snow metamorphism, melt rates & solute release
- Meltwater runoff, solute transport & (bio)chemical transformations in alpine watersheds

General Issues

- Role of snowpack in alpine hydrology and chemistry
- Important regional & interannual variations & trends
- Response to anthropogenic perturbations

Figure 4

MOTIVATION FOR DEVELOPING AHM

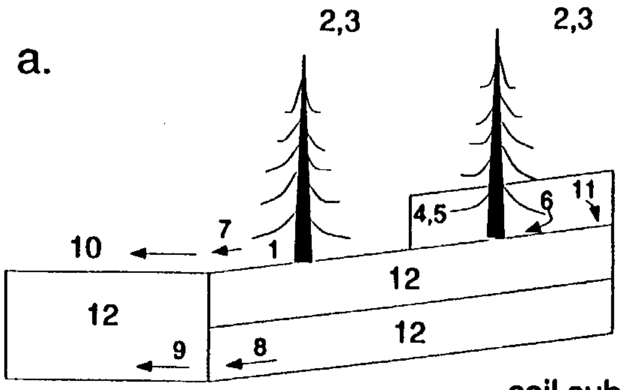
- Research tool to identify which hydrologic and hydrochemical processes were important and when changes due to these processes were occurring
  - Assist in interpreting field monitoring & process research
  - Help plan future research
- Predictive model for scenario analysis
  - Display watershed response to changing input conditions
  - Effects of natural or anthropogenic changes in climate
  - Effects of changes in atmospheric pollutant loading

Figure 5

AHM(Alpine Hydrochemical Model) is:
an integrated set of algorithms for
water and chemical balances that
describes hydrologic and chemical
processes in an alpine watershed.

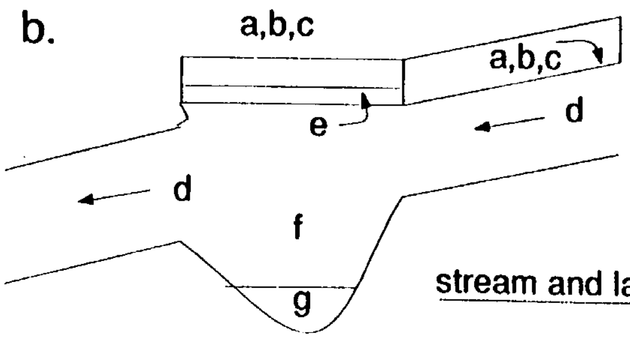
Applied to:
Emerald Lake Watershed
in Sierra Nevada, California
(120ha, elevation: 2800~3417m)

AHM -- Watershed Compartments



soil subunits

1. Rainfall litter interception
2. Snowfall canopy interception
3. Rainfall canopy interception
4. Snowpack
5. Snowpack liquid water
6. Snowpack drainage
7. Surface runoff (also 10, in/out)
8. Soil drainage (also 9, in/out)
11. Litter storage beneath snowpack
12. soil horizons



stream and lake subunits

a. Snowpack
b. Snowpack liquid water
c. Snowpack drainage
d. Streamflow
e. Ice
f. Epilimnion
g. hypolimnion

Figure 7

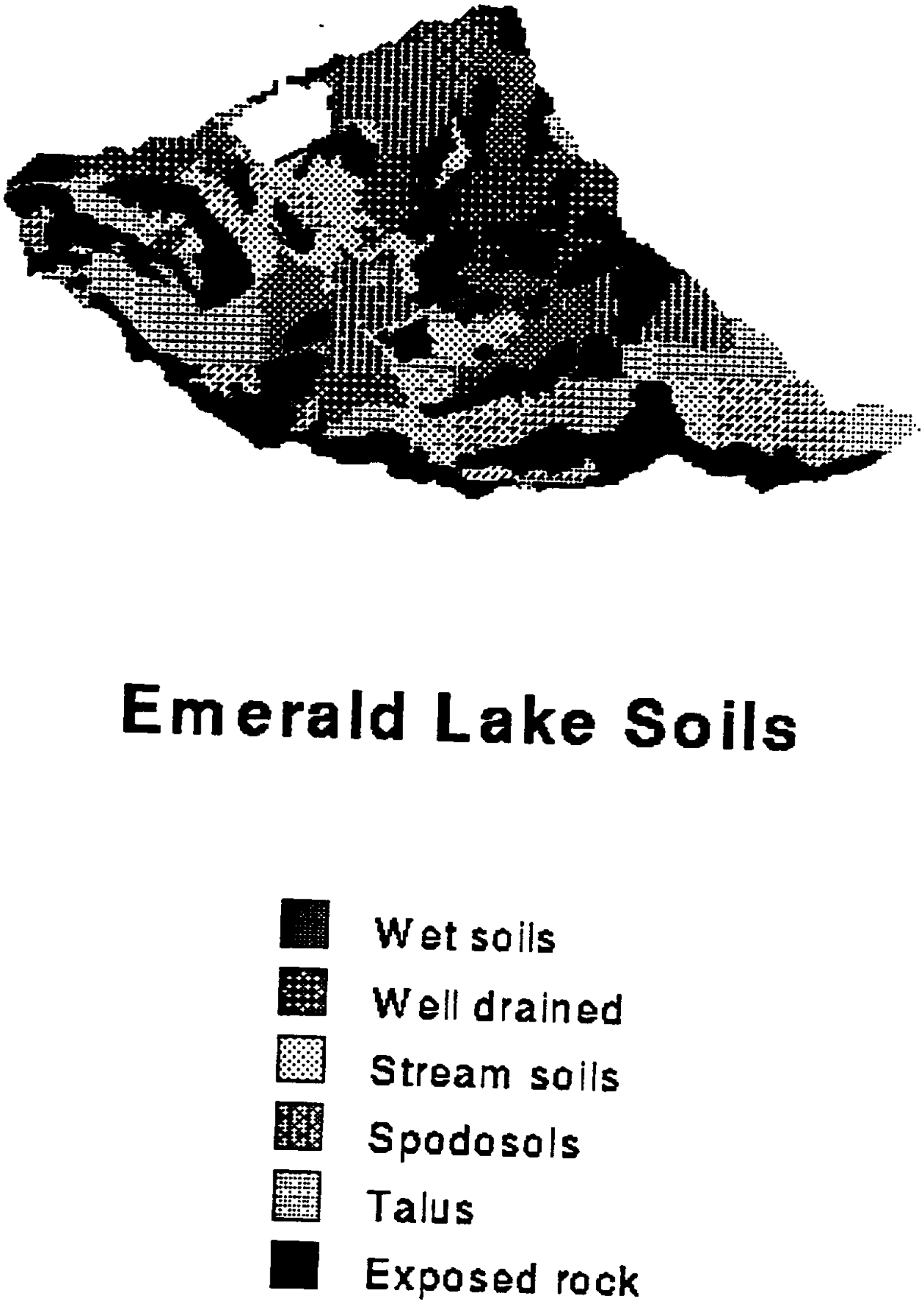
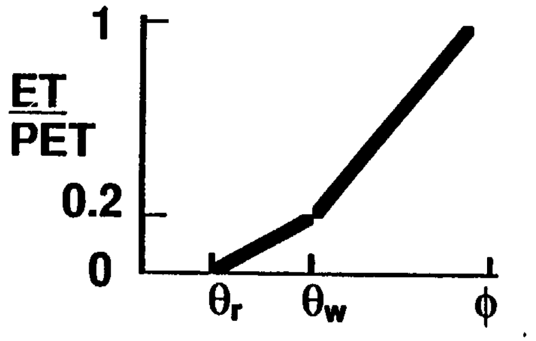

Emerald Lake Soils
Wet soils
Well drained
Stream soils
Spodosols
Talus
Exposed rock

Figure 8

AHM -- Water Balance

- Water storage
  - SCA, snowpack depth, SWE
  - Snowpack liquid water
  - Soil depth, ϕ, θ, θ_w, θ_r
  - Initial conditions



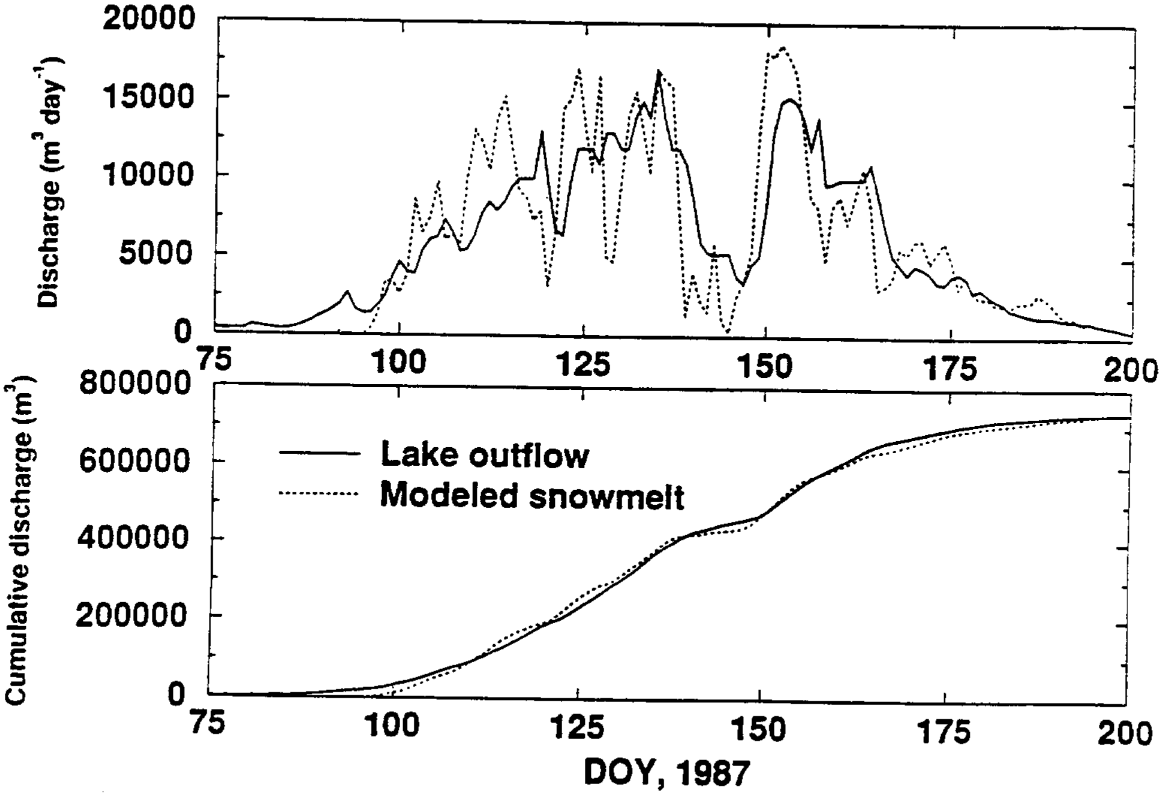
- Surface runoff: at a 1-day time step, all surface runoff enters stream
- Lake: stage-discharge relation; $Q = a\,(S - S_0)^b$
- Soil drainage (horizontal & vertical); $K_U = f(K_S, \theta, \phi, \theta_r, N)$
- PET & evaporation: data & Penman method
- ET: adjustable fraction of PET, each soil horizon
- Lake evaporation & sublimation: aerodynamic method following Brutsaert, as per Dozier et al. reports
- Routing: fraction snowmelt to soil vs. stream

Figure 9

AHM -- Chemical Balance

- Solute release from snowpack: $C = ABe^{-Bx} + (1-A)De^{-Dx}$
- Aqueous reactions: K_{eq} values
- Ion exchange: K_{eq}'s, X_{max}, PBS as initial condition
- Sulfate & silica adsorption: K_{eq}'s, Y_{max} Z_{max}
  - $Z\text{-}H_2SiO_3 = Z + H_2SiO_3$
  - K_{eq}'s & IC constrained by soil-solution data
- CO_2 partial pressure in soil: data
- Mineral weathering: $mol = A\, k_1[H+]^{\alpha}$
  - rock + CO_2 + H_2O = weathered rock + base cations + HCO_3^-
  - stoichiometry from rock & stream data
- Nitrogen transformations: 1st order in N:
  - fraction NH_4^+ --> org-N vs. NO_3^-
- Loss of organic acids: zero order

Figure 10



Discharge (m^3 day^{-1})
20000
15000
10000
5000
0
75
100
125
150
175
200
Cumulative discharge (m^3)
800000
600000
400000
200000
0
Lake outflow
Modeled snowmelt
75
100
125
150
175
200
DOY, 1987

Figure 11

Modeled vs. Surveyed SCA

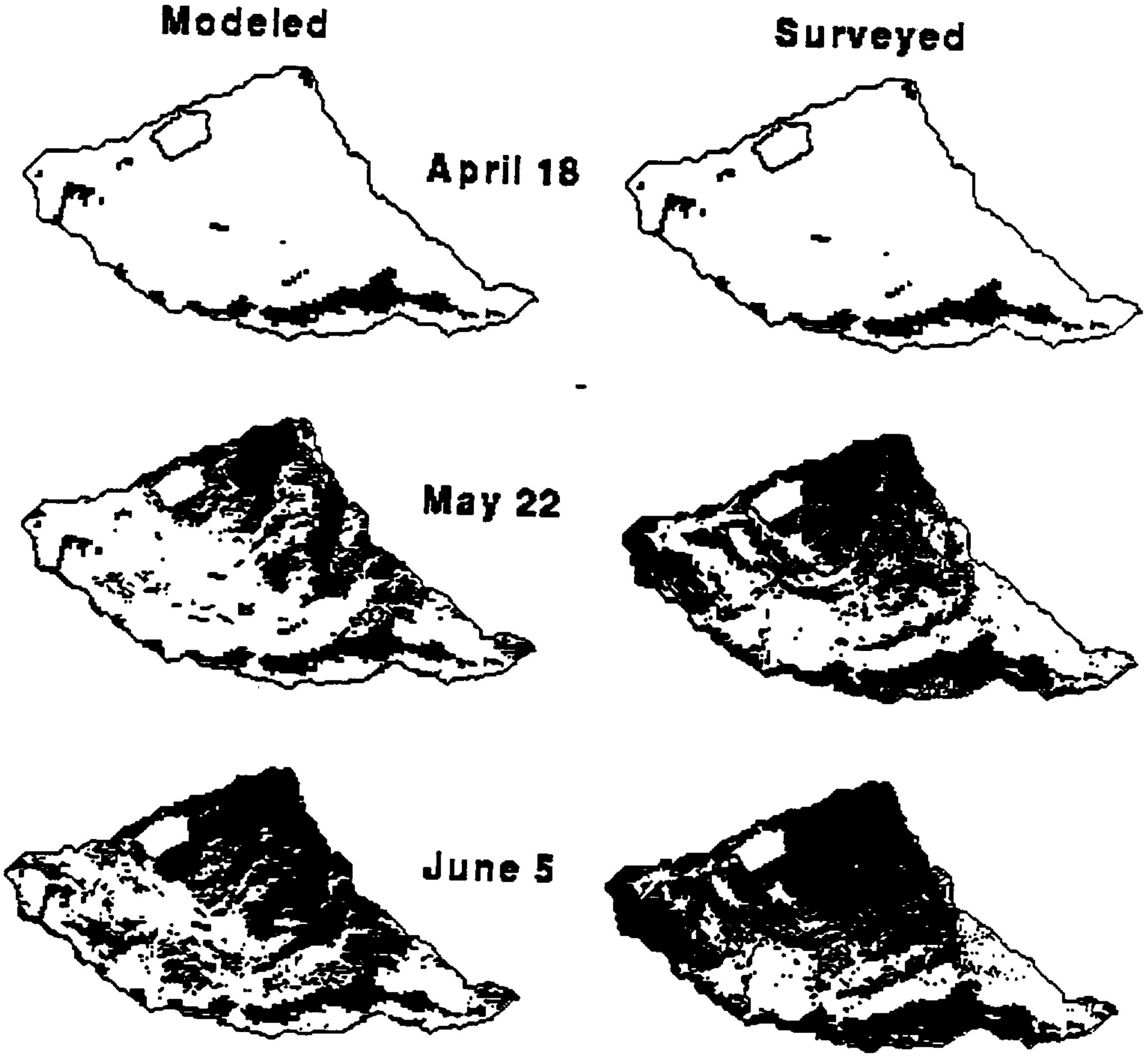
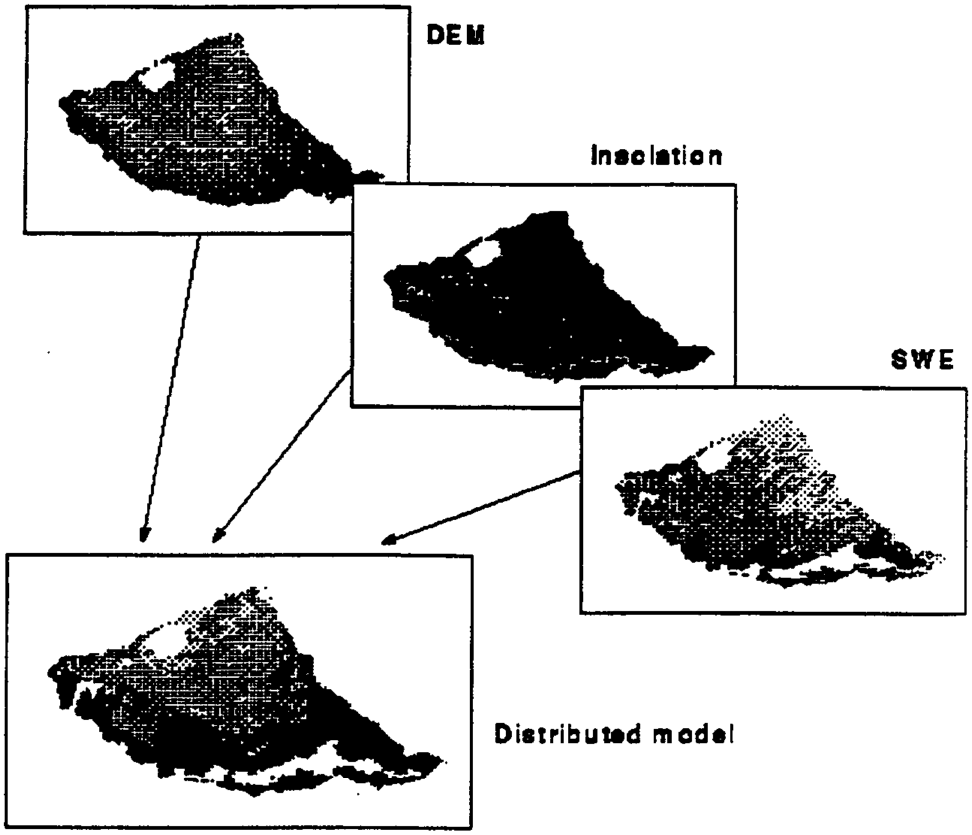


Figure 12

Snowmelt modeling



Procedure:

- Unsupervised classification of distributed data

- SNTHERM input files are generated for each class; model run for each class

- Post-processing

Figure 13

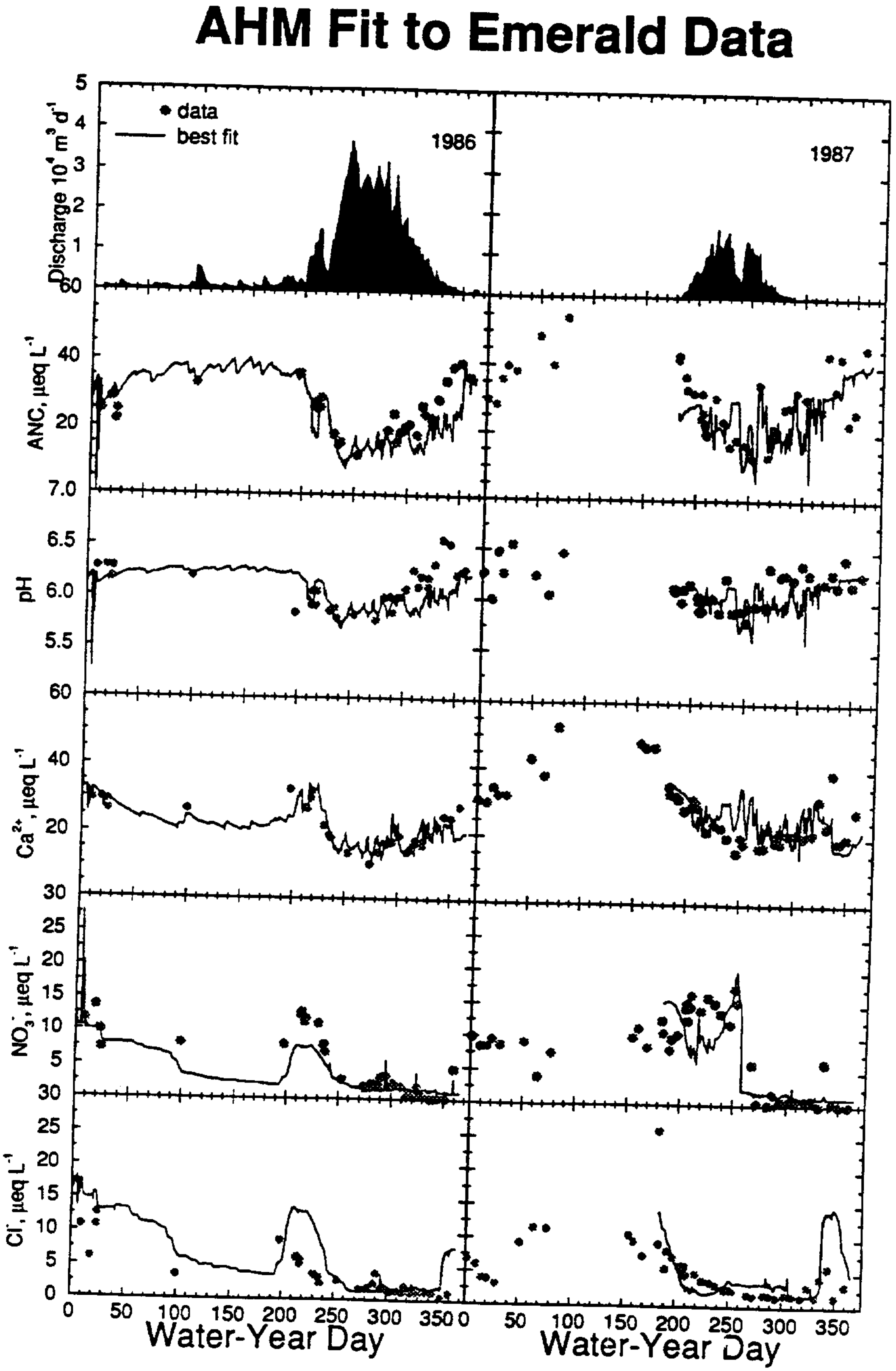

AHM Fit to Emerald Data
● data
best fit
1986
1987
Discharge 10^4 m^3 d^{-1}
ANC, µeq L^{-1}
pH
Ca^{2+}, µeq L^{-1}
NO$_3^-$, µeq L^{-1}
Cl$^-$, µeq L^{-1}
0 1 2 3 4 5
7.0 20 40 60
5.5 6.0 6.5
20 40 60
0 5 10 15 20 25 30
0 5 10 15 20 25 30
0 50 100 150 200 250 300 350
Water-Year Day
Water-Year Day

Figure 14

Hydrochemical Modeling Results

- Lumped parameter application of AHM to Emerald
  - Empirical estimation yielded physically realistic parameter set
  - Equally good simulation of calibration & validation years
- Automatic parameter estimation
  - Yielded slight improvement over empirical method
  - Multi-parametric sensitivity analysis reduced optimization time
  - Most sensitive parameters: ET, soil thickness, hydraulic conductivity, ion exchange coefficients, N reactions
- Response to perturbations
  - Emerald sensitive to climate warning & acid loading
  - Greater ionic pulse, faster snowmelt, drier summer

Figure 15

Emerald -- Response to Perturbations

- Evalute for 1986 & 1987, some of highest and lowest snowfall years on record

<u>Perturbations</u>

- 30% higher snowmelt rate
- Double chemical inputs in wet deposition
- 30% higher snowmelt rate & doubled chemical inputs
- Solute release from snow proportional to snowmelt
- Accelerated chemical elution from snow, Jan vs.Apr
- No nitrogen assimilation & only NH_4^+ assimilation
- 20% of runoff from rocks routed to stream

Figure 16

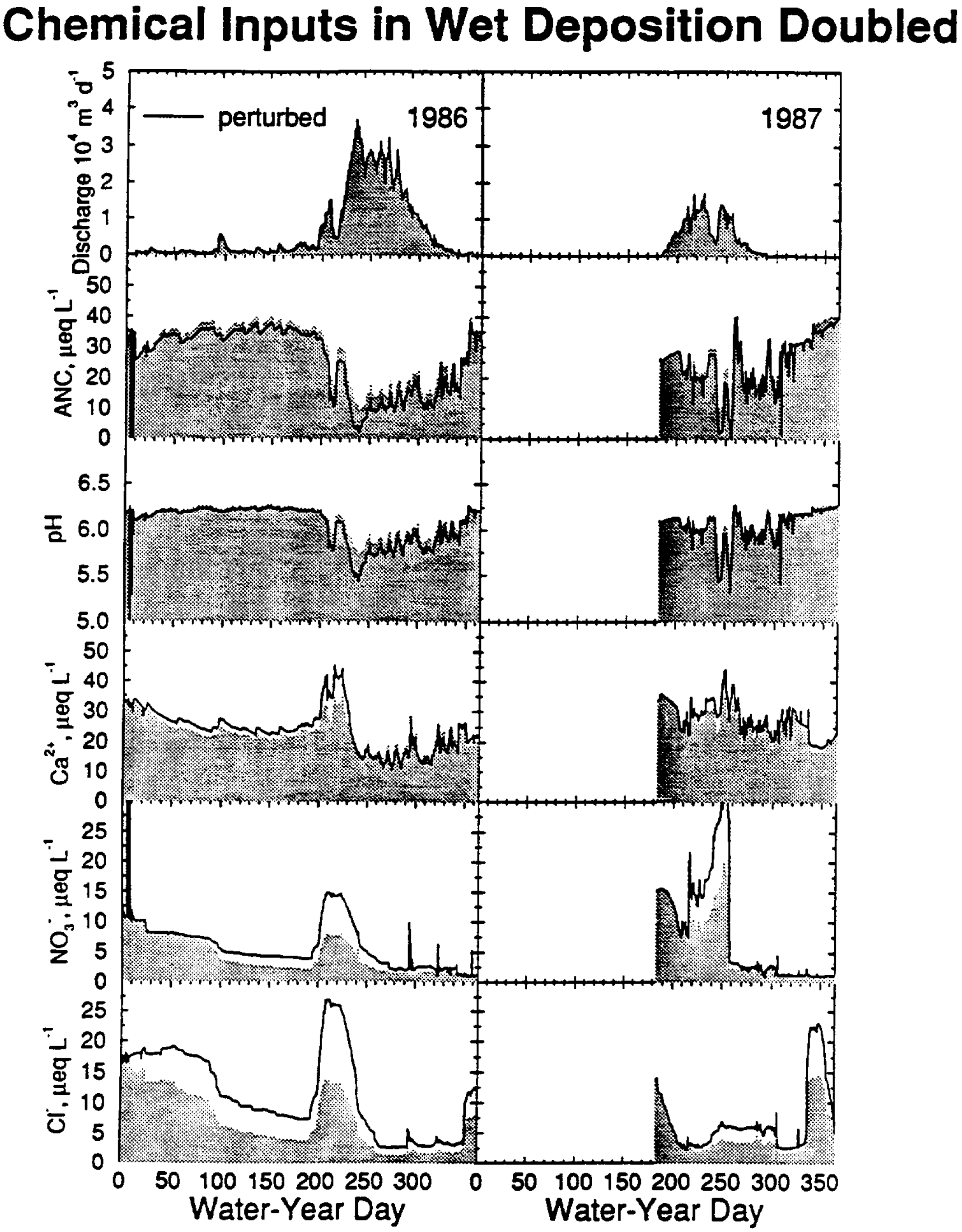

Chemical Inputs in Wet Deposition Doubled
perturbed
1986
1987
Discharge 10⁴ m³ d⁻¹
0
1
2
3
4
5
ANC, µeq L⁻¹
0
10
20
30
40
50
pH
5.0
5.5
6.0
6.5
Ca²⁺, µeq L⁻¹
0
10
20
30
40
50
NO₃⁻, µeq L⁻¹
0
5
10
15
20
25
Cl⁻, µeq L⁻¹
0
5
10
15
20
25
0
50
100
150
200
250
300
0
50
100
150
200
250
300
350
Water-Year Day
Water-Year Day

Figure 17

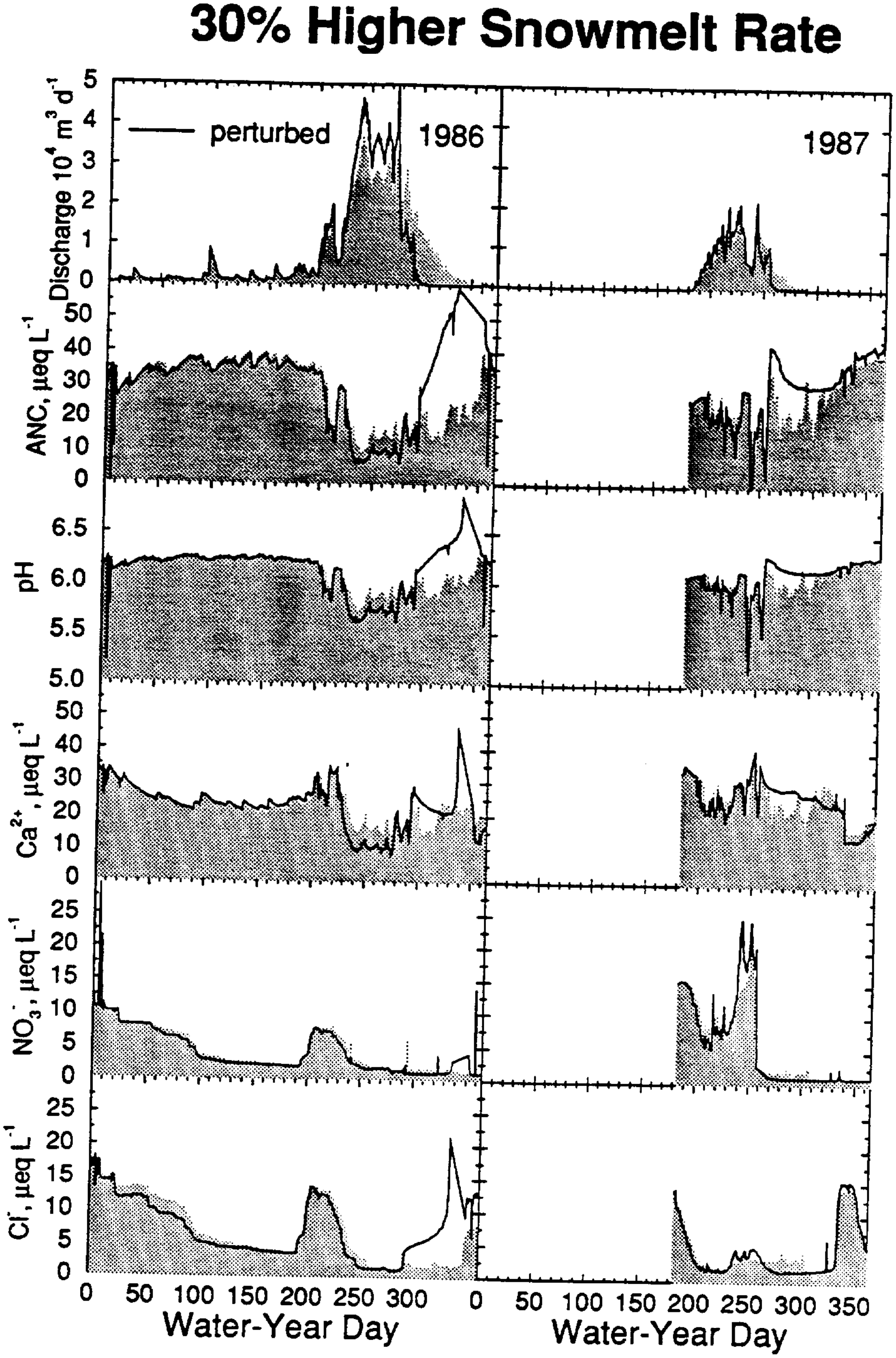

30% Higher Snowmelt Rate
perturbed
1986
1987
Discharge 10^4 m^3 d^{-1}
0
1
2
3
4
5
ANC, µeq L^{-1}
0
10
20
30
40
50
pH
5.0
5.5
6.0
6.5
Ca^{2+}, µeq L^{-1}
0
10
20
30
40
50
NO$_3^-$, µeq L^{-1}
0
5
10
15
20
25
Cl$^-$, µeq L^{-1}
0
5
10
15
20
25
0
50
100
150
200
250
300
0
50
100
150
200
250
300
350
Water-Year Day
Water-Year Day

Figure 18

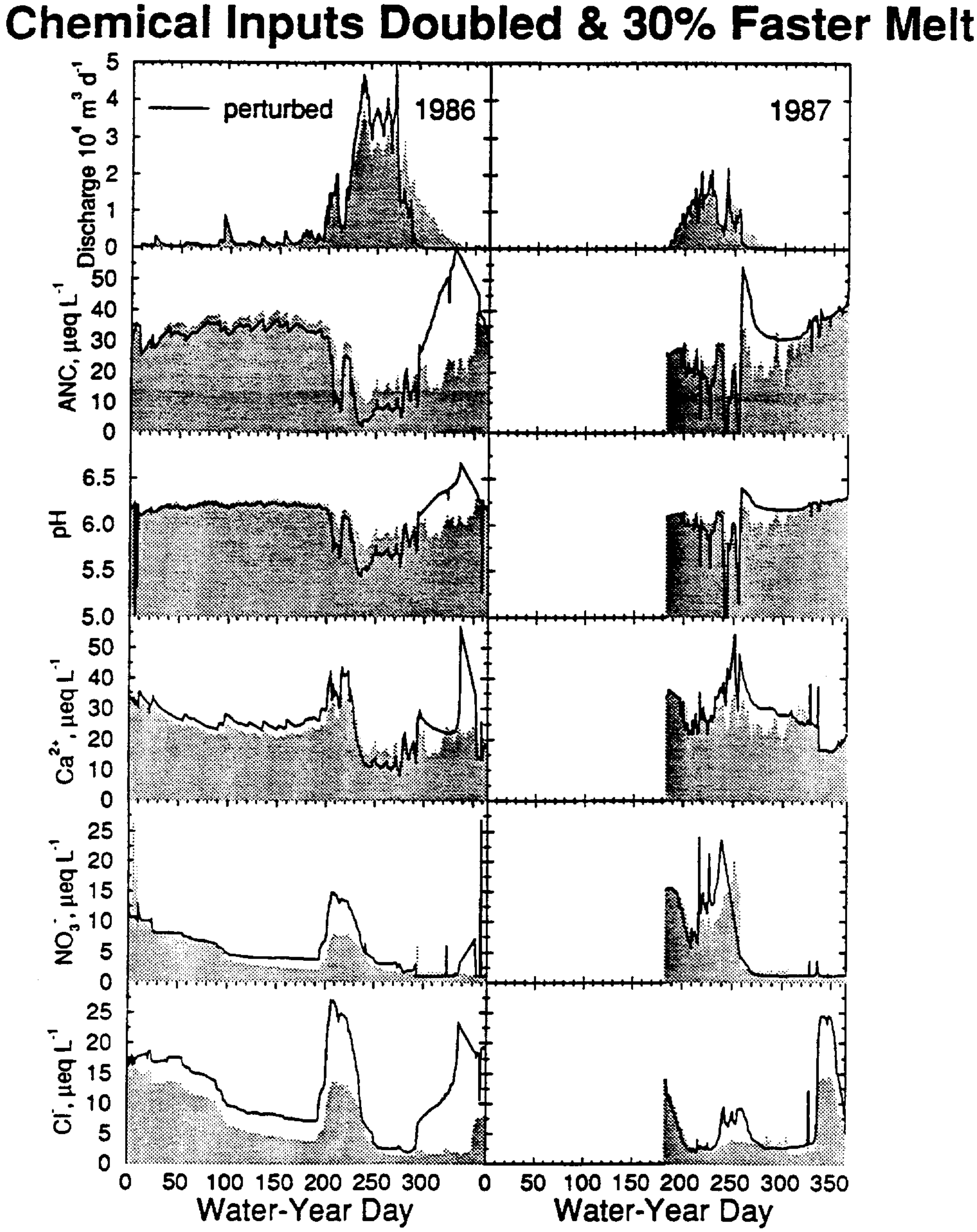

Chemical Inputs Doubled & 30% Faster Melt
perturbed
1986
1987
Discharge 10^4 m^3 d^{-1}
0 1 2 3 4 5
ANC, µeq L^{-1}
0 10 20 30 40 50
pH
5.0 5.5 6.0 6.5
Ca^{2+}, µeq L^{-1}
0 10 20 30 40 50
NO$_3^-$, µeq L^{-1}
0 5 10 15 20 25
Cl$^-$, µeq L^{-1}
0 5 10 15 20 25
0 50 100 150 200 250 300
0 50 100 150 200 250 300 350
Water-Year Day
Water-Year Day

Figure 19

Solute Release from Snow Proportional to Melt

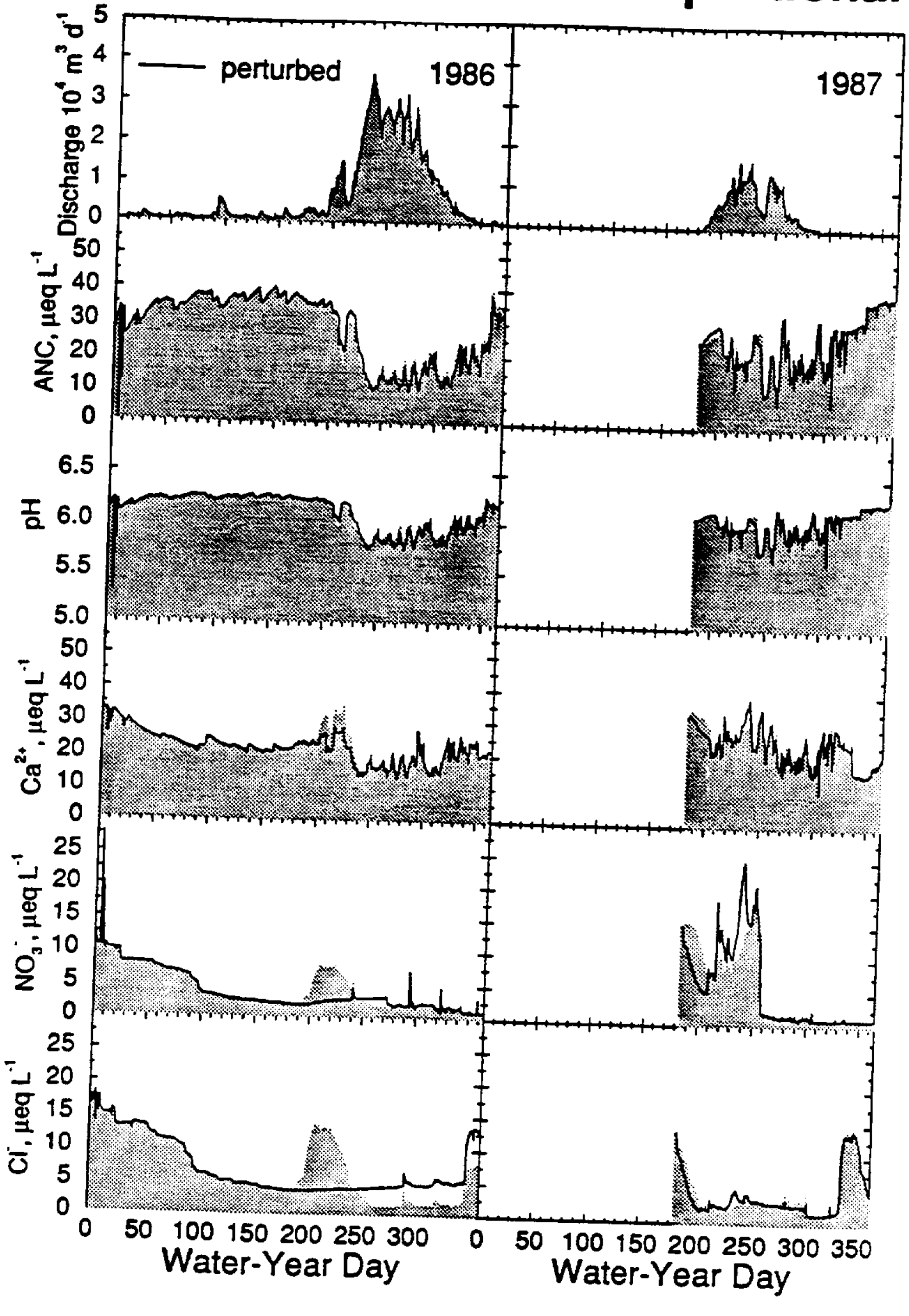


Figure 20

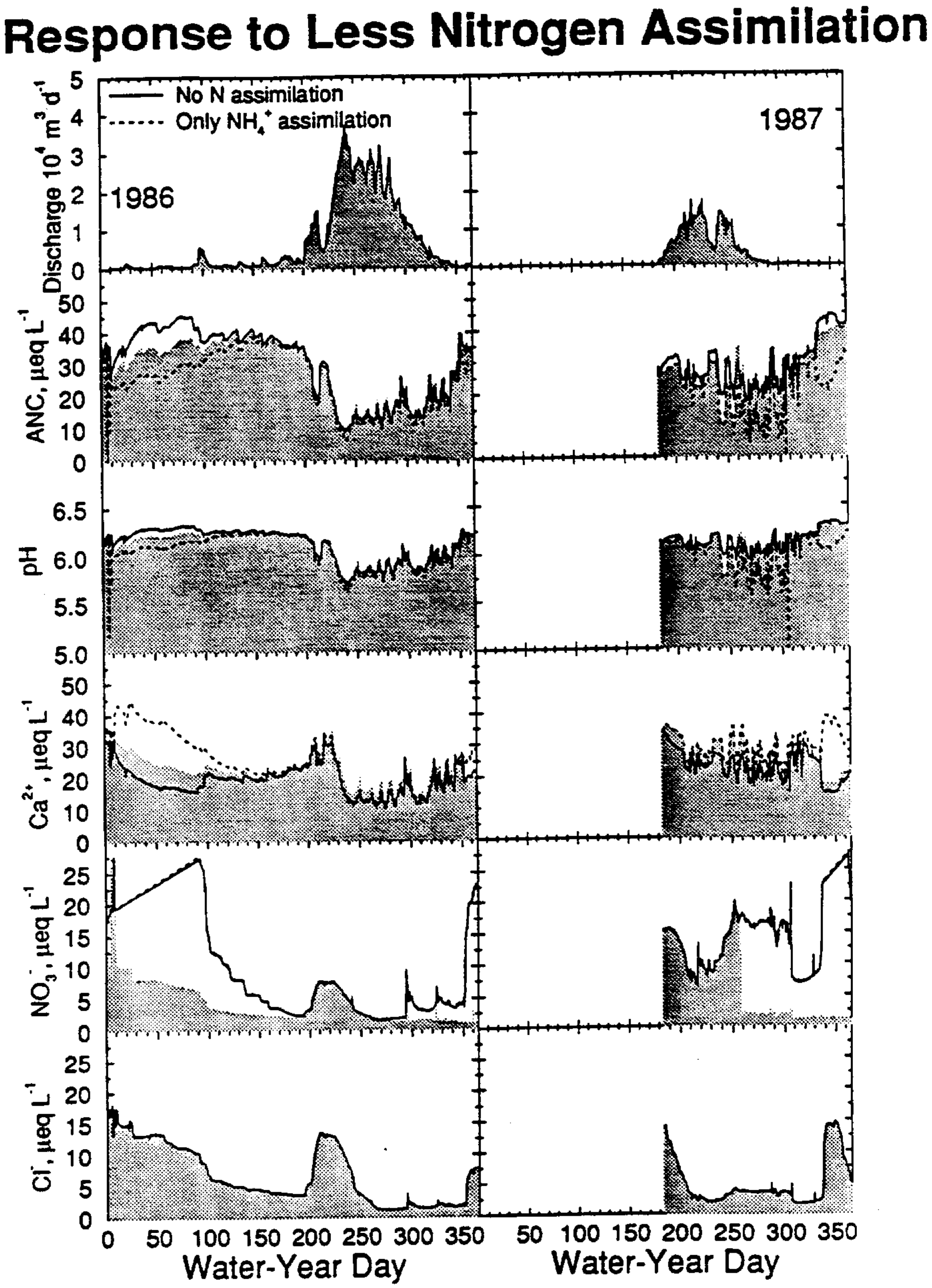

Response to Less Nitrogen Assimilation
No N assimilation
Only NH$_4^+$ assimilation
1986
1987
Discharge 10^4 m^3 d^{-1}
ANC, µeq L^{-1}
pH
Ca^{2+}, µeq L^{-1}
NO$_3^-$, µeq L^{-1}
Cl$^-$, µeq L^{-1}
0 1 2 3 4 5
0 10 20 30 40 50
5.0 5.5 6.0 6.5
0 10 20 30 40 50
0 5 10 15 20 25
0 5 10 15 20 25
0 50 100 150 200 250 300 350
50 100 150 200 250 300 350
Water-Year Day
Water-Year Day

Figure 21

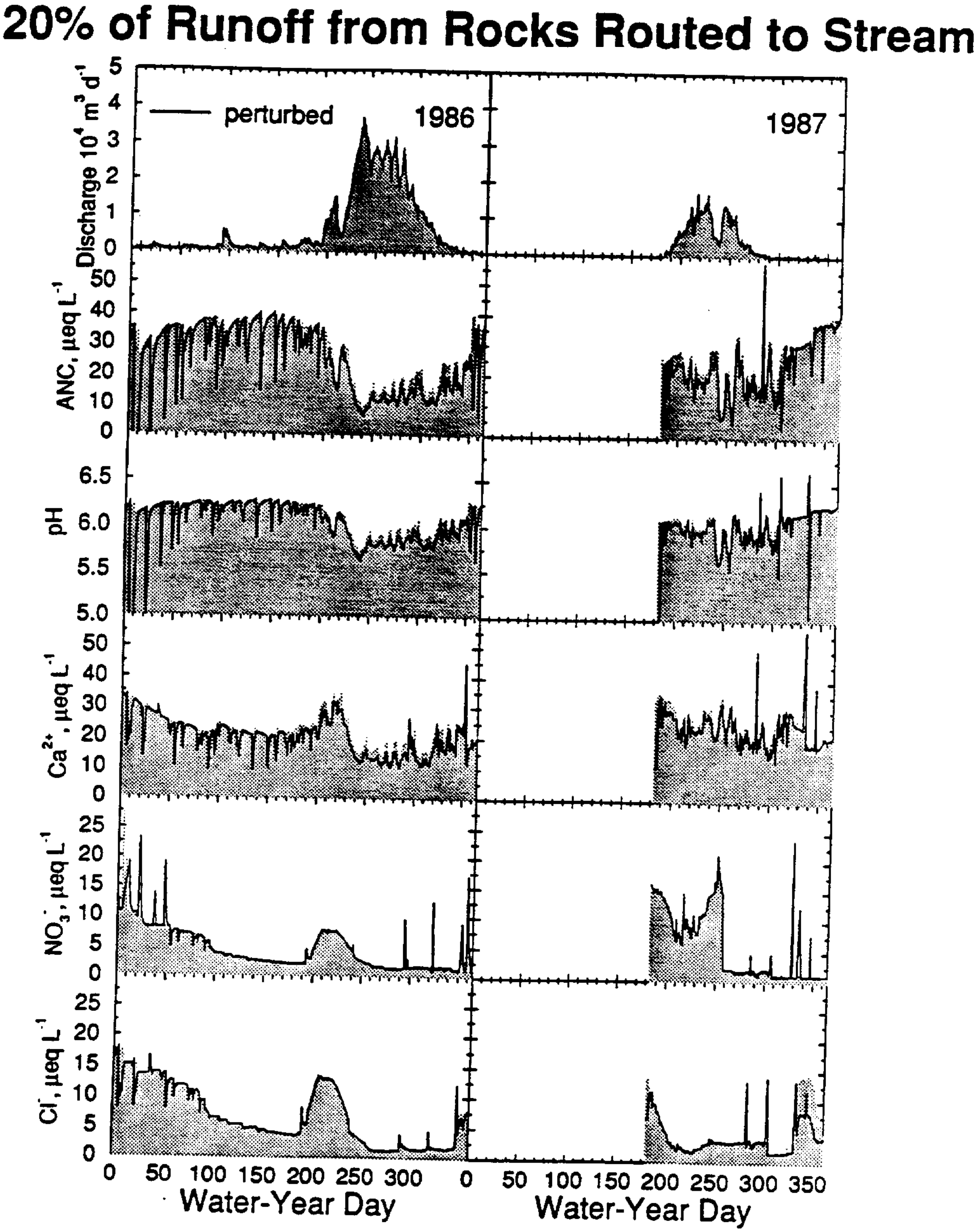

20% of Runoff from Rocks Routed to Stream
perturbed
1986
1987
Discharge 10^4 m^3 d^{-1}
0
1
2
3
4
5
ANC, µeq L^{-1}
0
10
20
30
40
50
pH
5.0
5.5
6.0
6.5
Ca^{2+}, µeq L^{-1}
0
10
20
30
40
50
NO_3^-, µeq L^{-1}
0
5
10
15
20
25
Cl^-, µeq L^{-1}
0
5
10
15
20
25
0
50
100
150
200
250
300
350
Water-Year Day
Water-Year Day

Figure 22

Modeling -- Future Directions

- Integrated snowmelt & hydrochemical modeling as a tool for regional analysis
- Alpine basins as sensitive indicators of climate change
- Distribution of headwater catchment responses with current interannual variability
    - 3 periods: recent monitoring, instrumental record, 1000 yr
    - Emerald as main test basin
    - Indicators: spring & summer stream conditions, summer soil
- Responses with changed regional climate & deposition
    - Parallel with evaluation under current conditions; MM4 and larger-basin modeling to define hydrology
    - Hypothesis: magnitude of changes larger than for current interannual
- Distribution of responses across different headwater catchments
    - Magnitude relative to interannual variability?
    - Extend to other basins in Tokopah, and Eastern Sierra