EFFECTS OF OZONE AND SULFUR DIOXIDE MIXTURES ON FOREST VEGETATION OF THE SOUTHERN SIERRA NEVADA

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ABSTRACT

In 1981 and 1982 a multidisciplinary study to assess the possible effects of ozone-sulfur dioxide mixtures on native vegetation was carried out within a 32-mile radius stretching from Oildale eastward to points in the Greenhorn, Breckenridge and Piute Mountain areas. The main objectives included: (1) continuous monitoring of ozone, sulfur dioxide and meteorological variables supplemented by a Huey sulfation plate network to detect sulfur dioxide at various elevations; (2) the measurement of sulfate content of surface soils and subsoils, and the sulfur content of pine needle and lichen tissue,including stable sulfur isotope ratios in tissues and soils along transects of increasing elevation; (3) determination of the stable sulfur isotope ratio of atmospheric sulfur in the source area and of soil and plant tissue sulfur in the receptor area; (4) fumigation of pine and giant sequoia seedlings with various mixtures of ozone and sulfur dioxide in outdoor open-top chambers; and (5) a survey of native vegetation.

Comparison of hourly averages of ozone and sulfur dioxide for July through October 1982 showed that ozone at Oildale was slightly lower by 1-2 pphm than at Democrat Springs (2400 ft) and Shirley Meadow (6600 ft). Sulfur dioxide hourly averages at Democrat Springs and Shirley Meadow were approximately one-fifth and one-tenth, respectively, of those at Oildale. The sulfation rates indicated by Huey plates were of dubious value in remote areas where SO_2 concentrations were less than 10 ppb. It might be helpful to increase the exposure time from six weeks to four months.

The concentrations of extractable sulfate in soils, and sulfur in pine needles and lichens along transects extending east of Oildale tend to decrease ($p < 0.01$) with increasing elevation in the 0-5 cm layer on the Breckenridge Mountain transect and in pine needle tissue on both the Greenhorn Ridge and Breckenridge Mountain transects. Sulfur concentrations on pine needles and lichen thalli had not reached toxic levels.

The $\delta^{34}S$ trend in soils and plant tissue ran counter to the expected result because the isotopic composition is more similar to the source area at greater distances from the source where total sulfur content of surface soil and plant tissue is the lowest. The moderately negative soil $\delta^{34}S$ at lower elevations tends to dilute the input of sulfur with a positive $\delta^{34}S$ from the atmosphere. This method remains promising for detecting the source of sulfur pollution, but additional sampling of the atmosphere, soils and plant tissue is required in California.

Recently germinated seedlings of digger, ponderosa and jeffrey pines and giant sequoia exposed to pollutant mixtures showed reductions in root growth ($p < 0.05$) at 10 pphm SO_2 and 20 pphm O_3. The SO_2*O_3 interaction was not significant for top and root growth. Top growth reductions were significant less frequently at the above concentrations.

Mixed gas fumigations of older pine and giant sequoia seedlings identified the visible symptoms of single and mixed gas injury by ozone and sulfur dioxide on older foliage comparable to adult trees.

Surveys of forest vegetation in the Greenhorn District of the Sequoia National Forest showed increases of ozone damage to pines at selected sites between 1977 and 1981. Foliar symptoms indicated that sulfur dioxide was not acting jointly with ozone.

Addition of sulfur dioxide to the San Jaoquin Valley air basin might accelerate forest deterioration if concentrations of both pollutants reach levels where joint action is possible.

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ACKNOWLEDGEMENTS

The diverse nature of tasks undertaken by the project required a high level of initiative and independent judgment by numerous individuals. The performance of all participants deserve recognition and some individuals merit special mention. Ken Stolte, the staff research associate assigned full time to the project, contributed sound scientific support in all phases of the project from data gathering to data analysis. He supervised laboratory helpers and assumed complete responsibility for the air monitoring stations, Huey plate exposure and analysis and all aspects of seedling fumigation experiments. He improved the method for germinating conifer seeds; poor germination impeded progress at one point. The unbounded enthusiasm that Ken brought to the project provided inspiration to both younger and older co-workers. Problems encountered in the analysis of soils and plant tissue for sulfur were worked out by Ed Betty. Linda Haag Verhoeven provided careful and skillful assistance in the laboratory analysis tasks and also in the preparation of seeds for germination and seedlings for fumigation experiments. Laboratory helpers who participated in various phases of the project include Melody Lardner, Craig Kazmier, Alfred Yamamota, Anne Smith, Nancy Leung, Mark Shaw and Regina Fuentes.

The open-top fumigation facility provided by the Air Resources Board at Riverside was managed and maintained by Dr. C. Ray Thompson, Phillip J. Dawson, Gerrit Kats and Joanne Wolf. An extraordinary effort was made to repair the chambers following wind damage in December 1981.

We were aided immeasurably in the analysis of stable sulfur isotope abundances by the full scientific collaboration of Dr. H. Roy Krouse and his laboratory staff at the Department of Physics, University of Calgary, Alberta. Dr. Krouse made two trips to Riverside to provide advice on sampling and interpretation of results. USDA, Forest Service Fire Laboratory technicians at Riverside who helped in the seedling fumigation and the SF_6 tracer experiment included Bob Van Doren, Bob Collins and Hector Martinez. Michael A. Fosberg and Bill Waite provided instrumentation and participated directly in the SF_6 tracer study. Anthony Gomez provided photographic documentation of experimental methods and results of both field and greenhouse studies.

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The U. S. Forest Service, Pacific Southwest Forest and Range Experiment Station, Forest Fire Laboratory funded a $4000 research agreement with the Department of Physics, University of Calgary that made possible the second set of sulfur isotope determinations in 1982.

We wish to express our gratitude to all of the individuals and organizations named above and to any others who we might have overlooked.

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

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I. PROJECT SUMMARY

INTRODUCTION

A survey of sulfur dioxide and sulfate in the Bakersfield area in 1977 and 1978 showed that the sulfur dioxide air quality standard was exceeded on 68 days in 1978 alone (Duckworth and Crowe 1979). This was the greatest number of occurrences of concentrations exceeding the 24-hour standard in the entire state. Sulfate levels were also exceptionally high. In the same survey, ozone maximum hourly concentrations in the range of 0.10 or 0.13 ppm frequently accompanied daily average sulfur dioxide concentrations of 0.052 to 0.076 ppm, particularly during the April through October period. The occurrence of frequent episodes of the combined pollutants raises concern about the possible additive or synergistic injury that may occur to both agricultural crops and native vegetation downwind from Bakersfield-Oildale.

The dispersion of air pollution from the Bakersfield-Oildale area during the summer months is heavily influenced by the general up-valley flow from the northwest (Unger 1974). The mountain barriers formed by the Tehachipi and the Greenhorn Mountains cause modifications of dispersion which are only partly understood. In other sections of the Central Valley to the north, the air quality data support the conclusion that ozone transport to the windward slopes of the Sierra results in elevated concentrations (Unger 1978, Miller and McCutchan 1972). Up-slope flows on the mountain slopes and up-canyon flows provide the major mechanisms for pollutant penetration into forested areas. The lower elevation digger pine stands and mid-elevation ponderosa or Jeffrey pine or mixed conifer forests are subjected to frequent exposure to ozone and possibly sulfur dioxide.

A 1977 survey of the southern sections of the Sequoia National Forest located sites where ozone injury to ponderosa and Jeffrey pines was described as none or very slight, slight and moderate (Figure VII-1) by Pronos et al. (1978). It is not known if a portion of this injury may be due to the combined effects of ozone and sulfur dioxide. Fumigation of ponderosa pine with high concentrations of SO_2 and O_3 (0.45 ppm each) combined has shown that substantially more foliage injury resulted from the combination than from exposure to the pollutants singly (Evans and Miller 1975). Dochinger et al. (1970) found that sensitive clones of eastern white pine experienced greater than additive injury when exposed daily to approximately 0.10 ppm each of ozone and sulfur dioxide.

Therefore, two important indications of potential effects were identified, namely chronic oxidant symptoms are present on foliage of ponderosa and Jeffrey pines in the southern Sequoia National Forest, and earlier fumigation studies have shown greater than additive injury resulting to pine species from ozone and sulfur dioxide combined.

Two conditions make this set of circumstances important and unique. First, the potential for serious permanent air pollution damage to certain ponderosa and Jeffrey pine dominated stands is exacerbated by the marginal site conditions typical of the extreme southern Sierra. Following chronic exposure, the decline in vigor and increased mortality of overstory trees from pine bark beetle attack results in thinner, poorly stocked stands. Stand perpetuation is dependent almost entirely on natural seeding because short spring and summer periods of adequate soil moisture make it difficult and inefficient to attempt replanting with bare root seedlings. As a result, the long-term outlook for maintaining a satisfactory forest cover is poor. Second, this is presently the only location where the effects of simultaneous exposure to both ozone and sulfur dioxide is suspected in natural forest stands in California.

A multifaceted study was undertaken to determine the present effects (if any) of ozone and sulfur dioxide on major pine species native to the mountains east of Bakersfield using a combination of field observations and greenhouse experiments. The objectives of the study were:

(1) Monitor ozone and sulfur dioxide with continuous monitoring instruments simultaneously at Kern Canyon (2400 ft) and Greenhorn Ridge (6400 ft) sites. Measure winds, temperatures and relative humidities at the same sites.

(2) Cooperate in an intensive two-day transport study designed around an SF_6 tracer release at Oildale.

(3) Use a Huey sulfation plate network with stations at 500 ft elevational intervals along three transects extending up to 32 miles east of Oildale.

(4) Determine the extractable sulfate content of surface (0-5 cm) and subsoils 5-15 cm, 15-30 cm and 70-100 cm at the same sites where Huey plates were located. Determine the sulfur content of pine foliage and lichens at sites where these species were present.

(5) Determine the stable sulfur isotope abundances ($\delta\ ^{34}S$ %) in a subset of the soil and foliage samples collected at increasing distances east of Oildale and in air samples collected at Oildale. Compare the sulfur isotope abundances of other possible sources of sulfur, e.g., agricultural sulfur, with that of soil and foliage samples.

(6) Fumigate pine seedlings to identify the effects of ozone and sulfur dioxide singly and in combination on symptom appearance and growth of tops and roots.

(7) Examine changes in tree condition at Forest Service plots established in 1977 and evaluate leaf symptoms on other woody species at varying distances from Oildale.

PROCEDURES

All monitoring and sampling activities were carried out at sites ranging from 1 to 35 miles east of Oildale. A preliminary sampling transect including 35 sites was used in 1981; in 1982 a slightly smaller version of the 1981 transect with 34 sites was used. The change in 1982 was in response to the need to sample more intensively in the mountain regions closer to Bakersfield-Oildale.

The air monitoring instrument support and seedling fumigation work was supported jointly by the Statewide Air Pollution Research Center and the U. S. Forest Service, Pacific Southwest Forest and Range Experiment Station. The Soil and Environmental Sciences Department at UCR managed all of the soil and plant tissue analysis for sulfur. Stable sulfur isotope analysis was done through research agreements with Dr. H. Roy Krouse, Department of Physics, University of Calgary. The U. S. Forest Service funded the second year of the agreement. The California Air Resources Board provided use of the open-top chamber fumigation facility at UCR and participated directly in the SF_6 tracer study scheduled on September 15, 1982. The continuous air monitoring sites were provided through the cooperation of the Greenhorn District of the Sequoia National Forest.

RESULTS

Comparison of hourly averages of ozone and sulfur dioxide for July through October showed that ozone at Oildale (Manor Street) was slightly lower by 1-2 pphm than either mountain station. This difference in ozone between sites is due in part to the advanced "photochemical age" of the air masses at Democrat Springs (2400 ft) and Shirley Meadow (6600 ft). Sulfur dioxide hourly averages at Democrat Springs and Shirley Meadow were approximately one-fifth and one-tenth, respectively, of those at Oildale. Data describing vertical mixing and mass flux between Bakersfield and the Kern River drainage obtained during the intensive study on September 15, 1982 indicated that pollutants from Oildale would have been mixed upward through a deep layer and transported eastward into the Kern River drainage at ridge-top level. The lower gorge of the Kern River is too narrow to allow the mass flux observed in the mid- to upper canyon; it was suggested that the upper canyon flux is derived from air entering over ridge tops lateral to the canyon (Appendix 1). The synoptic weather pattern on September 15 was a 500 millibar low and surface low; ozone levels decreased at mountain stations during the day. Further analysis of the synoptic weather during the summer of 1982 showed that the highest ozone pollution was present during periods dominated by a 500 millibar high and a surface low. The diurnal winds at Democrat Springs and Shirley Meadow were compared during each of four distinct synoptic patterns. Sustained winds from the west after nightfall seemed to be associated with ozone concentrations remaining above 8-10 pphm at Shirley Meadow.

The sulfation rates indicated by Huey plates were of dubious value in remote areas where SO_2 concentrations were less than 10 ppb. Closer to Bakersfield where exposures may not be influenced by the sheltering and diverting effects of terrain and where SO_2 concentrations often reach 30-50 ppb, there may be an appropriate use for the method. At remote sites, the exposure time might be lengthened from six weeks to four months in order to exceed the lower detection limits of the method. In spite of its limitations, the method appeared to faithfully reflect the decreasing SO_2 concentration in a transect extending from Oildale up the Kern River gorge. On the Greenhorn and Breckenridge Mountain transects, there was a hint of increased sulfation rates at higher elevations. These observations tend to support the hypothesis that greater mass flow of pollutants occurs at ridge-top levels.

The concentrations of extractable sulfate in soils, and sulfur in pine needles and lichens along transects extending east of Oildale tend to decrease ($p < 0.01$) with increasing elevation in the 0-5 cm layer on the Breckenridge Mountain transect and in pine needle tissue on both the Greenhorn Ridge and Breckenridge Mountain transects. Two lichen species, _Letharia vulpina_ and _Hypogymnia enteromorpha_, accumulated higher concentrations of sulfur at elevations ranging from 4500 to 7200 ft than the highest concentrations accumulated by digger pine at its lowest elevation and closest distance to Oildale. The lichen tissue was probably older than the oldest pine needles (four years old) sampled and thus had more time to accumulate sulfur or was a more efficient accumulator of atmospheric sulfur. At the same elevation, sugar pine needles accumulated more sulfur than Jeffrey pine but less than the lichens. There was no indication by the appearance of pine needles and lichen thalli that sulfur concentrations had reached toxic levels.

The stable sulfur isotope ratio of atmospheric and fuel samples obtained at Oildale ranged from +2 to +7 ($\delta^{34}S\%$). Surface and subsoil layers between 800 and 2500 ft elevation (the area close to Bakersfield) were in the range of -12 to 0. Across the whole range of elevation difference from 800 to 7200 ft, the mean $\delta^{34}S$ of the 0-5 cm layer was always more positive than subsoil layers, but differences were not significant ($p < 0.05$). The $\delta^{34}S$ of pine needle sulfur became more positive with increasing elevation; slopes were significant for the Greenhorn Mountain ($p < 0.05$) and Breckenridge Mountain ($p < 0.01$) transects. The $\delta^{34}S$ trend in soils and plant tissue runs counter to the expected result because the isotopic composition is more similar to the source area at greater distances from the source where total sulfur content of surface soil and plant tissue is the lowest. One interpretation is that the moderately negative soil $\delta^{34}S$ at lower elevations tends to dilute the input of sulfur with a positive $\delta^{34}S$ from the atmosphere. Comparisons of the $\delta^{34}S$ of pine needle tissue with surface and subsoil layers between 3000 and 7000 ft show that foliage isotopic composition is more positive than all soil layers on both transects, but the difference is not significant. This comparison suggests that atmospheric deposition at elevations above 3000 ft may originate from a source area where the isotopic composition of the atmosphere ranges up to +7. Additional sampling of the atmosphere, soils and plant tissue is required in order to obtain a better evaluation of sulfur isotope composition in both polluted and pristine environments in California.

Two experiments in which recently germinated seedlings of digger, ponderosa and Jeffrey pines and giant sequoia were exposed to mixtures of ozone and sulfur dioxide showed significant reduction ($p < 0.05$) in root growth from 10 pphm SO_2 and 20 pphm O_3. Top growth reductions were significant less frequently at the above concentrations. Exposure to 5 or

10 pphm of SO_2 alone occasionally stimulated both top and root weight compared to the filtered air control. Root growth rates are very important during the early phases of seedling establishment. These results suggest that forest regeneration may be affected if pollutant mixtures were present.

Mixed gas fumigations of older pine and giant sequoia seedlings served to help in the identification of the symptoms of single and mixed gas injury by ozone and sulfur dioxide on older foliage comparable to adult trees. Visible injury ratings showed significant interactions between pollutants resulting in greater than additive injury from concentrations as low as 5 pphm sulfur dioxide and 10 pphm ozone. These concentrations could be reached frequently in atmospheres downwind from uncontrolled sulfur dioxide sources.

Surveys of forest vegetation in the Greenhorn District of the Sequoia National Forest encompassing the Greenhorn, Breckenridge and Piute Mountain areas have shown increases of ozone damage to pines at selected sites between 1977 and 1981. Foliar symptoms did not suggest that sulfur dioxide was acting jointly with ozone to cause existing injury.

Ozone pollution in the San Joaquin air basin shows no trend toward improvement (California Air Quality Data, Vol. XIV, No. 3). The protection of forest resources from further deterioration is extremely difficult if only ozone is involved. The introduction of additional sources of sulfur dioxide to the basin could accelerate forest deterioration if concentrations of both pollutants reach levels where joint action may cause additives or more than additive injury. The air monitoring and transport phases of this study suggest that the introduction of tall stacks may cause pollutants to accumulate in laminae at heights equivalent to the elevations of forested slopes and ridges at locations where most of the mass transfer of pollutants to the east takes place. This possibility requires further study.

II. CONTINUOUS MEASUREMENTS OF POLLUTANTS AND METEOROLOGICAL VARIABLES

INTRODUCTION

A survey of sulfur dioxide and sulfate in the Bakersfield area in 1977 and 1978 showed that the sulfur dioxide air quality standard was exceeded on 68 days in 1978 alone. This was the greatest number of occurrences of concentrations exceeding the 24-hour standard in the state. Sulfate levels were also exceptionally high (Duckworth and Crowe 1979). In the same survey, ozone maximum hourly concentrations in the range of 0.10 or 0.13 ppm frequently accompanied daily average sulfur dioxide concentrations of 0.052-0.076 ppm, particularly during the April through October period. The occurrence of frequent episodes of the combined pollutants raises concern about the possible additive or synergistic injury that may occur to both agricultural crops and native vegetation.

The dispersion of air pollution from the Bakersfield-Oildale area during the summer months is heavily influenced by the general up-valley flow from the northwest (Unger 1974). The mountain barriers formed by the Tehachapi and the Greenhorn Mountains have an important modifying effect on dispersion by guiding portions of the polluted air mass into up-canyon and up-slope flows in the afternoon. In other sections of the Central Valley to the north, the air quality data support the conclusion that ozone transport to the windward slopes of the Sierra results in elevated concentrations (Unger 1978, Miller and McCutchan 1972, Carroll and Baskett 1979).

The purposes of this portion of the study were to observe the summer month concentrations of ozone and sulfur dioxide in the lower Kern River Canyon and the Greenhorn Ridge and compare these with those at Oildale; observe the relationship of pollutant concentrations to surface winds, temperature and relative humidity on a monthly basis; compare pollution concentrations and surface meteorological variables during distinct synoptic patterns and to participate in a multi-agency transport study centered around a one-day release of SF_6.

PROCEDURES

Democrat Springs (2400 ft) was the only monitoring station operated in September and October 1981. During the July through October period in 1982, stations were maintained at both Democrat Springs and Shirley Meadow Ski Area (6400 ft), Figure II-1.

At Democrat Springs, the instruments were housed in an air conditioned trailer, and at Shirley Meadow a concrete block building was used; at 6400 feet, the daytime temperatures were usually not high enough to require air conditioning. At both stations, the air monitoring instruments sampled from the center of an air stream flushed down a vertical pipe (six inches in diameter); the shielded intake was between 20 and 30 feet above the ground.

Monitor Labs Model 8850 sulfur dioxide analyzers and Dasibi Model 1003AH ozone analyzers were used at both stations. Field calibrations were done by the Air Resources Board, Division of Technical Services on September 24 and 30, 1981 and on August 4, 1982. Data was recorded on strip chart recorders. All instruments were checked and serviced once weekly.

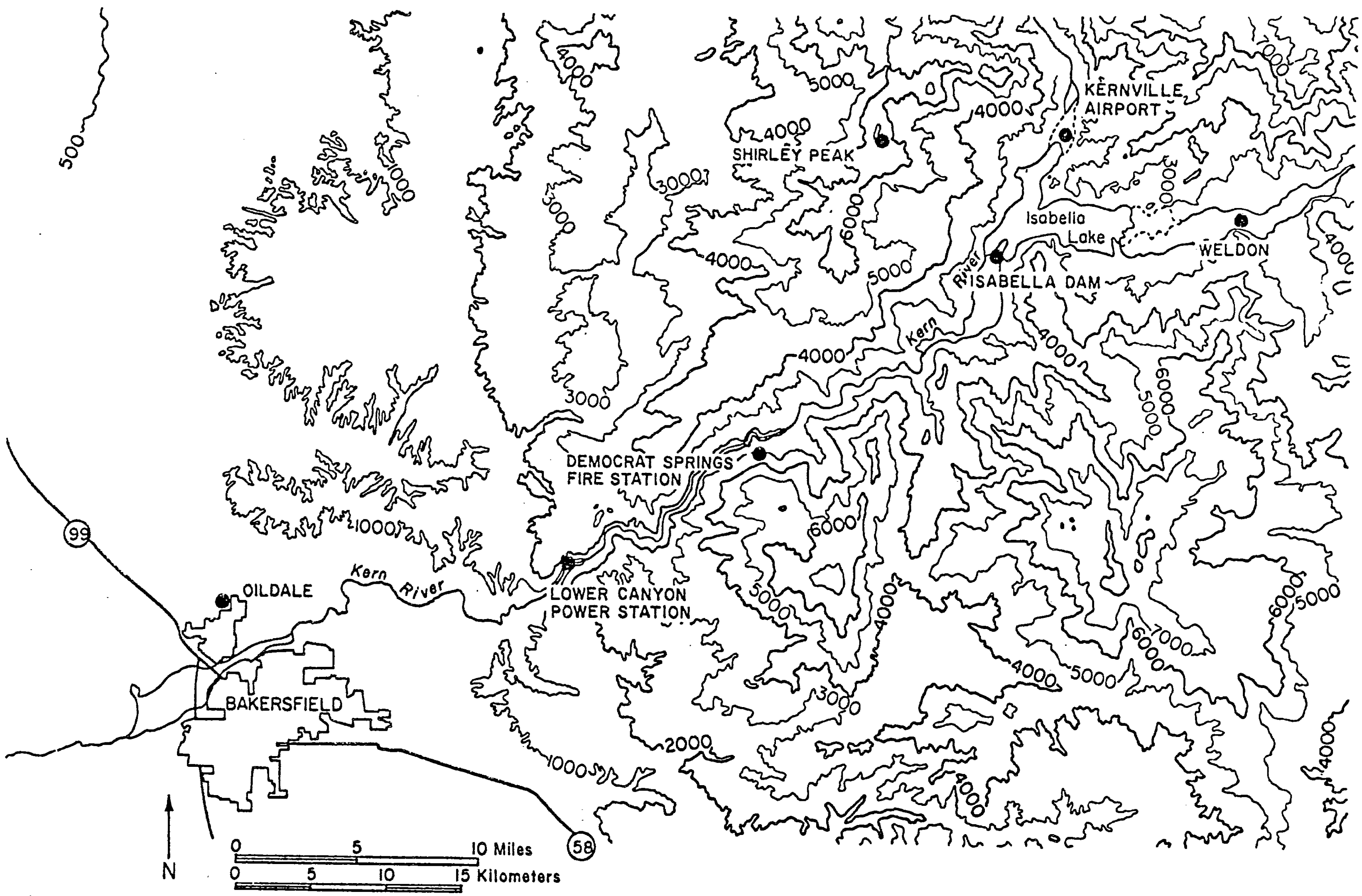


Figure II-1. Topographic features of the Bakersfield-Kern River drainage area showing locations of continuous air monitoring sites at Democrat Springs and Shirley Peak.

Wind direction and wind speed were measured at a height of 20 feet at both stations using Climatronics and MRI equipment. Air temperature and relative humidity were measured at four feet using Climatronics sensors or hygrothermographs in standard enclosures. Temperature and relative humidity sensor calibration was checked weekly with an aspirated psychrometer.

Monitoring was done from September 1 to October 28, 1981 and from July 8 to October 27, 1982. On September 15 and 16, 1982 an intensive study was done to investigate the transport of pollutants from the Bakersfield area using four additional surface wind stations, a tetroon tracking system and an SF_6 tracer release at Oildale. The principal participants included scientists from the California Air Resources Board; University of California, Riverside; U. S. Forest Service, Fire Laboratory; State Air and Industrial Hygiene Laboratory; California Institute of Technology; Sonoma Technology, Inc. and the China Lake Naval Weapons Center. A detailed account of surface wind and the tetroon tracking results obtained on September 15 and 16 are included in Appendix 1.

RESULTS

Democrat Springs, September-October 1981

The weather during September was normal for this month. October was a little cooler than normal even including substantial snowfall at higher elevations on the 29th. A description of the relationship between weather and pollutant concentrations at the Democrat Springs station follows for September and for selected days in October. The variables described are temperature, relative humidity, surface winds and synoptic weather patterns in relation to ozone and sulfur dioxide concentrations.

The average hourly values for the selected variables in September are summarized in Figure II-2a, b and c for the 0900-1900 period. At 1500 hours, the average maximum temperature was 31^{o}C with a corresponding relative humidity of 30%; at this hour the daily up-canyon flow (250 degrees azimuth) reached its maximum of 6 mph. The average hourly maximum ozone concentration also reached a maximum of 10.2 pphm at 1500 hours and sulfur dioxide reached its average hourly maximum of 3 ppb at 1400 hours (Figure II-2c). In September, the maximum hourly concentrations for ozone and sulfur dioxide were 15 pphm and 3 ppb, respectively.

In October, duration of detectable sulfur dioxide was from 1000-2200 hours compared with 1200-1900 hours in September (Figure II-3a). The concentration remained at about 4 ppb from 1400-1600 hours in October. In September, it peaked at 1400 with a maximum of 3 ppb. The difference in average concentrations between months was the opposite for ozone because ozone concentrations were lower in October (Figure II-3b). However, due to Dasibi lamp failure only 20 days of ozone data were available for October, so these hourly averages are not representative of the whole month.

The interval including October 20-27, 1981 was characterized by several consecutive days with higher afternoon sulfur dioxide concentrations. In Figure II-4a, b and c, the hourly average temperature, relative humidity, winds and pollutant concentrations are shown for this period. In contrast to September days with lower sulfur dioxide, October 20-27 show lower temperatures, similar relative humidities, a shorter duration of up-canyon winds in the afternoon and a wind speed sustained at 3 mph even after wind direction shifted to the evening down-slope direction (170-180 degrees).

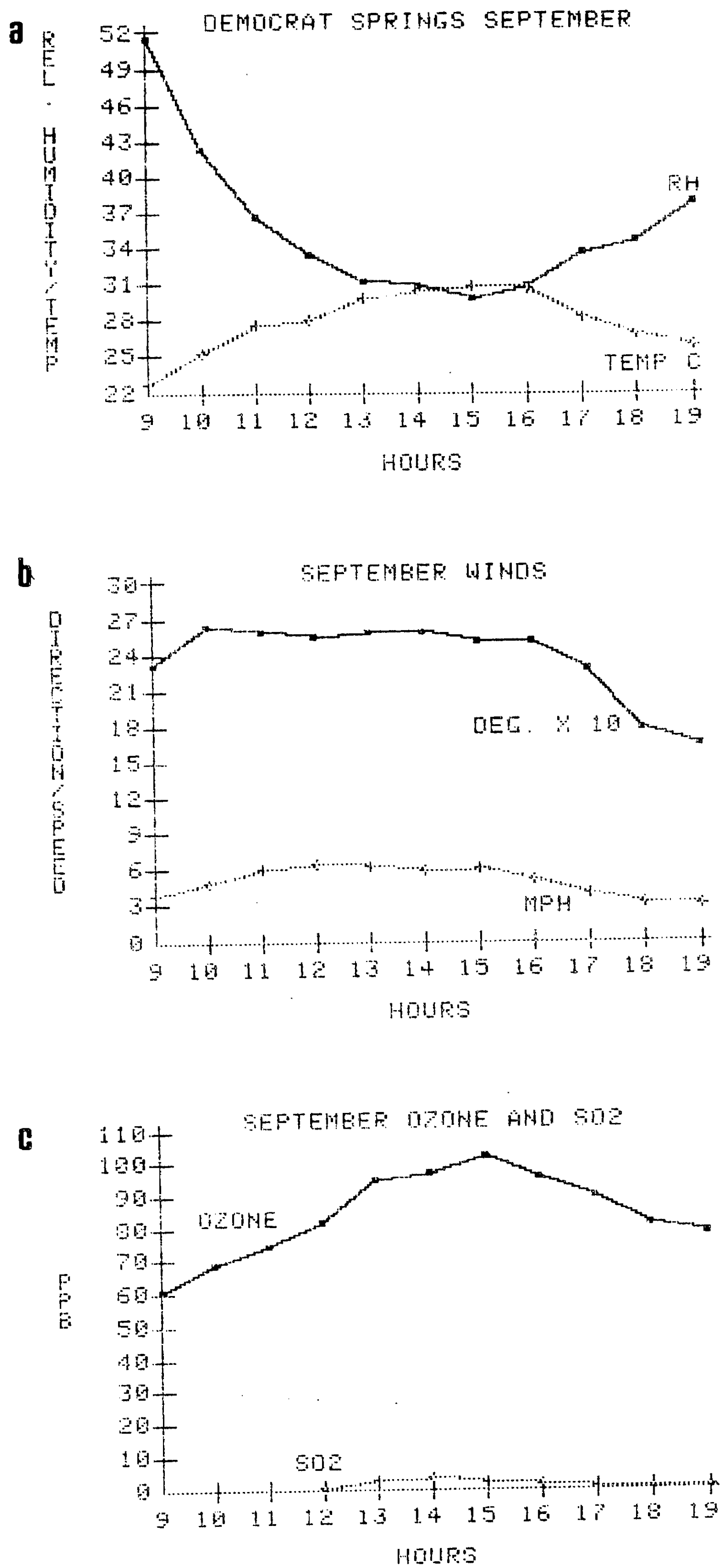
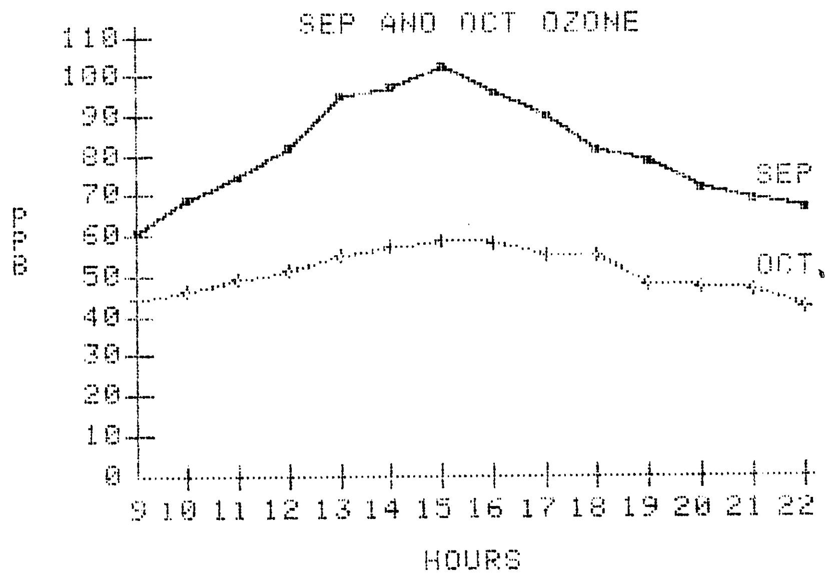


Figure II-2. (a) Temperatures, relative humidities, (b) winds, (c) ozone and sulfur dioxide at Democrat Springs in the Kern River Canyon during September 1981.

a



b

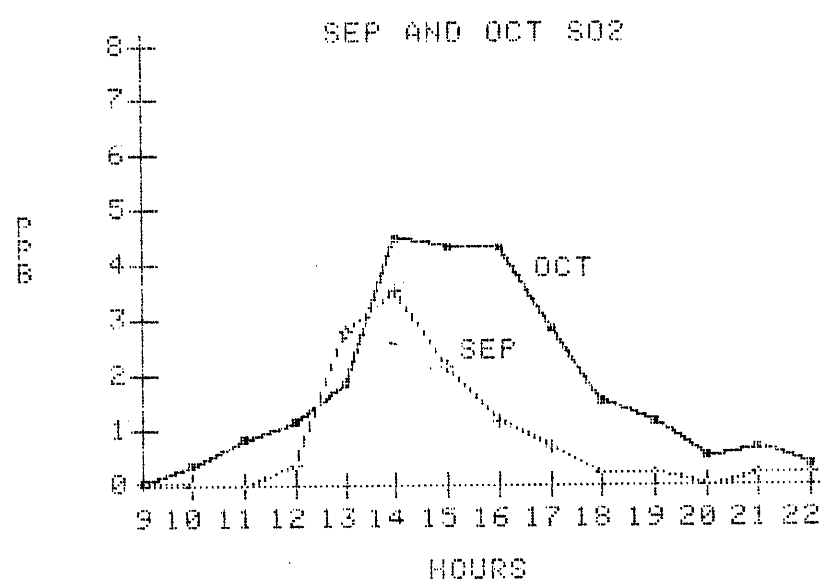


Figure II-3. Comparison of average hourly concentrations for (a) ozone and (b) sulfur dioxide during daylight hours of September and October 1981 at Democrat Springs in the Kern River Canyon.

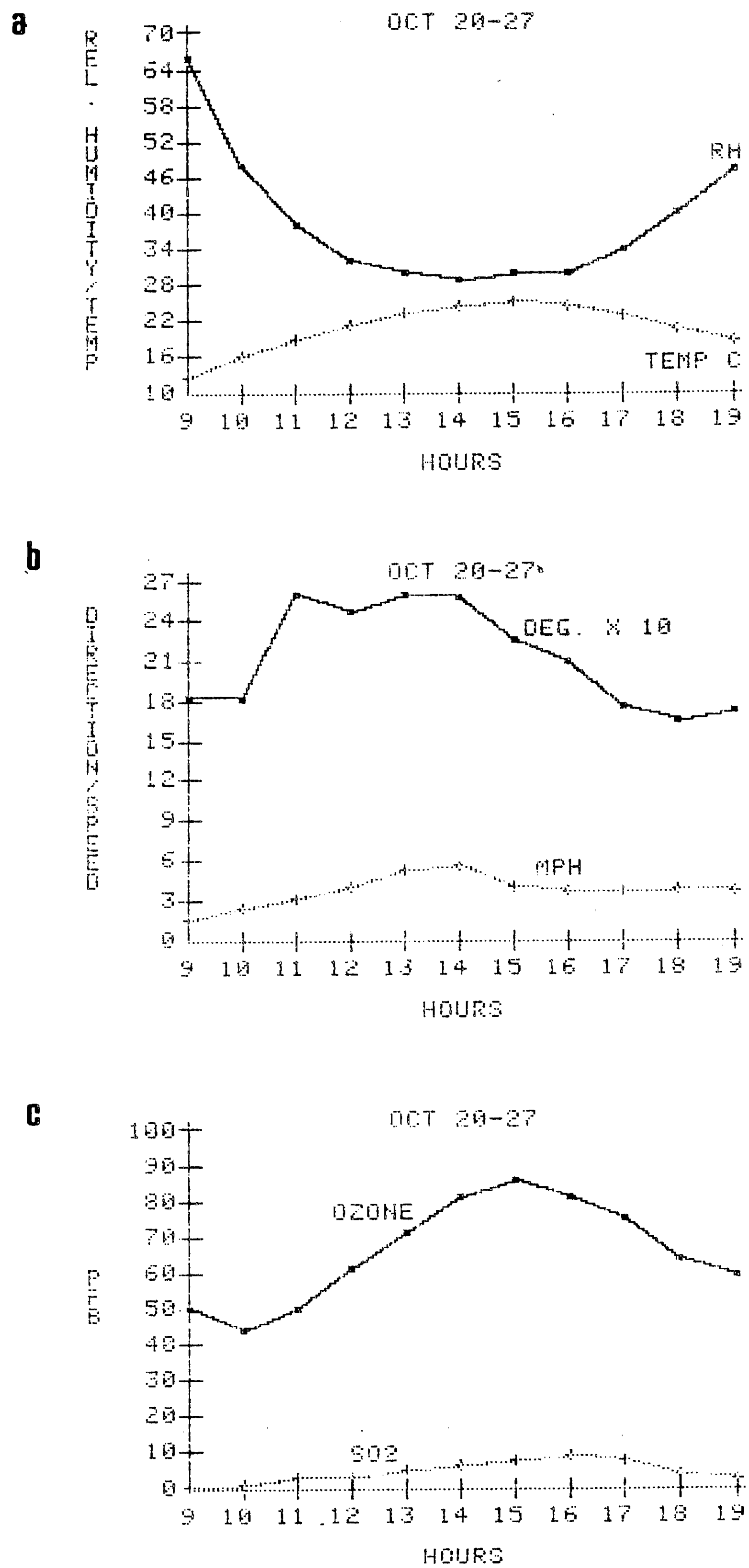


Figure II-4. (a) Temperatures, relative humidities, (b) winds, (c) ozone and sulfur dioxide at Democrat Springs in the Kern River Canyon during October 20-27, 1981, a period with relatively high sulfur dioxide.

October 15 and 25 were selected for further study of the influence of synoptic weather on surface winds at both Bakersfield and Democrat Springs and hence on pollutant transport up-canyon. On the 15th, sulfur dioxide was almost below detection (<1 ppb), while on the 25th the concentration reached the highest value (20 ppb) measured during the entire September-October period.

On October 15, 1981, an elongated surface high pressure system extended from Washington State to Nebraska, and a surface low was centered over northern Mexico. This created an offshore surface pressure gradient (higher surface pressure to the northeast) between Bakersfield and Tonopah, Nevada and a fairly strong onshore gradient between Bakersfield and Las Vegas. As the day progressed, a surface low was forming over Utah as surface pressure was building along the coast. By the end of the day, this had created higher surface pressure at Bakersfield than at both Tonopah and Las Vegas.

The main synoptic weather feature on October 25, 1981 was a weak surface high centered near Salt Lake. A weak surface trough extended from Yuma, Arizona to northern California early that morning. The surface pressure gradient between Bakersfield and both Tonopah and Las Vegas was in an offshore direction for the entire day. Because of a surface high building just off the coast of southern California surface pressure was higher at Los Angeles than at Bakersfield.

Winds at Democrat Springs on the mornings of both October 15 and 25 veered from south-southeasterly to westerly as they often do under days with weak synoptic patterns. The main difference, however, was that on October 15, winds from 0900 on generally remained from a westerly direction until 1700, but winds on October 25 became north-northeasterly at 0900 and remained steady from that direction until near 1300. Windspeeds during this time were slightly stronger than those on the 15th, and also when westerly winds prevailed after 1300, they were from 3-4 mph stronger than those on the 15th.

At Democrat Springs on October 15, ozone remained at background concentrations all day, and sulfur dioxide was barely detectable (1 ppb) for one hour. On October 25, ozone concentrations were average, but the most interesting feature of this day is the 20 ppb sulfur dioxide peak which appeared abruptly at 1300 hours.

To further explain the type of wind pattern found at Democrat Springs on the 25th, winds at Bakersfield would need to be examined. On October 25, Bakersfield had opposing winds during the late morning-early afternoon hours from those of Democrat Springs (until near 1300). This would have naturally created a frontal area of the two different air masses--that from the north-northeast at Democrat Springs and that from a westerly direction at Bakersfield. For example, if Bakersfield had had the same northerly flow as recorded at Democrat Springs, the air at both places would be of the same source--no frontal area would prevail. When winds did become westerly at Democrat Springs, the 8 mph speed was sufficient to rapidly move the sulfur dioxide accumulated in the frontal area from the Bakersfield region into the Democrat Springs area or other canyon areas where the northerly flow had subsided.

Comparison of Oildale O_3 and SO_2 with Democrat Springs and Shirley Meadow, July through October 1982

The differences among the means of maximum hourly concentrations of ozone and sulfur dioxide at Democrat Springs and Shirley Meadow are compared with Oildale, Table II-1. Maximum hourly ozone concentrations at

Table II-1. Comparison of Maximum Hourly Concentration Means for Ozone and Sulfur Dioxide at Oildale, Democrat Springs and Shirley Meadow in 1982

Month	Oildale[a]/Democrat		Oildale/Shirley		Democrat/Shirley	
	No. Days	Means	No. Days	Means	No. Days	Means
Ozone (pphm)						
Jul	24	11.9/12.3[b]	15	9.0/8.9	15	12.0/8.9
Aug	25	8.6/10.1	31	8.4/11.3	25	10.1/11.4
Sept	26	7.6/10.1	30	7.1/8.6	26	10.1/9.0
Oct	21	5.6/7.0	26	5.8/7.0	20	7.0/6.6
Sulfur Dioxide (ppb)						
Jul	22	29.0/9.0	16	30.2/0	15	7.6/0
Aug	31	35.0/7.0	24	36.0/3.0	24	7.5/3.0
Sept	31	31.0/5.0	31	31.0/3.0	30	5/3.0
Oct	27	36.0/7.3	27	36.0/1.4	27	7.3/1.4

[a]Oildale (Manor) data obtained from California Air Quality Data, Vol. XIV, Numbers 3 and 4.

[b]Oildale mean/Democrat Springs mean.

Democrat Springs and Shirley Meadow were between 1 and 2 pphm higher than Oildale in seven of eight possible comparisons. Regardless of the source of ozone at these remote sites, the higher concentrations are due primarily to the older "photochemical age" of the air mass compared to Oildale.

Sulfur dioxide concentrations at Democrat Springs were usually about one-fifth of Oildale, while those at Shirley Meadow were one-tenth of those at Oildale. It is probable that the lower concentrations at Democrat Springs represent downwind dilution of sulfur dioxide originating at Oildale because the lower Kern River Canyon is the most likely transport route from Oildale. At Shirley Meadow, it is much more difficult to implicate a single source; the one- to two-hour long traces of 3-5 ppb could have originated from a series of urban/industrial sources in the San Joaquin Valley.

Characteristics of Air Monitoring and Meteorological Variables at Democrat Springs and Shirley Meadow During July Through October 1982

Hourly values for ozone, sulfur dioxide, windspeed, wind direction, wind run, air temperature and relative humidity are included in Appendix 2. The following sections contain a more detailed analysis of this data base.

For each month, we have examined ozone and sulfur dioxide data in terms of the frequency distribution of concentrations and the average hourly concentration for each hour; Shirley Meadow and Democrat Springs are compared in Figures II-5, II-6, II-7 and II-8. The primary interest here is to identify possible effects of terrain features, difference in elevation and distance from the source area on pollutant concentrations. Democrat Springs is located 21 miles east of Oildale at an elevation of 2400 feet in the Kern River Canyon. Shirley Meadow is on the crest of the Greenhorn Ridge at 6400 feet and is 32 miles northeast of Oildale (Figure II-1). We cannot predict the effect of terrain, elevation and distance from this limited data base, but some inferences can be made about pollutant doses at the two locations.

The frequency distribution of ozone concentrations indicated higher concentrations at Democrat Springs during July and August (Figures II-5a and II-6a), but not in September and October (Figures II-7a and II-8a). The diurnal pattern of ozone concentrations at both stations indicates the

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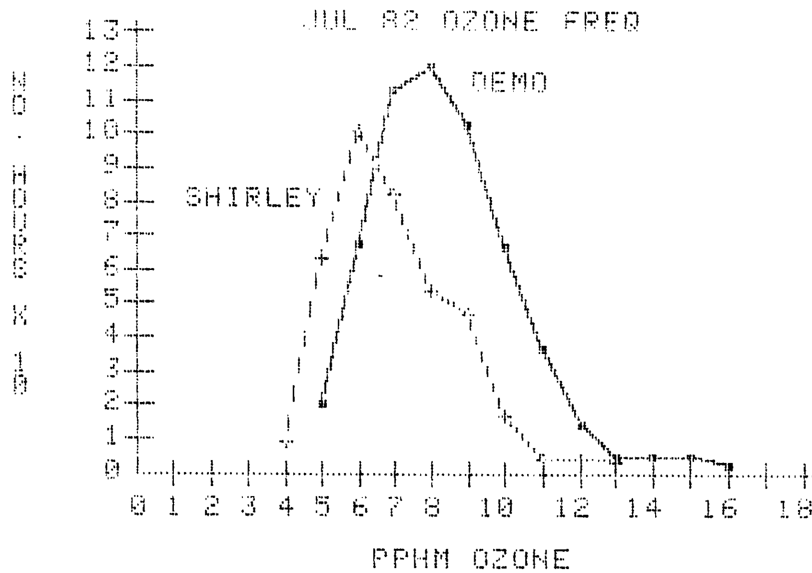

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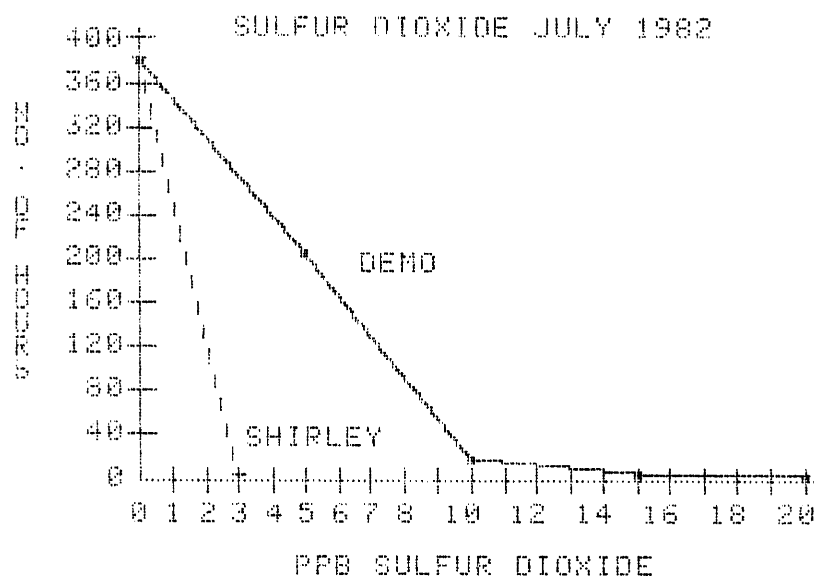

Figure II-5. Frequency distributions for July 1982 of hourly averages of (a) ozone and (b) sulfur dioxide concentration, (c) wind direction, and (d) wind speed, including diurnal changes in hourly averages of (e) ozone, (f) SO_2, (g) temperature and (h) relative humidity.

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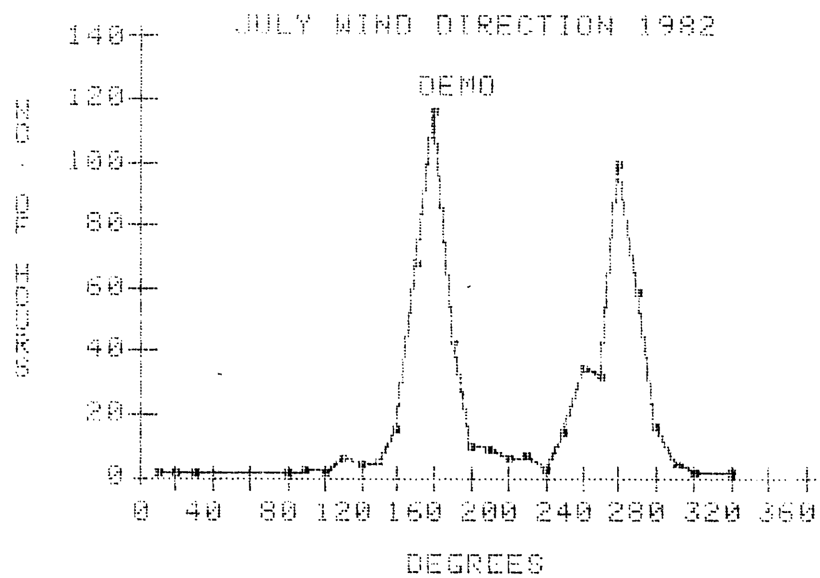

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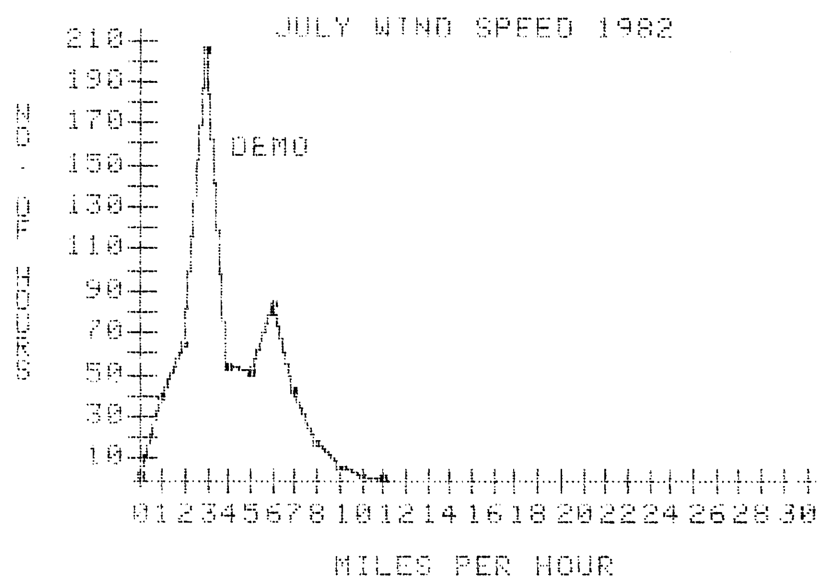

Figure II-5. (Continued)

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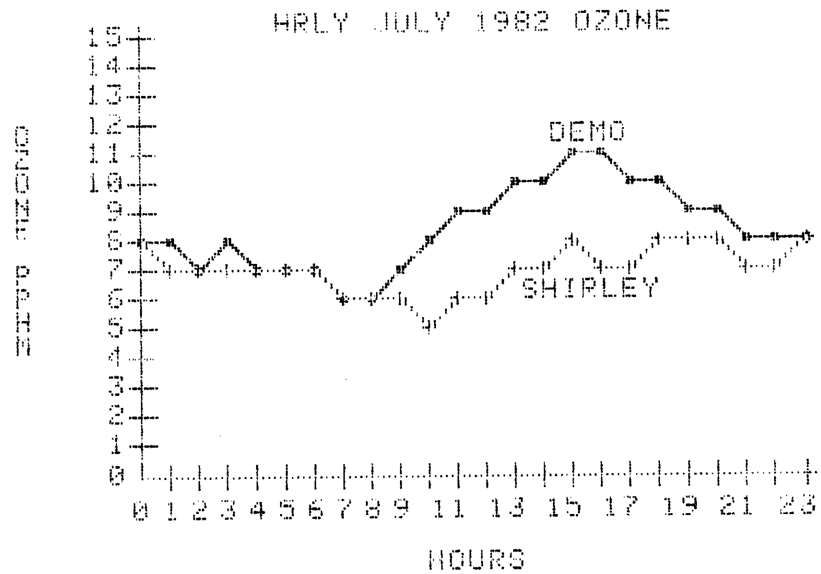

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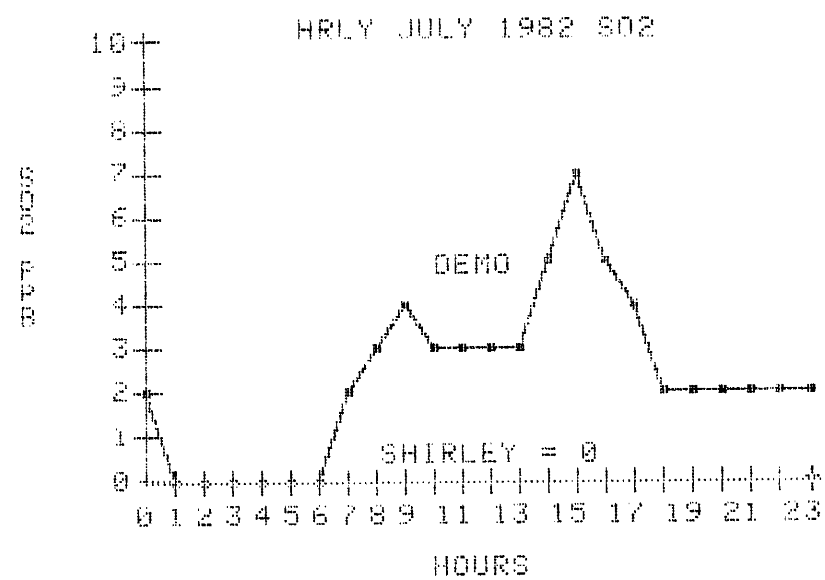

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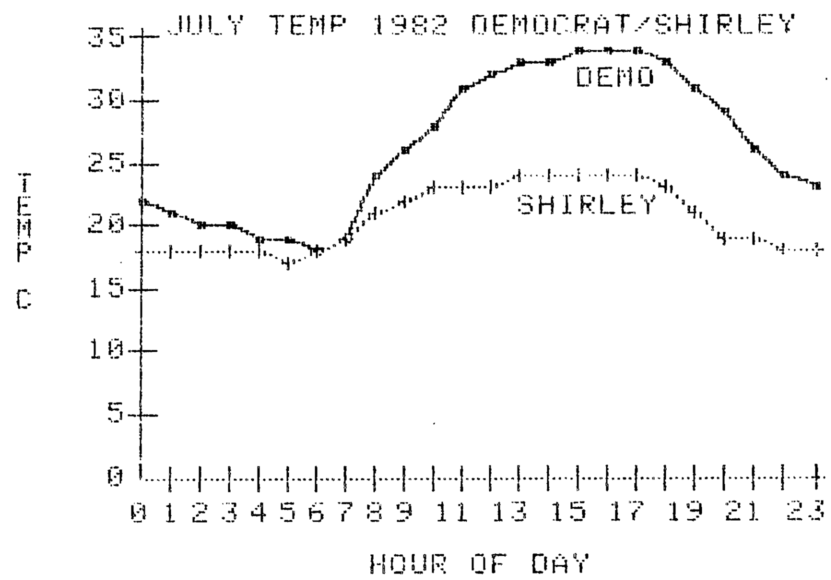

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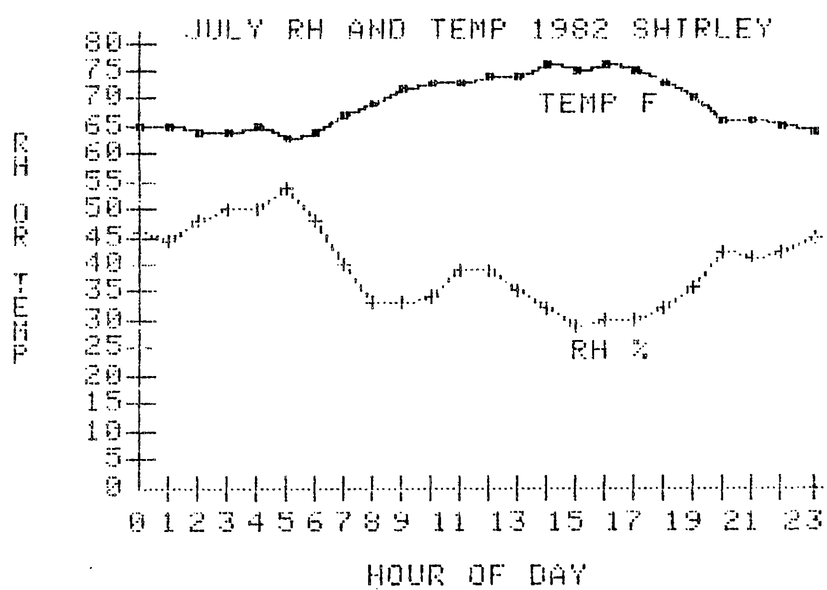

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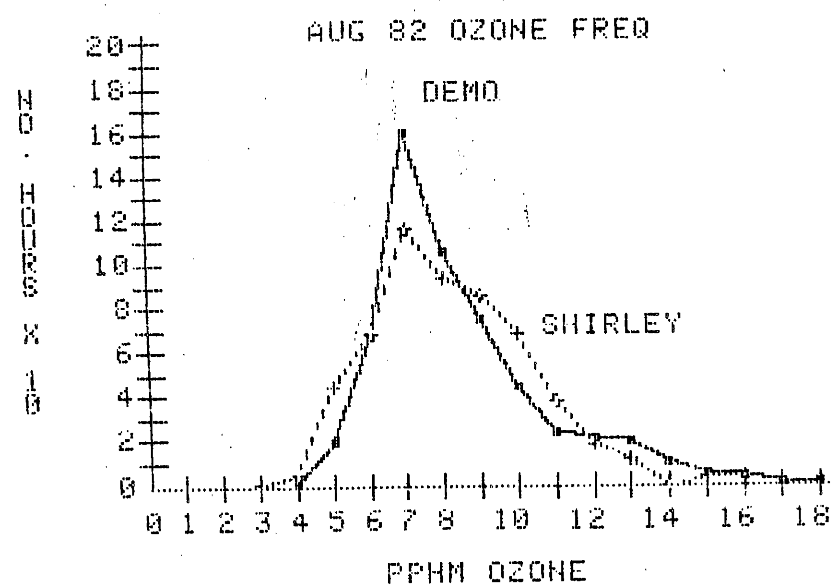

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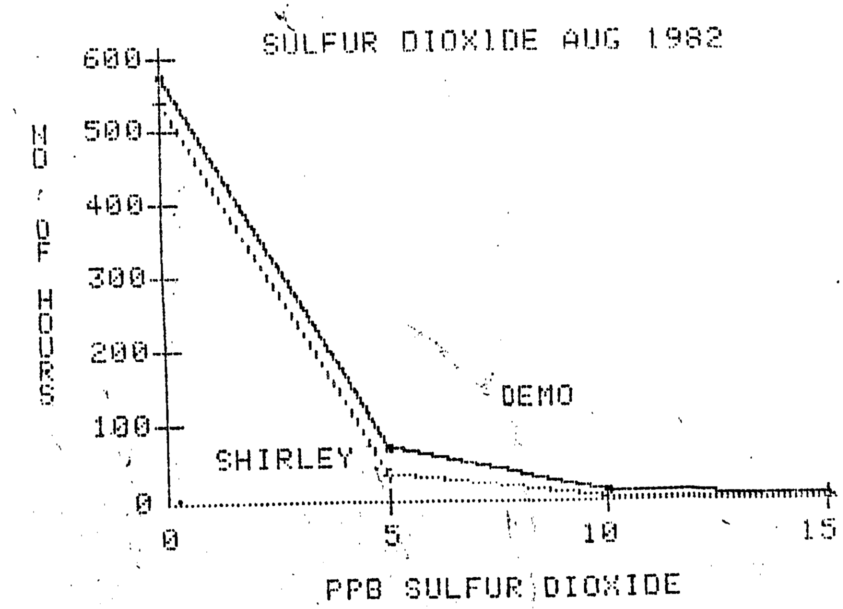

Figure II-6. Frequency distributions for August 1982 of hourly averages of (a) ozone and (b) sulfur dioxide concentrations, (c) wind direction, and (d) wind speed, including diurnal changes in hourly averages of (e) ozone, (f) SO_2, (g) temperature and (h) relative humidity.

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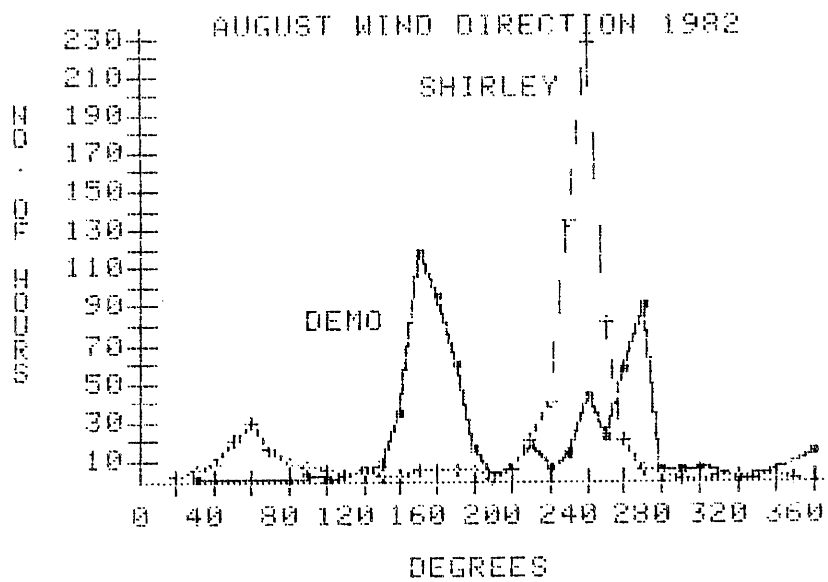

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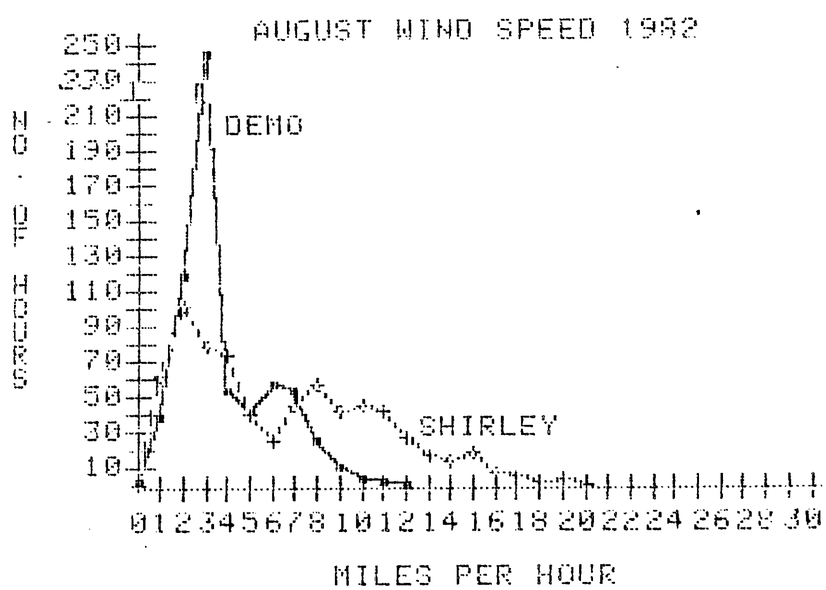

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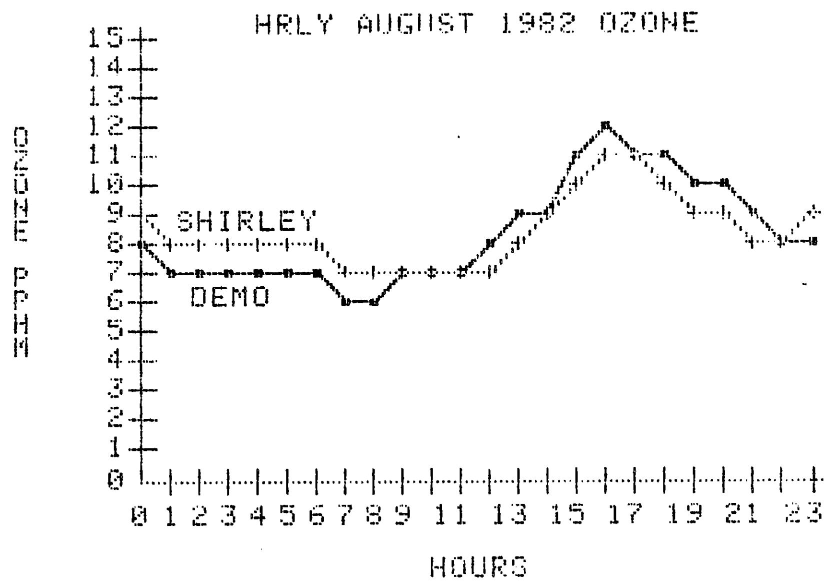

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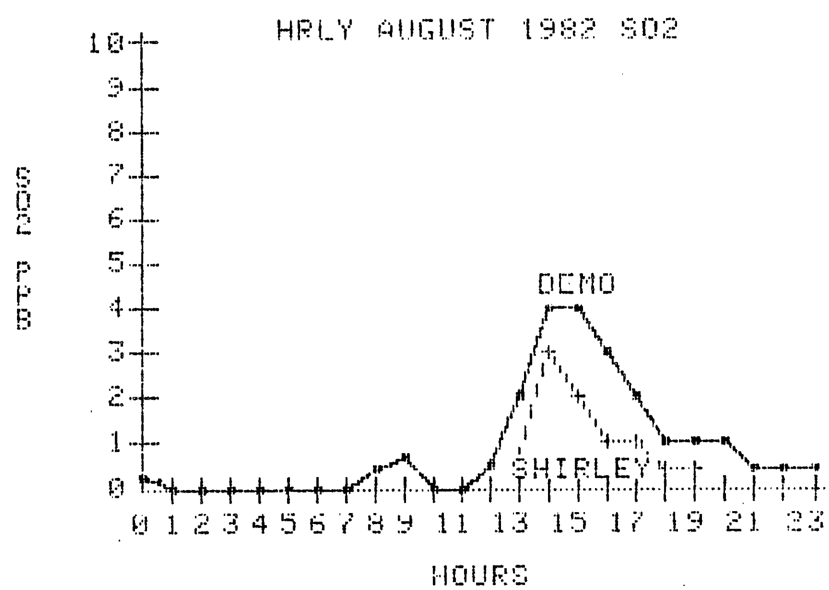

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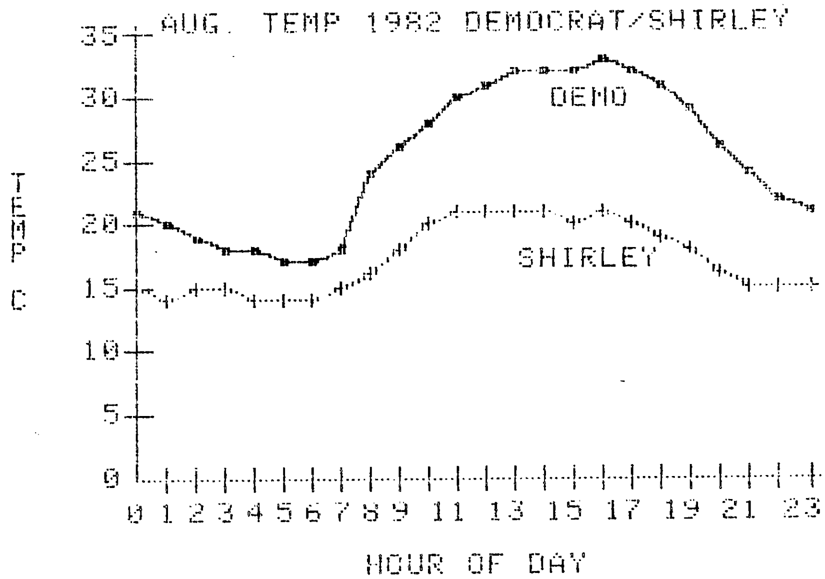

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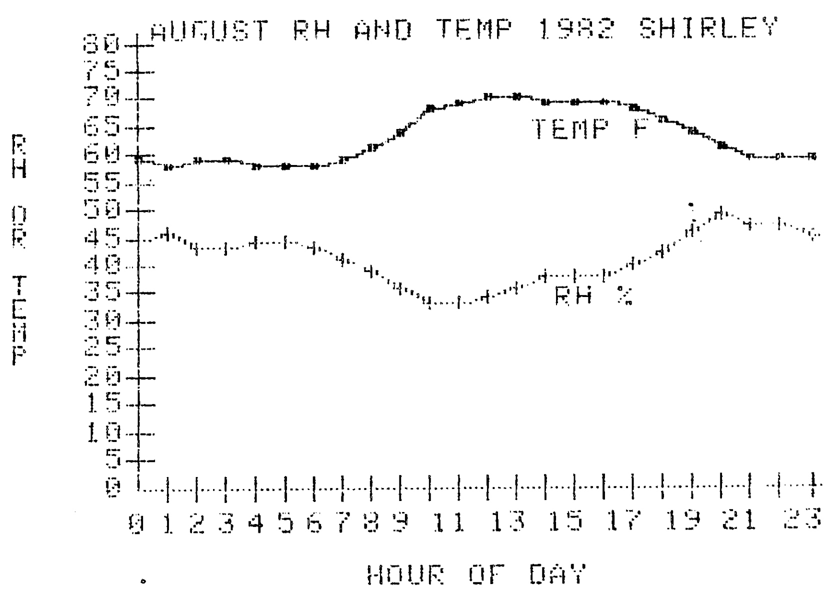

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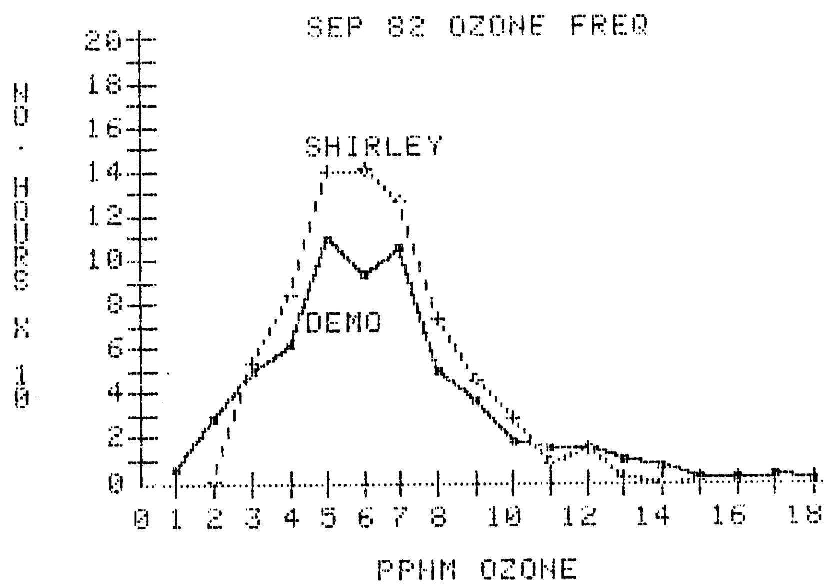

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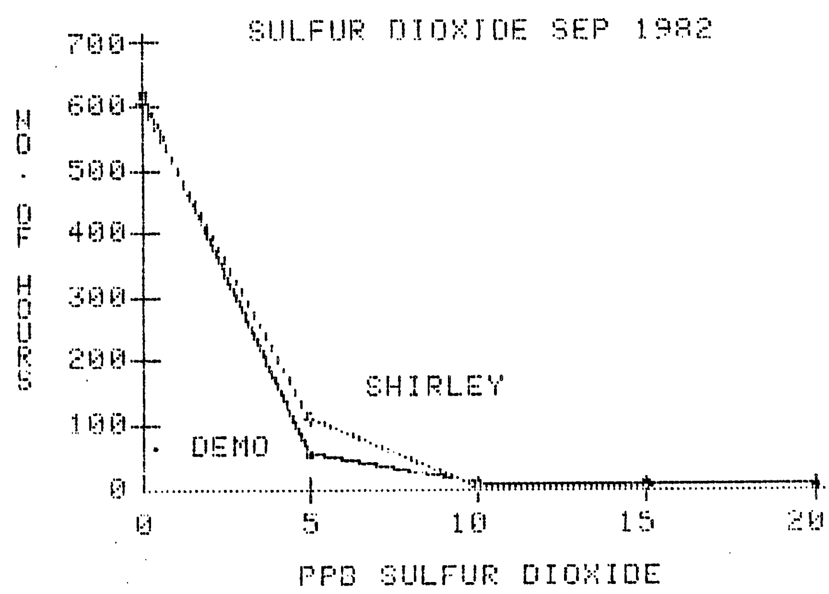

Figure II-7. Frequency distributions for September 1982 of hourly average (a) ozone and (b) sulfur dioxide concentrations, (c) wind direction, and (d) wind speed, including diurnal changes in hourly averages of (e) ozone, (f) SO_2, (g) temperature, and (h) relative humidity.

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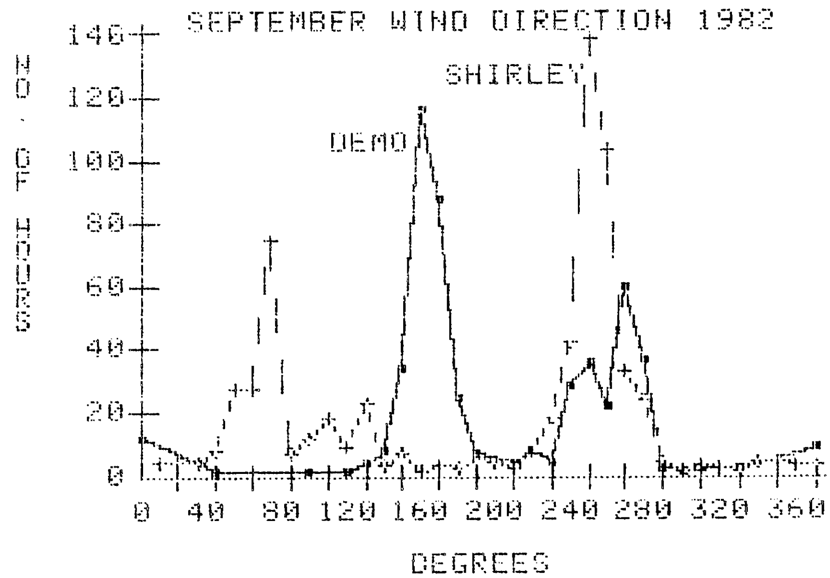

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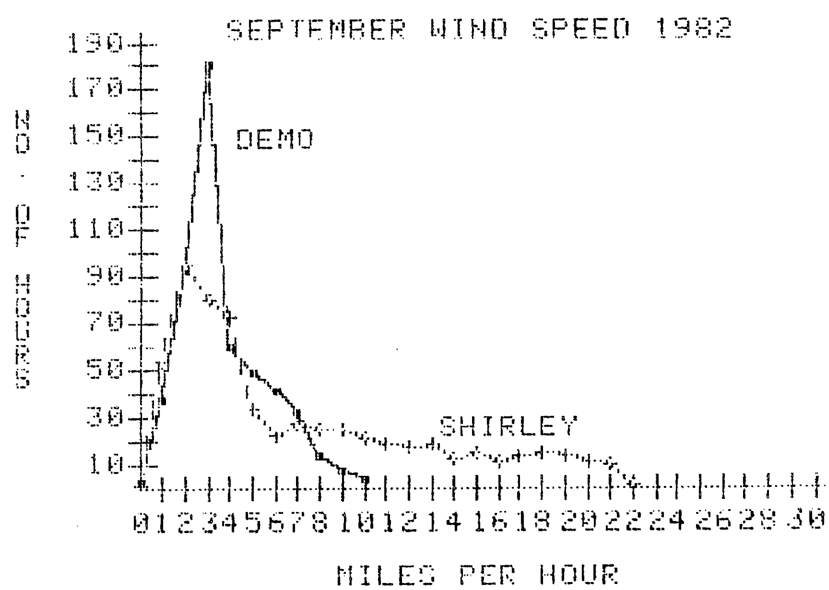

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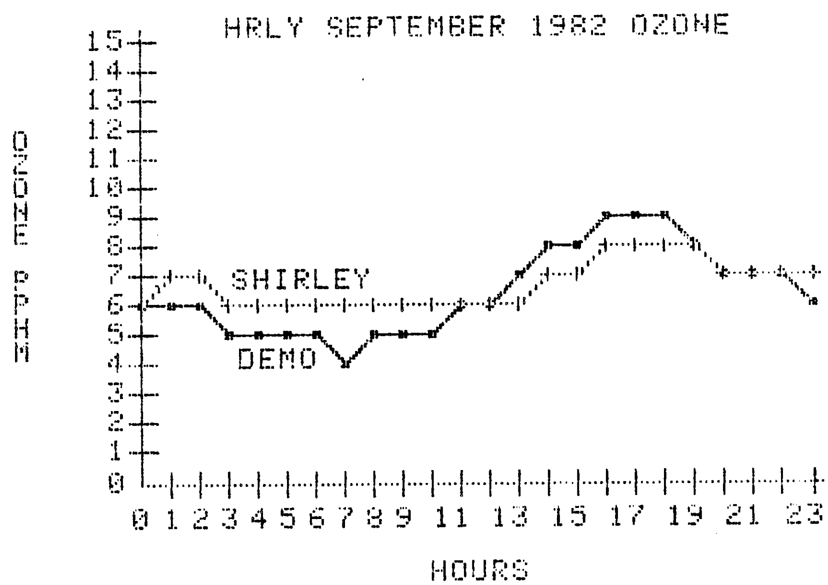

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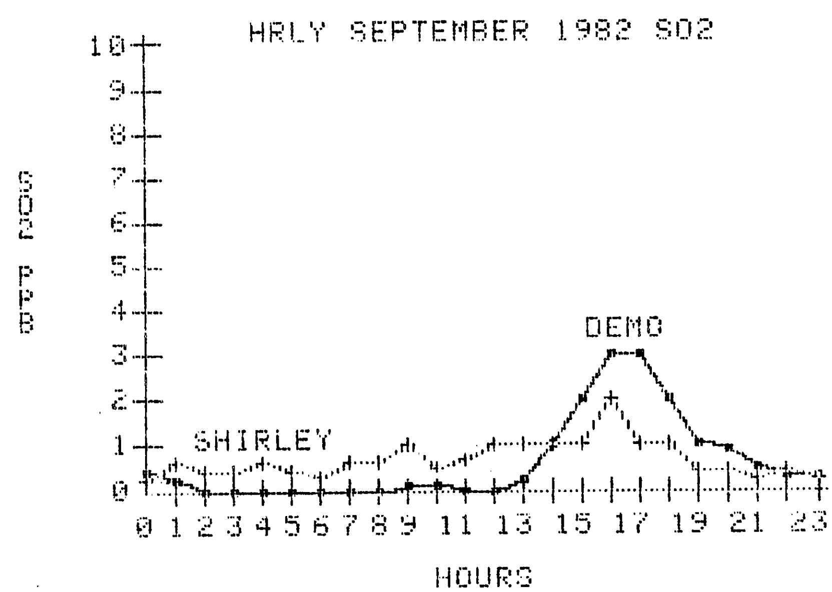

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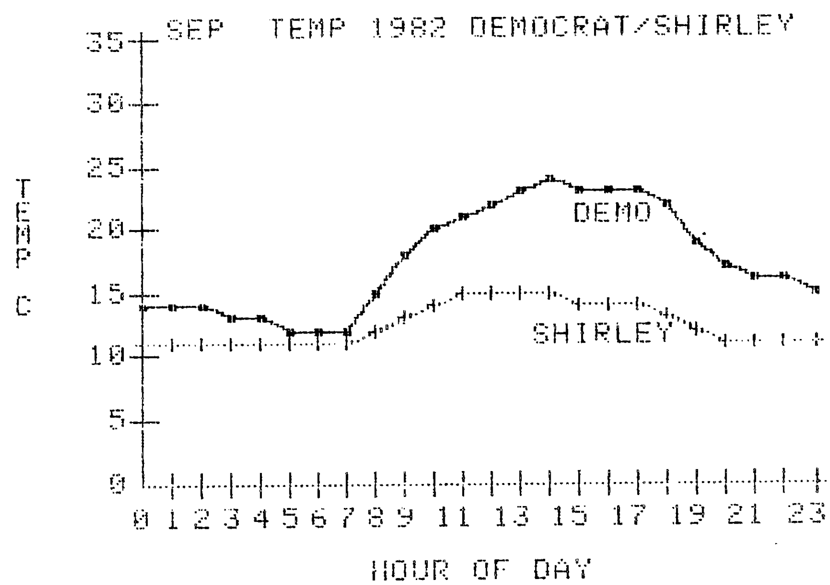

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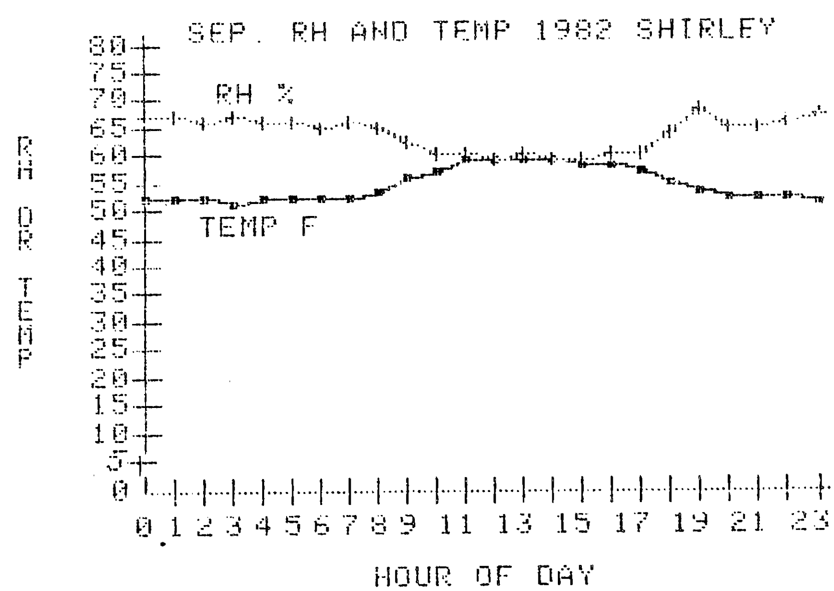

Figure II-7.(Continued)

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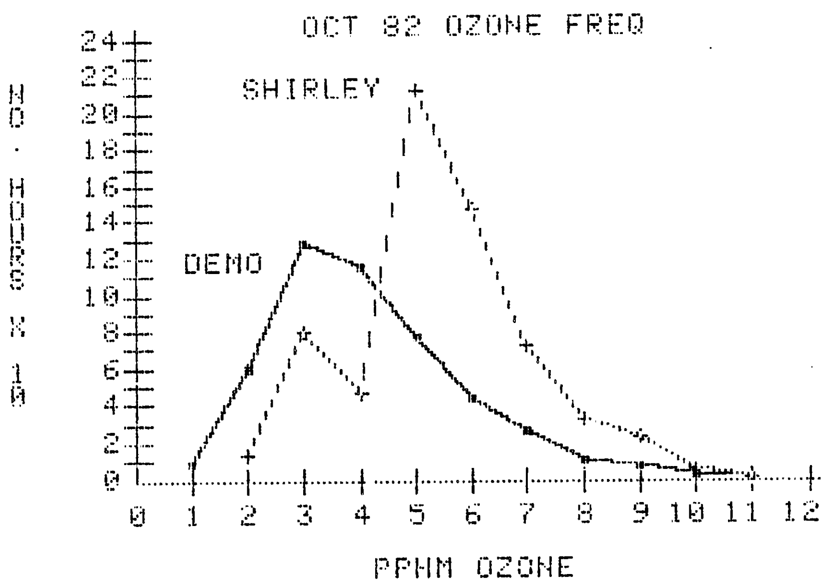

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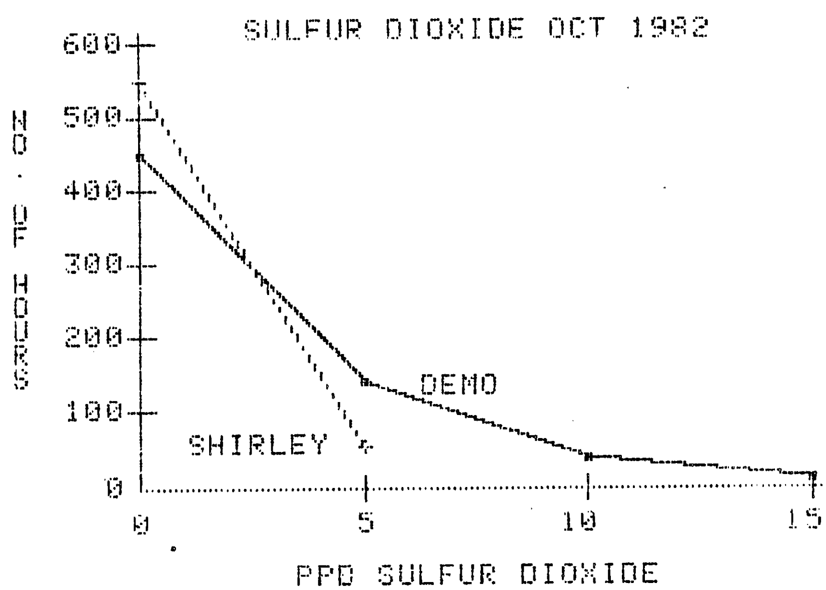

Figure II-8. Frequency distributions for October 1982 of hourly average (a) ozone and (b) sulfur dioxide concentrations, (c) wind direction, and (d) wind speed, including diurnal changes in hourly averages of (e) ozone, (f) SO_2, (g) temperature, and (h) relative humidity.

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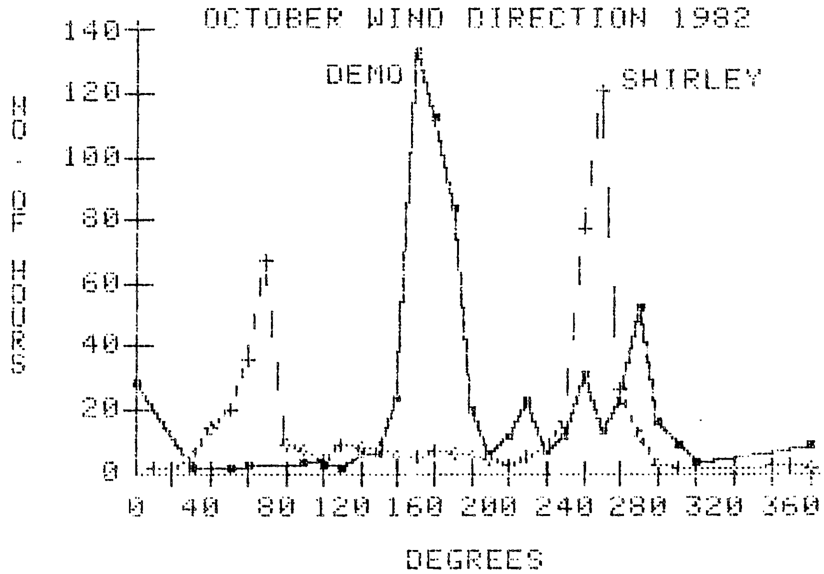

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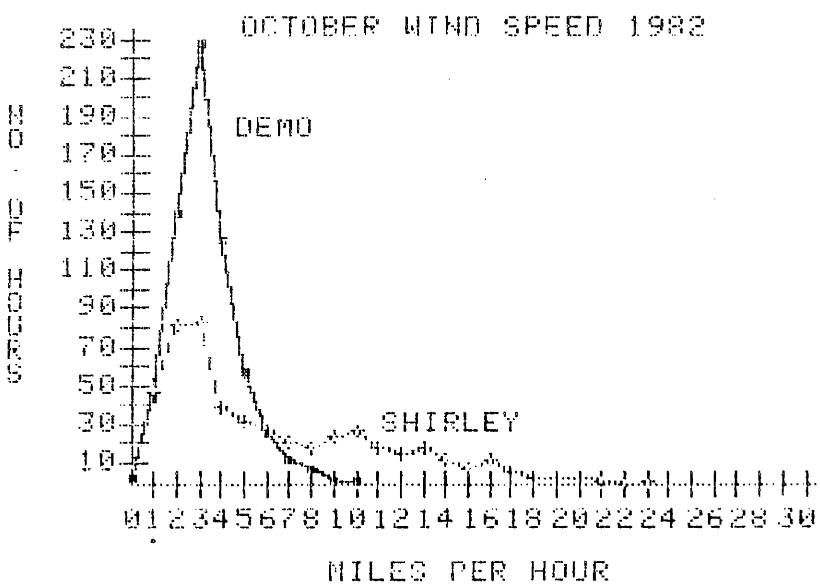

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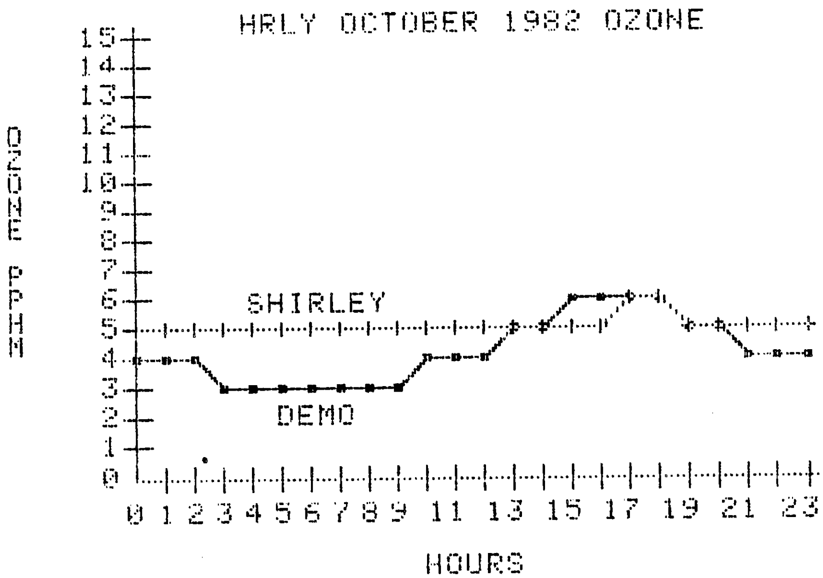

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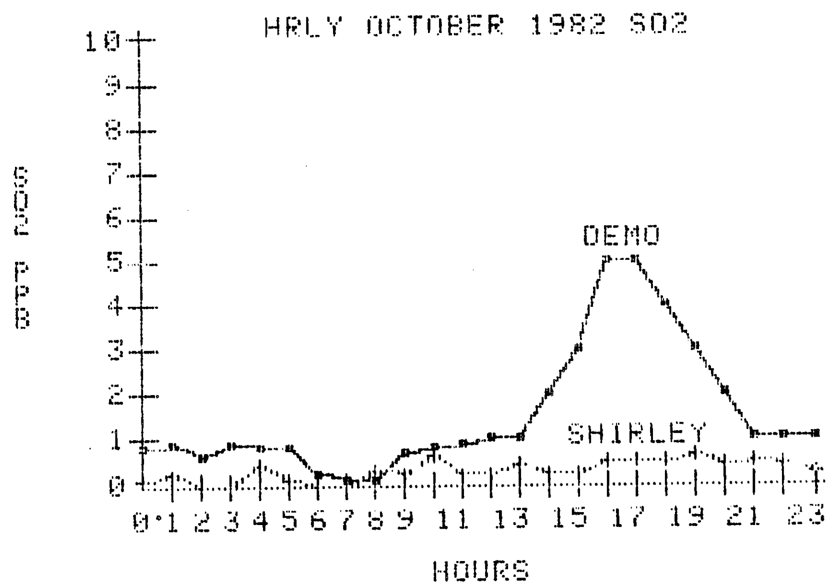

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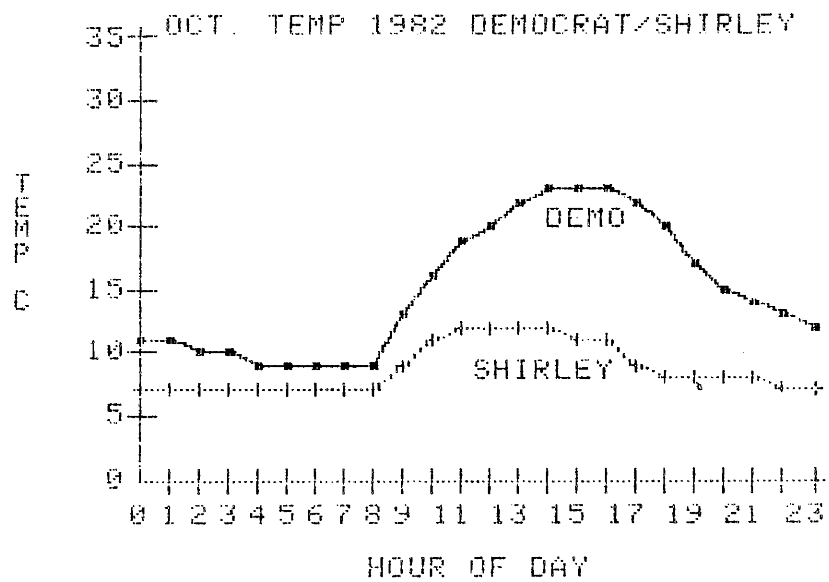

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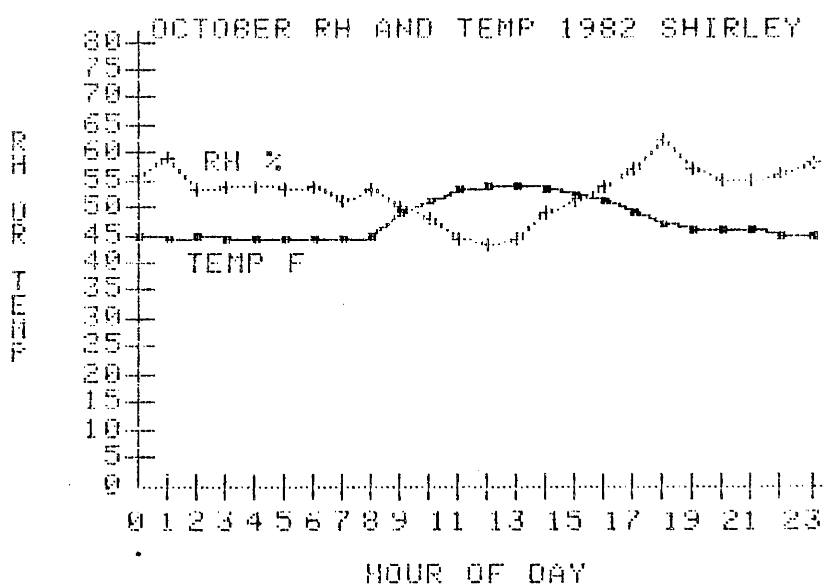

Figure II-8. (Continued)

expected late afternoon-early evening peaks consistent with transport from a distant upwind source area (Figures II-5e, II-6e, II-7e and II-8e). Even though Shirley Meadow is about 14 miles northeast of Democrat Springs, the afternoon ozone peaks occurred at about the same time in August and September (Figures II-6e and II-7e), but in October, the peak occurred two to three hours later at Shirley Meadow (Figure II-8e). In August, September and October, the nocturnal ozone concentrations at Shirley Meadow (6600 ft) were 1-2 pphm higher than at Democrat Springs (2400 ft). This is consistent with findings in other mountainous areas.

Sulfur dioxide hourly maximum concentrations ranged up to 20 ppb at Democrat Springs and 10 ppb at Shirley Meadow on a few occasions (Figures II-5b, II-6b, II-7b and II-8b). The daily sulfur dioxide peak at both stations was concurrent with the late afternoon ozone peak (Figures II-5f, II-6f, II-7f and II-8f). At Shirley Meadow, the average sulfur dioxide concentrations were highest in August and September, while at Democrat Springs, July and October had higher concentrations (Table II-1). The 1981 sulfur dioxide measurements at Democrat Springs also revealed higher concentrations in October compared to September. The cooler surface air temperatures in October (Figure II-8g) may limit vertical mixing; therefore, air masses polluted with sulfur dioxide are transported up-canyon with less dilution.

Frequency distributions for wind direction at Democrat Springs show two dominant flows, namely, daytime up-canyon (270^{o}) and nighttime downslope (160^{o}) from the higher terrain of Breckenridge Mountain (Figures II-5c, II-6c, II-7c and II-8c). This pattern remained fairly constant from July through October; however, the daytime wind speeds decreased gradually from July to October (Figures II-5d, II-6d, II-7d and II-8d).

Frequency distributions for wind direction were also bimodal at Shirley Meadow, with afternoon and night winds flowing mainly from the southwest (240-270°); early to mid-morning winds were from the east-northeast (60-70°) in August, September and October (Figures II-6c, II-7c and II-8c), but not in July when they were from the southeast (Figure II-5c).

At Shirley Meadow, daytime wind speeds frequently ranged up to 18 and occasionally 22 mph; Democrat Springs winds rarely exceeded 10 mph (Figures II-5d, II-6d, II-7d and II-8d).

Air temperatures at Democrat Springs and Shirley Meadow were often within 1-3 C of one another at about 0700 PDT regardless of the month. During afternoon hours, the maximum daily temperature at Shirley Meadow was usually 10-12 C cooler than Democrat Springs (Figures II-5g, II-6g, II-7g and II-8g). Daily peak ozone and sulfur dioxide concentrations were usually coincident with the maximum air temperature.

The relative humidity during the late afternoon hours at Shirley Meadow was 30-40% in July, 35-45% in August, 60-70% in September and 55-65% in October (Figure II-5h, II-6h, II-7h and II-8h). These ranges suggest that September may have had the conditions most favorable for plant injury in the vicinity of Shirley Meadow. Democrat Springs relative humidity was not available in 1982 because it was not possible to maintain a suitable calibration of the aspirated dry and wet thermocouples used there.

Influence of Synoptic Weather Patterns on Meteorological and Pollutant Variables at Democrat Springs and Shirley Meadow

The 24-hour records for ozone, sulfur dioxide, air temperature, wind speed and direction were compared for distinct types of days selected from the daily weather maps for August 1982. The four selected conditions included one day each characterized by: (1) 500 millibar (mb) high-surface high, August 31; (2) 500 mb high-surface low, August 21; (3) 500 mb low-surface low, August 25; (4) 500 mb low-surface high, August 26.

The hourly changes in pollutants, temperatures and winds for four selected days are shown in Figures II-9, II-10, II-11 and II-12. Wind direction at Democrat Springs was the same for the high-high, high-low and low-high days (Figures II-9d, II-10d and II-11d); on the low-low day the wind was from the north from 0900-1000. At Shirley Meadow winds originated from 220-240 degrees for most of the 24-hour period during the high-high and high-low days; on the low-low and low-high days, winds shifted from the usual 220-240 degrees to 0-50 degrees during the 0700-1000 period. At Democrat Springs winds shifted from the predawn 120- to 160-degree direction through west to north for a few hours after dawn on the high-high, high-low and low-high days. However, on the low-low days, the same shift was through east to north (Figures II-9d, II-10d, II-11d and II-12d).

At Democrat Springs the wind speed peaked at midday and at Shirley Meadow the peak was at about 1800 on high-low, low-low and low-high days. On the high-high day, wind speeds were similar for the whole 24-hour period at both stations (Figures II-9e, II-10e, II-11e and II-12e).

On the high-high day, wind speed decreased to less than 4 mph by 2000 hours, and there was an abrupt decrease of ozone from 12 pphm to 5 pphm at Shirley Meadow; the same wind pattern at Democrat Springs was associated with a more gradual decline of ozone (Figure II-9a). At Shirley, on the low-low and low-high days, wind speeds averaging 12-14 mph at about 1700-1800 were associated with ozone concentrations that did not decline

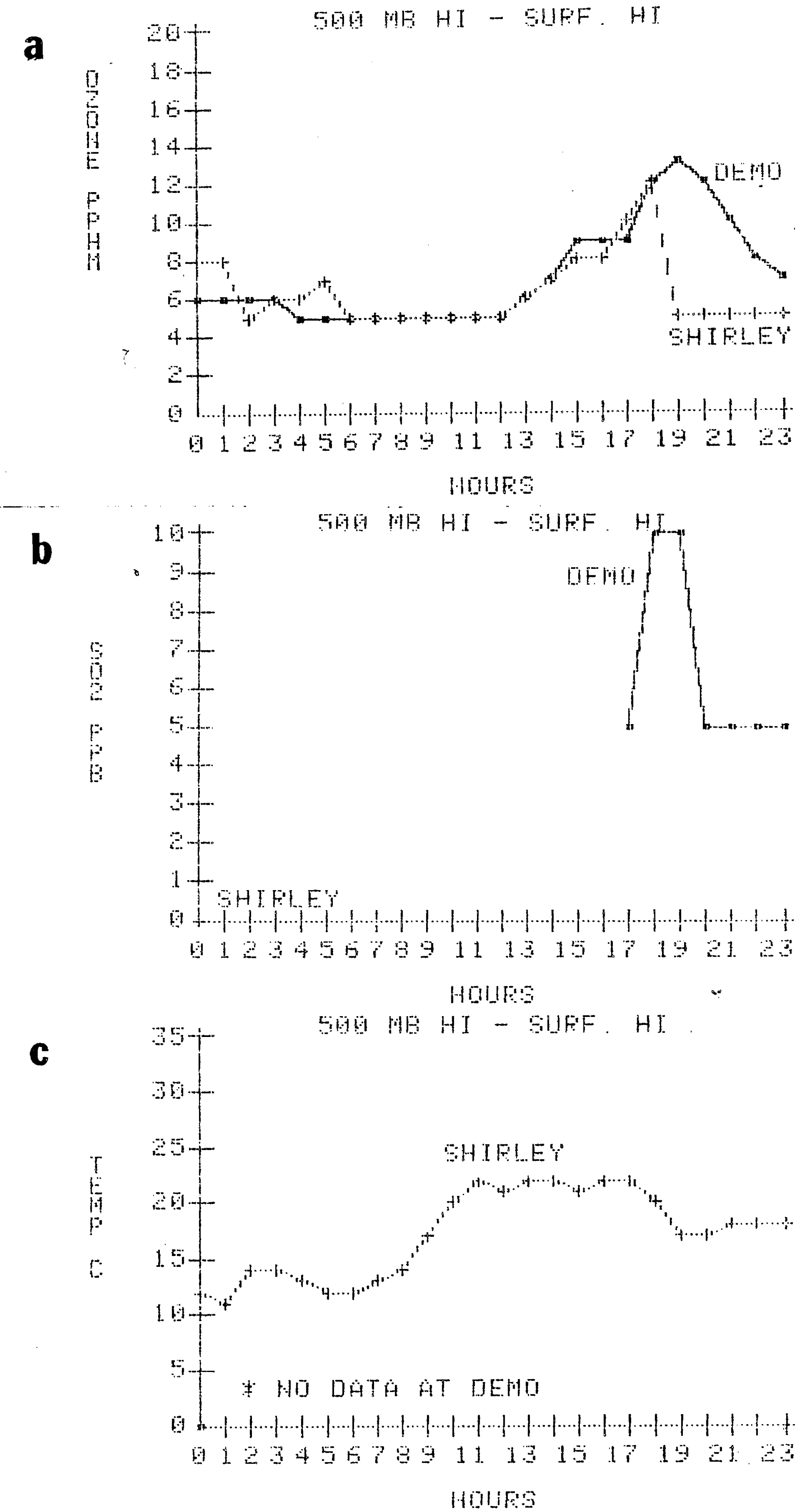

Figure II-9. Hourly values for (a) ozone, (b) sulfur dioxide, (c) air temperature, (d) wind speed and (e) wind direction on August 31, 1982 at Democrat Springs and Shirley Meadow characterized by a 500 millibar high and a surface high pressure.

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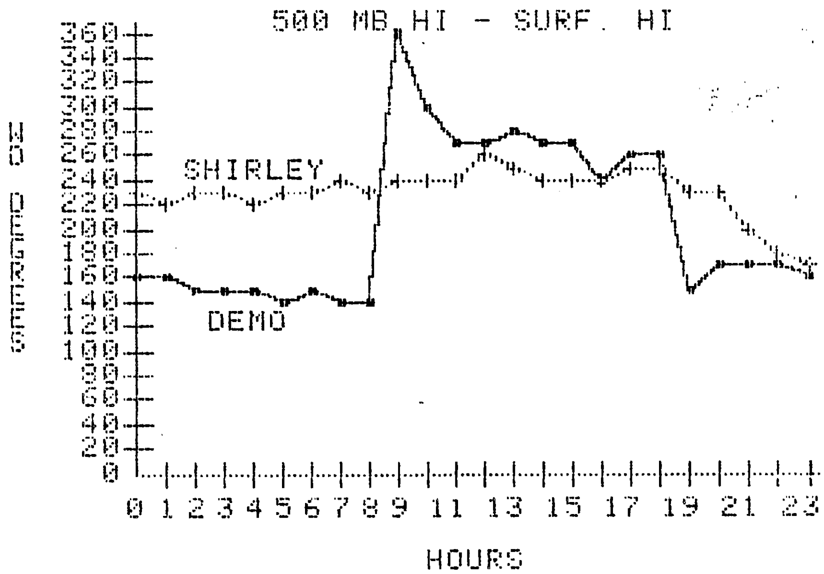

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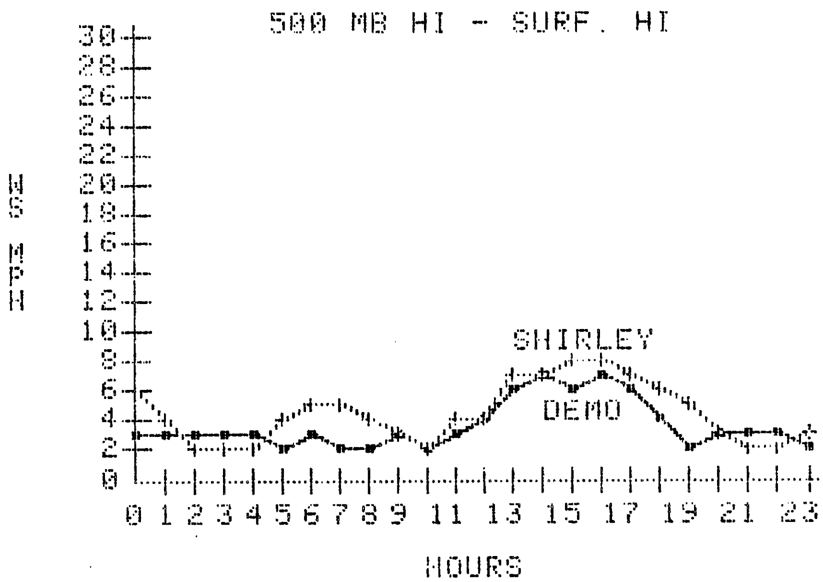

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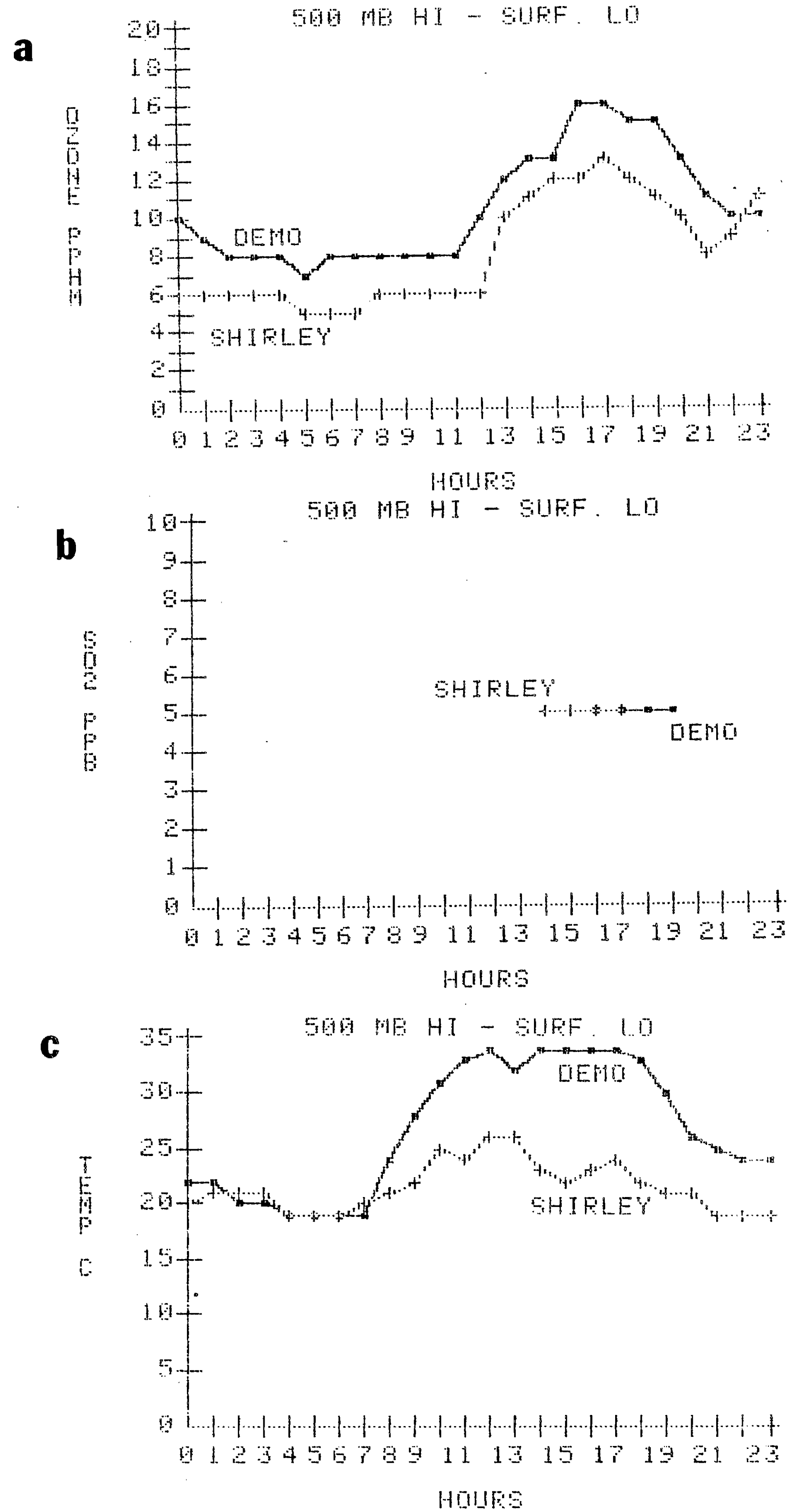

Figure II-10. Hourly values for (a) ozone, (b) sulfur dioxide, (c) air temperature, (d) wind speed and (e) wind direction on August 21, 1982 at Democrat Springs and Shirley Meadow characterized by a 500 millibar high and a surface low pressure.

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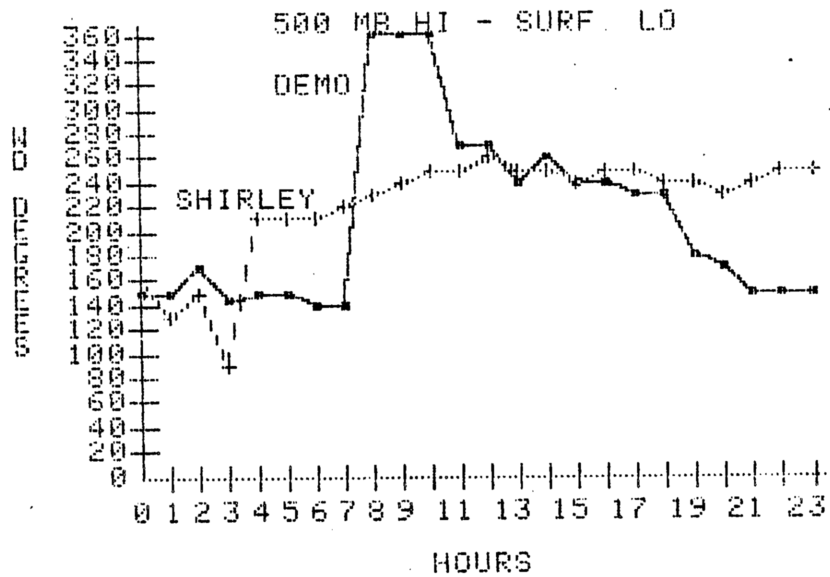

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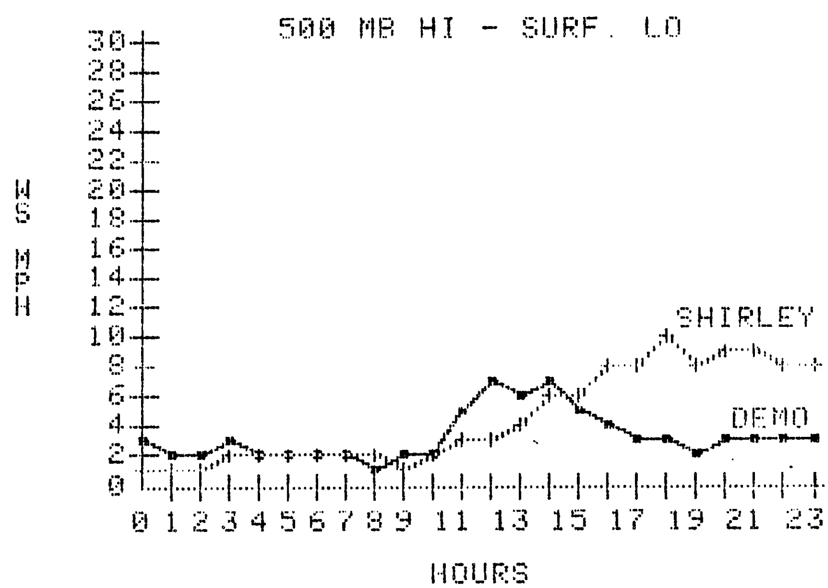

Figure II-10. (Continued)

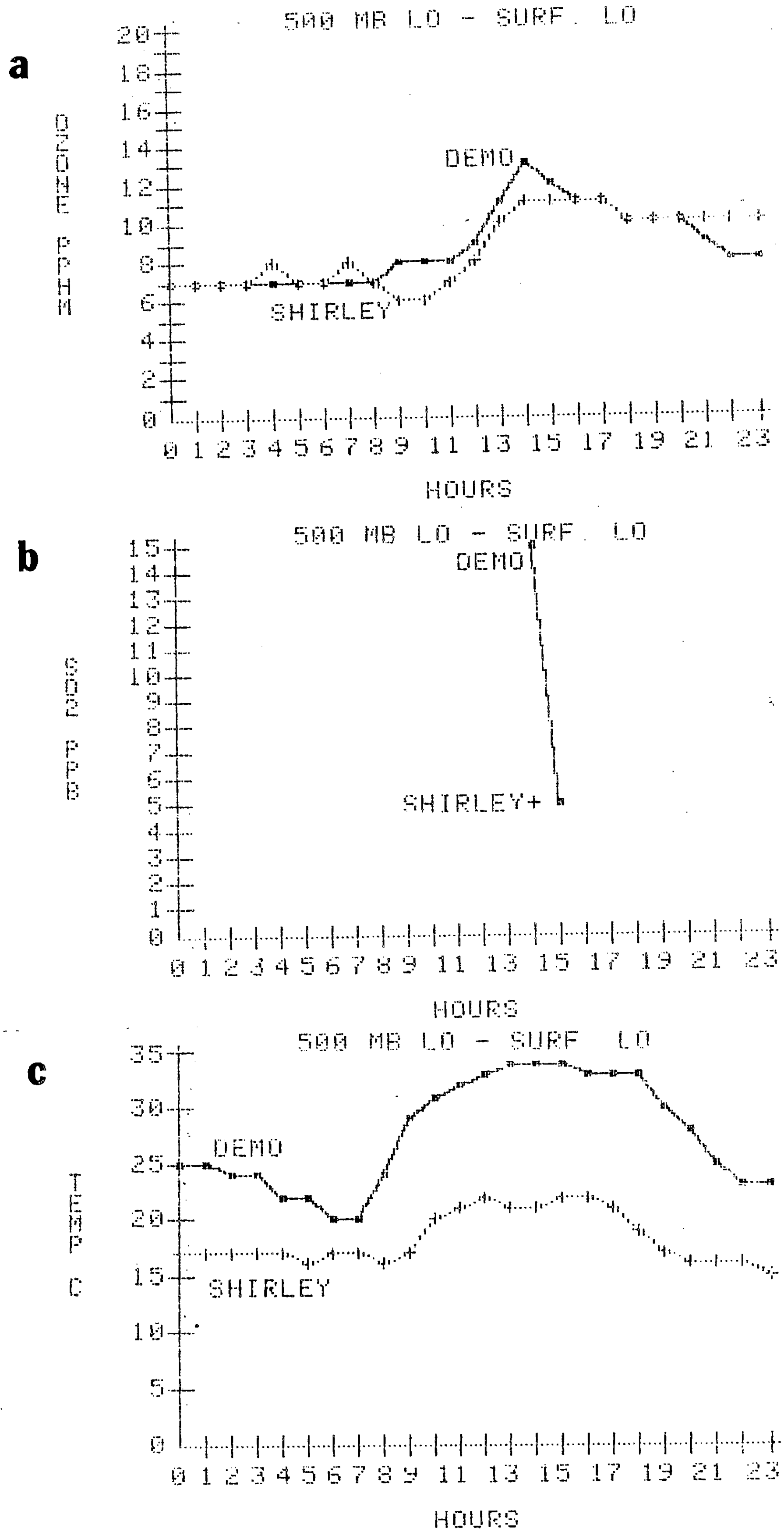

Figure II-11. Hourly values for (a) ozone, (b) sulfur dioxide, (c) air temperature, (d) wind speed and (e) wind direction on August 25, 1982 at Democrat Springs and Shirley Meadow characterized by a 500 millibar low and a surface low pressure.

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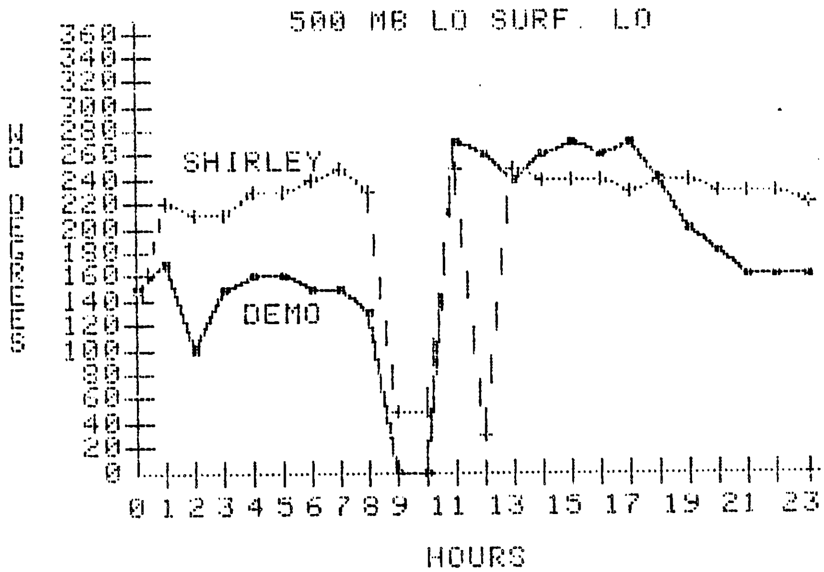

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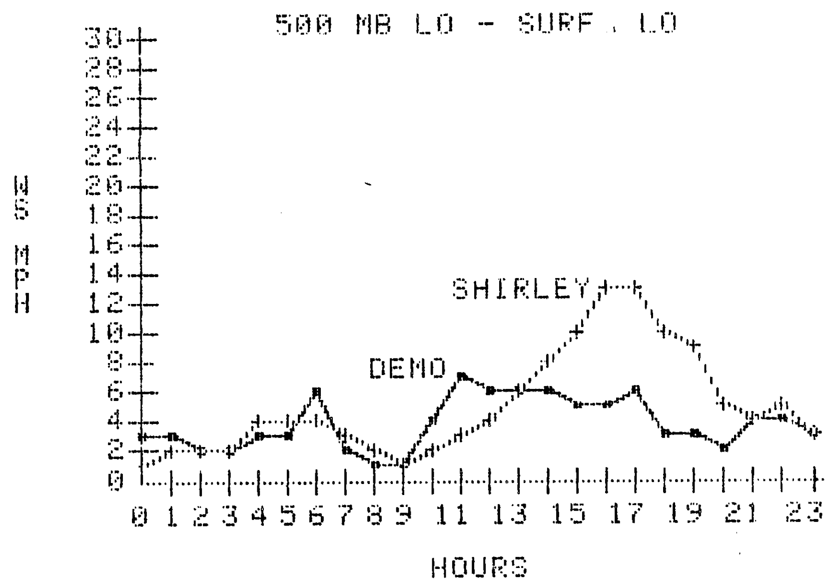

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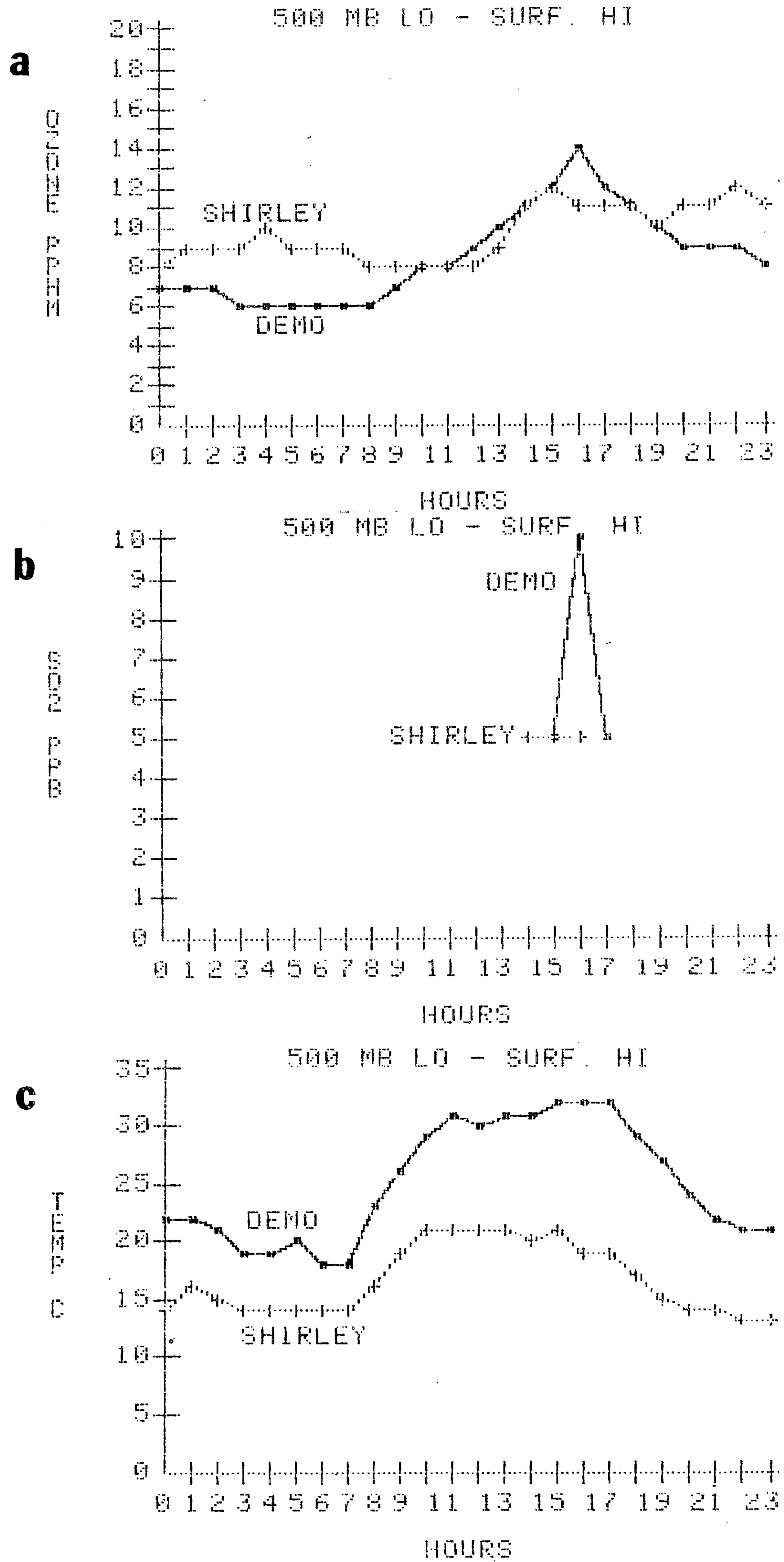

Figure II-12. Hourly values for (a) ozone, (b) sulfur dioxide, (c) air temperature, (d) wind speed and (e) wind direction on August 26, 1982 at Democrat Springs and Shirley Meadow characterized by a 500 millibar low and a surface high pressure.

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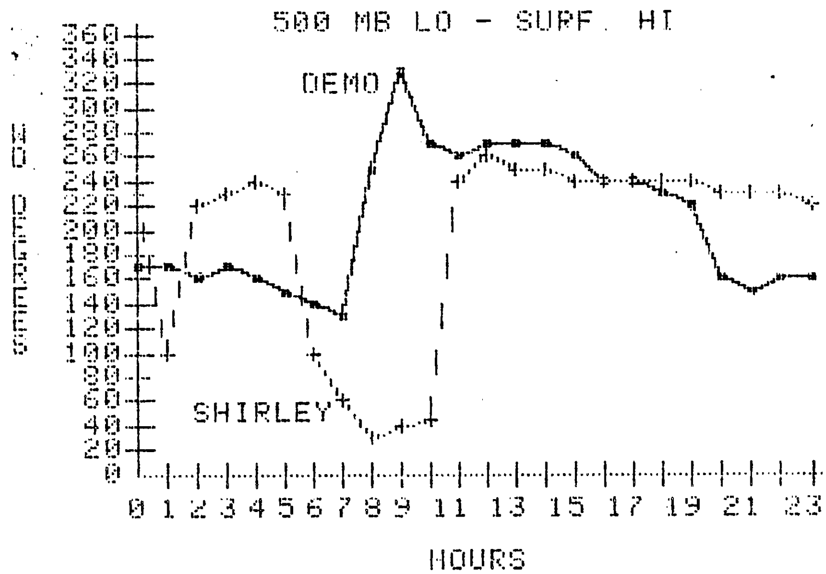

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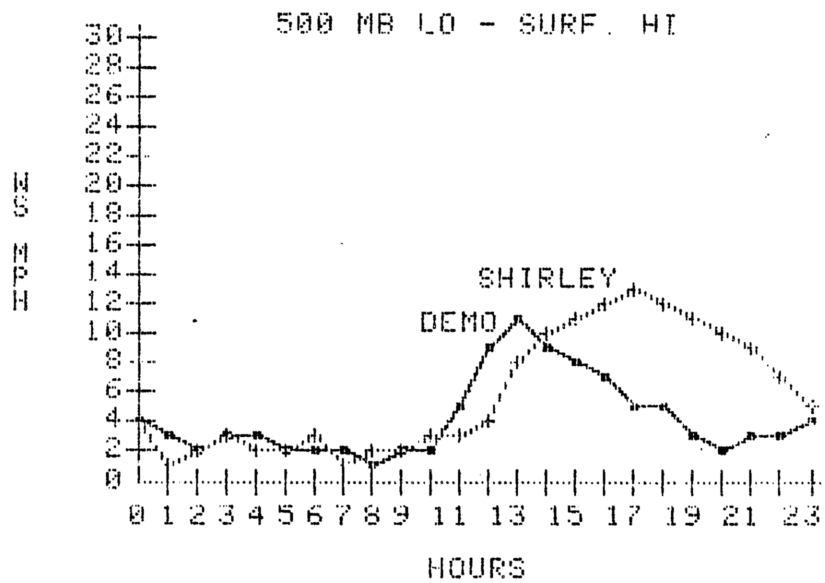


Figure II-12. (Continued)

significantly during the 1800-2300 hour period (Figures II-11a and II-12a). On the high-low day, wind speeds remained near 8 mph until 2300 hours at Shirley Meadow, and ozone concentrations increased from 8 to 11 mph between 2100 and 2300 (Figure II-10a). Ozone concentrations always declined at Democrat Springs after dark regardless of the type of synoptic pattern.

It was difficult to distinguish any definite influences of the four synoptic patterns on sulfur dioxide concentrations except that Democrat Springs had the longest duration at 10 pphm on the high-high day (Figure II-9b).

Limited interpretation is possible from a sample limited to one day for each synoptic pattern. The majority of days during the July through September period were better characterized as transitional types from one to another of these four extremes. However, the 500 mb high, surface low day appears to result in the longest duration of high ozone concentrations at both stations. During August 17 to 21, each day was categorized as having a 500 mb high, surface low synoptic pattern. The means of hourly values for wind direction, wind speed and ozone at both stations indicate a very active transport of ozone from west to east lasting into the evening hours (Figures II-13a, II-13b and II-13c). Air temperature at Shirley Meadow showed at 25 C maximum on the high-low day, while the maximum days representing other synoptic patterns did not exceed 21 C. When pollutant records are not available, it may be useful to use temperature as an identifier of the frequency of high ozone pollution days at elevations in the 5000-7000 foot zone. A second indicator of high ozone days at this elevation is the sustained late afternoon and evening wind >8 mph from about 240 degrees. The high-low day appears to be the synoptic pattern that results in deep penetration of polluted valley air into the southern Sierra and into the desert to the east; therefore, a study was designed to further define the influences of terrain on surface flow of polluted air.

Intensive Pollutant Transport Study During September 13-17, 1982

The study was centered around SF_6 and radar-tracked tetroon releases at Oildale. We installed and maintained four surface wind stations in addition to Democrat Springs and Shirley Meadow (Figure II-1).

The specific objectives of this part of the multi-agency study carried out by the USDA, Forest Service Fire Laboratory and the Statewide Air Pollution Research Center were: (1) to determine the transport patterns from Oildale, (2) to determine the mass balance in the lower and mid-regions of the Kern River drainage, and (3) to make a preliminary estimate of the mixing and dispersion processes at the valley-mountain interface.

Equipment and personnel were assembled so that the maximum sampling effort could be done on September 15. We had very little flexibility to change the date because of the high cost of maintaining personnel on travel status. Unfortunately, the 13th through the 19th were characterized by a low-low synoptic pattern, and it would have been necessary to wait until the 21st through the 24th when a high-low pattern returned, which would have provided conditions for maximum pollutant accumulation and transport from Oildale eastward as indicated by the data for August 17-21 (Figure II-13a,b,c). Surface winds were westerly at Democrat Springs and Shirley Meadow on the 15th of September, but ozone concentrations did not increase because precursors had ceased to

a

b

c

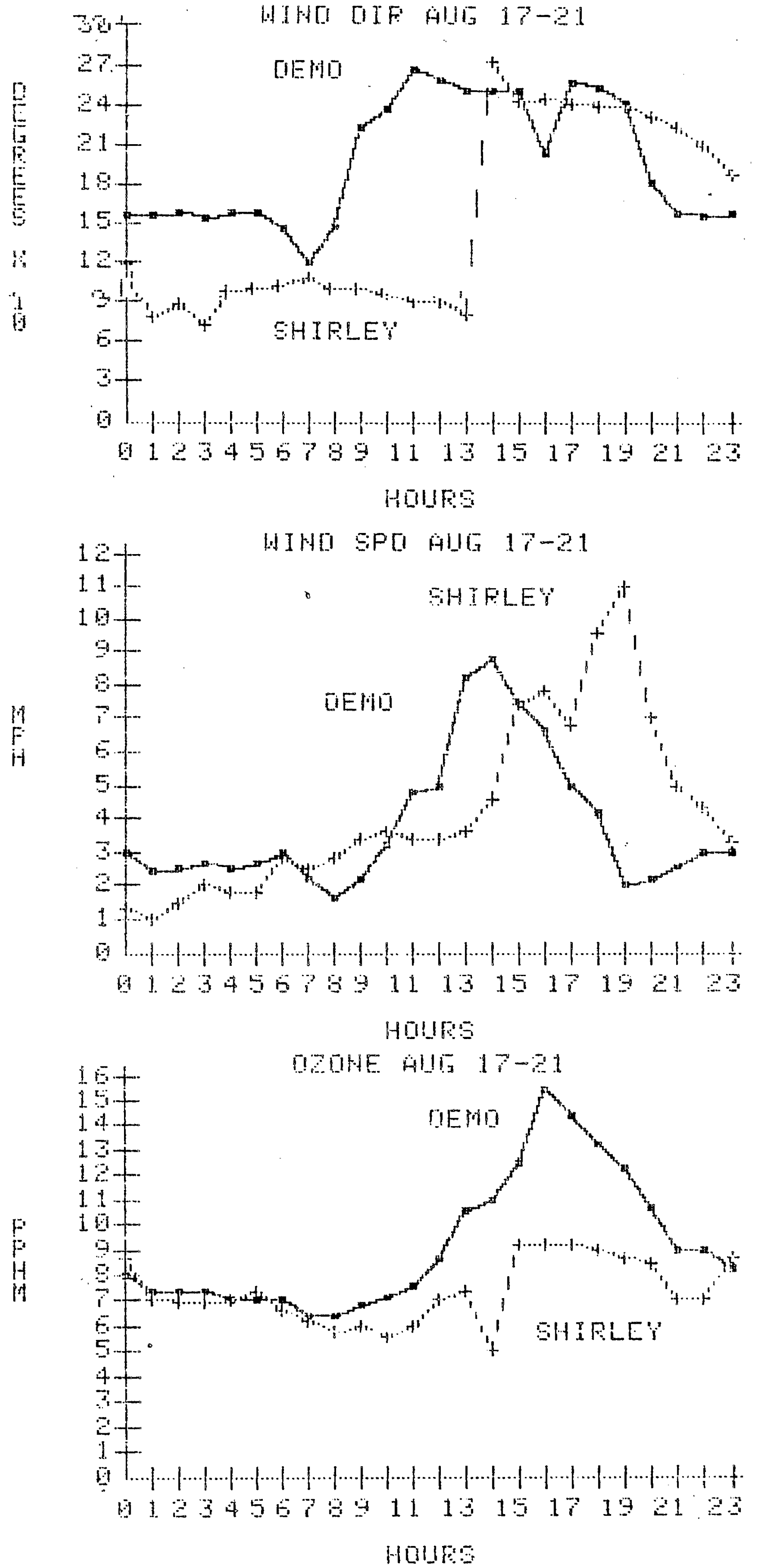


Figure II-13. Hourly (a) wind directions, (b) wind speeds and (c) ozone concentrations, during August 17-21, a period dominated by a 500 millibar high pressure and surface low pressure.

accumulate sufficiently in the source area during this persistent low-low synoptic pattern (Figure II-14a,b,c). Additional data pertaining to transport patterns, mass balance in the mid- to lower Kern Canyon and vertical mixing and dispersion at the valley-mountain interface are described in Appendix 1 prepared by Michael A. Fosberg, Research Meteorologist at the USDA, Forest Service Fire Laboratory, Riverside.

SUMMARY

Frequent transport of ozone and sulfur dioxide to Democrat Springs (2400 ft) and Shirley Meadow (6400 ft) was observed during the summers of 1981 and 1982. The synoptic pattern associated with long durations of ozone concentrations in the range of 10-15 pphm at these monitoring sites was a 500 mb high and surface low. Averages of maximum hourly ozone concentrations were consistently higher at the remote sites than at Oildale, but sulfur dioxide concentrations at Democrat Springs and Shirley were about one-fifth and one-tenth, respectively, of those at Oildale. Winds were consistently from the west during high pollution days, but this does not implicate only the Bakersfield-Oildale area as the source region. Valley winds undoubtedly deliver pollutants from communities to the north. Mass flow through the lower Kern River Canyon is restricted by the narrow dimensions of the gorge. Transport of mass from the San Joaquin Valley is more likely to take place at ridge level with subsequent entrainment into the local circulation that develops above the gorge. On the day of the multi-agency transport study, deep mixing was observed above Oildale, to the level of the upper southwesterly flow. This lends support to the hypothesis that transport of mass takes place mainly at the level of the ridges flanking the lower Kern River Canyon.

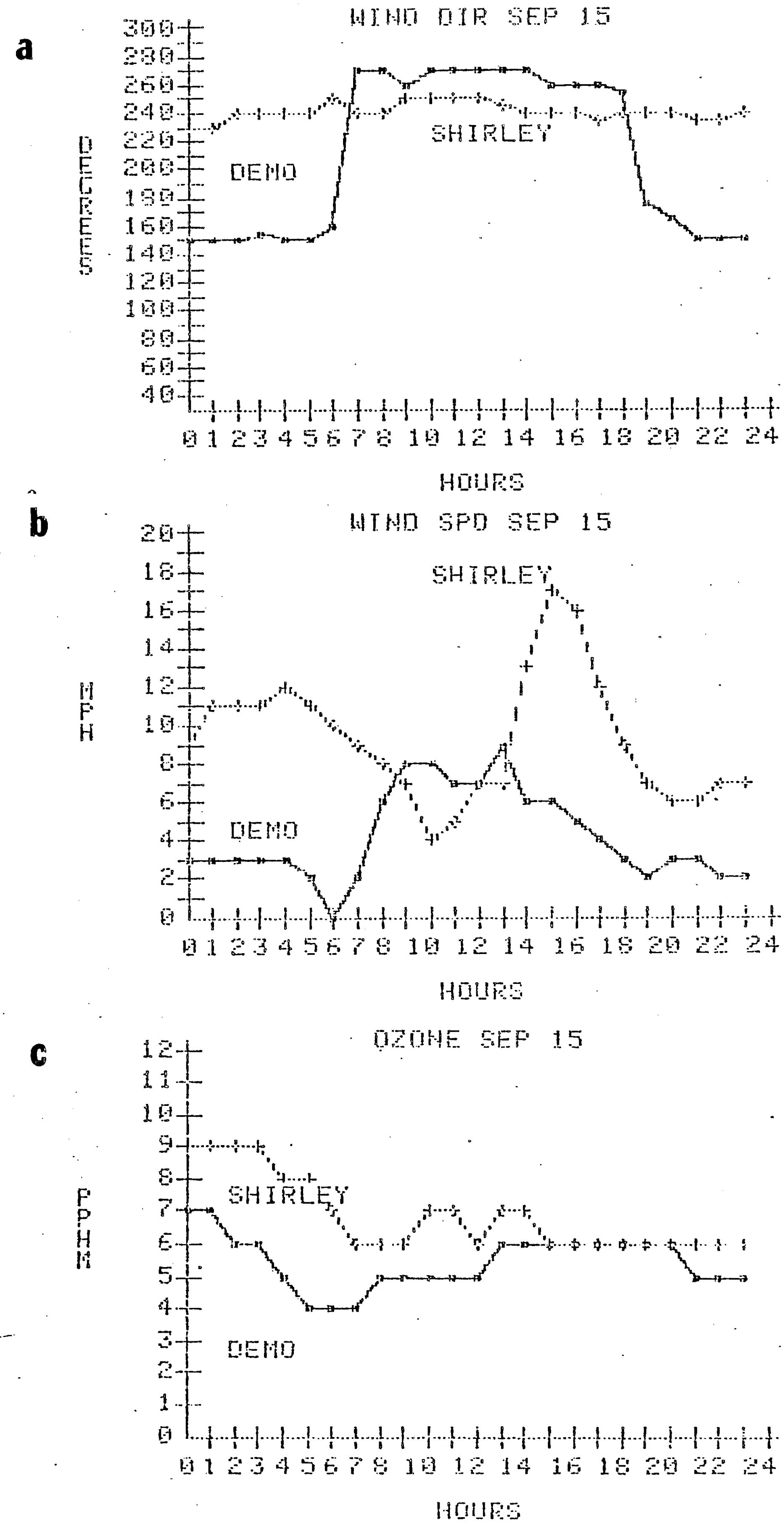


Figure II-14. (a) Wind directions, (b) wind speeds and (c) ozone concen rations at Democrat Springs and Shirley Meadow on September 15, 1982 during SF_6 release at Oildale.

III. HUEY SULFATION PLATE MEASUREMENT OF THE EXTENT OF DETECTABLE SULFUR DIOXIDE

INTRODUCTION

Huey sulfation plates were used to complement the continuous instrumental monitoring of sulfur dioxide in the study area. The following discussion will evaluate some of the background data on the method. Sulfation plates are 5 cm diameter plastic petri plates with a dry, solid coating of lead peroxide in the bottom of the dish. They are exposed in an inverted position for four to eight weeks. The measured response results from the reaction of SO_2 with PbO_2 to form $PbSO_4$. Plate holders can be mounted on trees, fence posts, etc.

The use of lead peroxide cylinders has also been reported. Thomas and Davidson (1961) reported that the rate of reactivity of sulfation cylinders increased with temperature and wetting of the lead peroxide surface but not with wind speed or changes in relative humidity. They noted that the consideration of meteorological, environmental and cultural factors were important in site selection. Drainages were considered more desirable than hills and ridge tops. Single point sources generally resulted in low sulfation and poor correlation of sulfation with SO_2 dosage compared to metropolitan or dispersed industrial areas. At some sites the sulfation present was not sufficient for effective analysis by barium sulfate precipitation. It was not possible to correlate sulfation values with sulfur in the foliage of trees when the content of sulfur in the foliage was low. Seasonal spread in reactivity values differed by two to three magnitudes between seasons. Huey (1968) reported that in plates the relationship between sulfation (μg $SO_3/cm^2/day$) and ppm SO_2 is variable from location to location and season to season.

Although there are obvious limitations to the use of the lead peroxide method, a number of attributes make it a desirable tool for the evaluation of SO_2 concentrations. Sulfation plates are relatively inexpensive and can be easily placed in many locations. They have been used to reveal the non-homogeneous distribution of SO_2 pollution, and can be useful in locating sites for continuous air monitors (Huey 1968). Sulfur dioxide isopleths have been constructed with data obtained from a network of sulfation plates. Replicate values obtained at the same site are constant and seldom differ by more than 10%. The reactivity of sulfation cylinders were relatively stable over exposure periods of up to four months. Sulfation plates are more sensitive than cylinders (Huey 1968); both may be effective in measuring sulfation at distances up to 40 miles from an emission source (Thomas and Davidson 1961).

In this study, the sulfation plate network was intended as a supplement to instrumental air monitoring in order that the eastward extent of SO_2 transport might be indicated. There was no intent to examine possible correlations between sulfation rates and accumulation of sulfate in plant tissue or surface soils.

PROCEDURE

Huey plates were obtained from Sanitary Engineering Laboratories, Inc. (Serco), Cedar Falls, Iowa. Two lead peroxide-coated plates were placed in an inverted position in a standard plate holder available from the manufacturer. The holder supported two plates at a distance of 3-17 cm away from the surface to which it was attached. In 1981 the standard holders were attached about six feet above the ground on tree trunks, utility poles or stakes, depending on what was conveniently available. In 1982, the standard holder was replaced by a hardware cloth cage with two holes in which plates were inverted. This change was made to exclude woodpeckers. Cages were mounted mainly on metal fence posts placed in clearings; a few were mounted on tree trunks.

During July through October 1981, the transects along which plates were exposed were defined as the Piute Mountains (including the Caliente-Bodfish Road leading to Tehachipi Pass), Breckenridge Mountain, Greenhorn Mountains and the lower Kern River Canyon (Figure III-1). In 1982, the Piute Mountains were excluded, Sawmill road sites and additional sites along the road to Breckenridge Mountain and Rancheria Road and Greenhorn Ridge were added mainly to have stations located at 500-ft elevational intervals on slopes and in drainages facing the valley (Figure III-2).

In 1981, the greatest number of plates were exposed between July 29 and October 28. The exposure period in 1982 extended from July 16 to October 27. Each year these exposure times were split into July-August and September-October exposure periods of approximately six weeks each.

Plates collected from the field were stored in sealed plastic bags at room temperature prior to analysis. Plates were analyzed in a single batch about three to five months after collection using the turbidimetric barium sulfate method (Huey 1968). Values of $\mu g\ SO_4$ per plate were derived from a standard curve prepared for each batch and SO_2 concentrations were derived by Huey (1968) using a factor of 0.0035 for converting $\mu g\ SO_3/cm^2/day$ to ppm SO_2. This factor is one that is normally used when volumes considered are approaching an infinite value (the atmosphere). A duplicate set of plates from both exposure intervals in

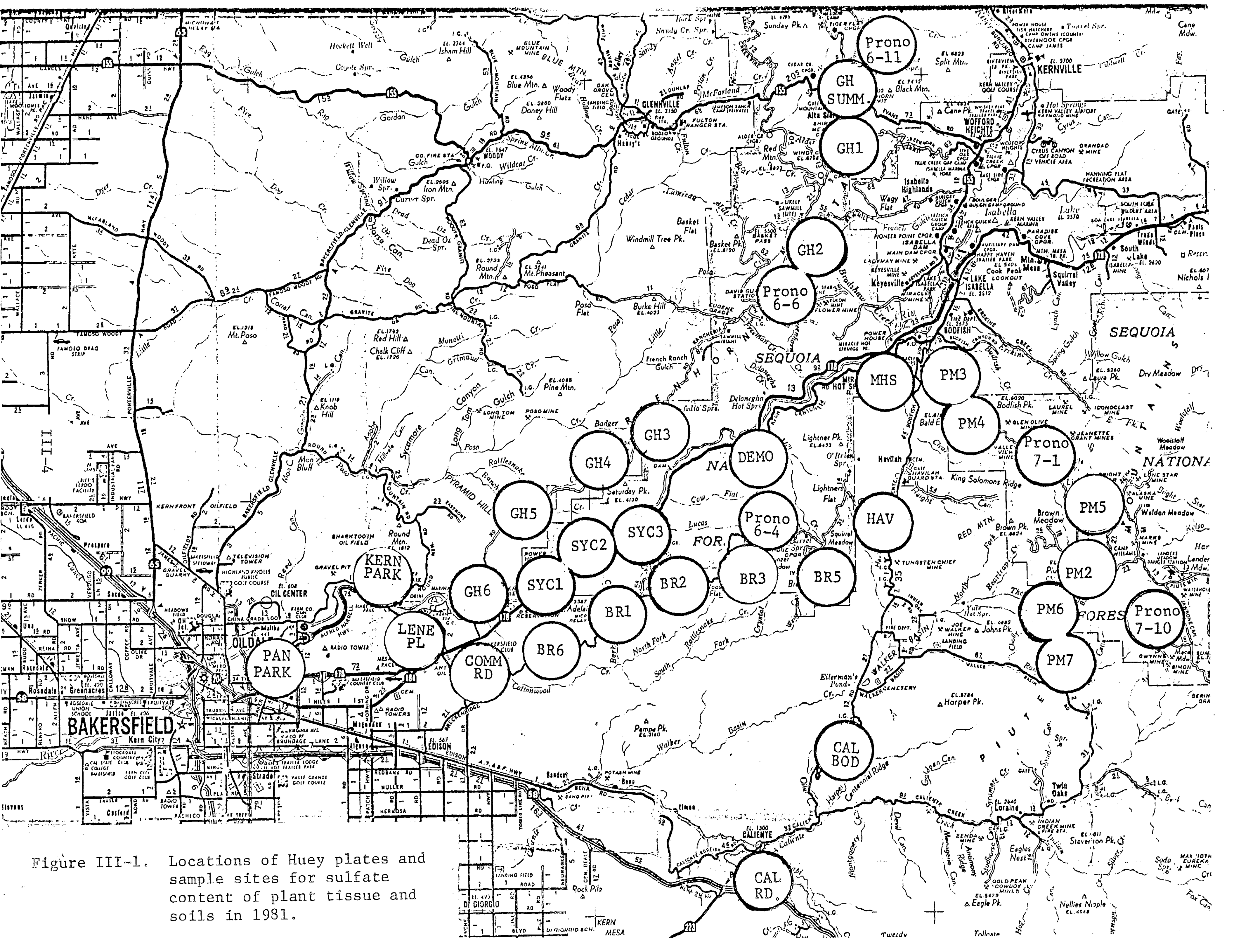


Figure III-1. Locations of Huey plates and sample sites for sulfate content of plant tissue and soils in 1981.

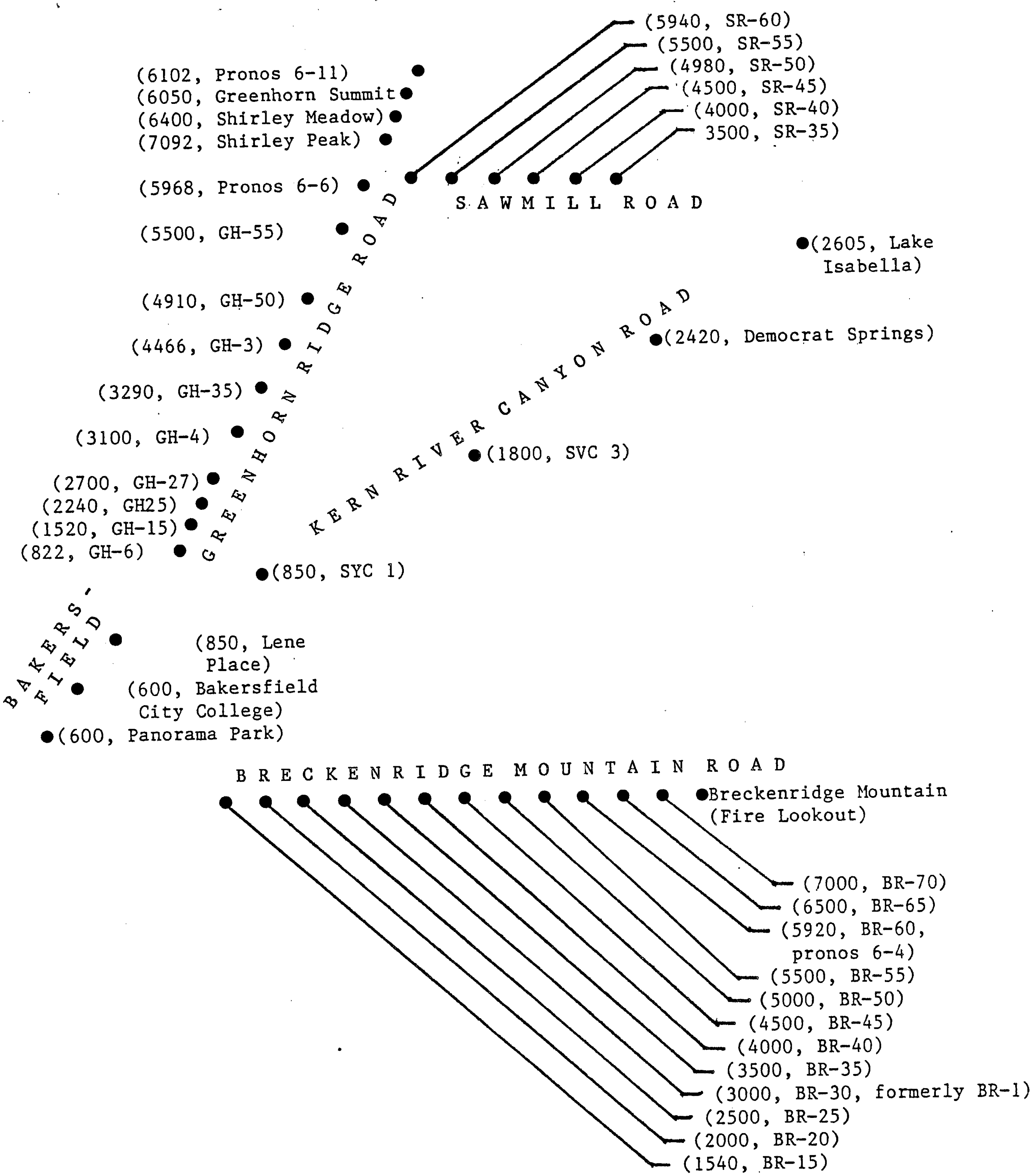


Figure III-2. Relative elevations and locations, based on the map scale of Figure III-1, of sites where Huey plates were deployed and samples were gathered for analysis of sulfur content of soils and plant tissues in 1982. Elevation (ft) and place name or code name of the site is included in parenthesis, e.g. (6102, Pronos 6-11). GH = Greenhorn Ridge, BR = Breckenridge Mountain and SR = Saw Mill Road.

1981 were sent to Serco for analysis. The trends from site to site and sulfation rates determined by their analysis compared sufficiently well to ours that we felt confident in continuing the analyses in our laboratory. The usual maximum values for optical density and micrograms sulfate are 0.10 and 500, respectively, for the standard curve. The values obtained in our study were always in the lower one-third of the standard curve.

RESULTS

The data set obtained in both 1981 and 1982 have revealed some serious limitations of the Huey plate method. Unexpected problems were encountered in the field exposure phase. Some plates were either damaged or lost during the exposure phase due to failure of the wire cage to retain the plates or due to destruction by curious birds and human vandalism. Both the accuracy and precision of the laboratory analysis process required careful scrutiny.

The mean sulfation rates, expressed as hourly mean SO_2 concentration (ppb), during 1981 are shown for 31 stations in Table III-1. No distinct trends emerge from these data. Sites close to Bakersfield did not have sulfation rates that were consistently higher than the most remote Piute Mountain sites. There were no major differences between exposure periods. In 1982, there were also wide variations between replicate plates at the same site. Typical variation was evident as a measurable sulfation rate for only one of four plates exposed at the same site. This type of variation was typical of remote sites where hourly SO_2 averages were $\lesssim$ 10 ppb such as at Democrat Springs and Shirley Meadow (Table II-1).

Table III-1. Hourly Mean Sulfur Dioxide Concentrations Determined with Huey Sulfation Plates During July through October 1981 in the Southern Sequoia National Forest

General Location	Plot	Distance and Elevation Direction from Oildale			Hourly Mean Sulfur Dioxide Concentration (ppb x 10^{-1})				
		Miles	Deg.	Ft.	6/30 to 7/30	7/13 to 8/21	7/29 to 9/4	8/21 to 10/6	9/25 to 10/28
Piute Mountains	Havila	24.9	82	3000			0.84	0.84	
	PM #3	28.1	71	3800			0.32		0.80
	PM #4	29.0	75	5740			0.61	0.62	<0.01
	PR 7-1	31.9	80	6600	0.51		0.32	0.51	0.07
	PM #5	32.6	84	7880			0.35	1.0	
	PM #2	31.9	88	8000	0.51		0.42	0.67	0.12
	PM #6	31.4	90	6600			0.24	0.25	
	PM #7	31.6	95	4800					
					0.51 ± 0		0.48 ± 0.22	0.71 ± 0.29	0.25 ± 0.37
Oildale/ Kern Canyon	Panorama Park	1.8	180	600		0.77		0.34	0.89
	Kern Co. Park	5.3	85	500		0.22		0.23	<0.01
	Lene Place	6.7		700		0.82		0.84	0.43
	Commanche Road	9.0		1000		0.80		0.75	0.55
Kern Canyon/ Caliente	Democrat Springs	20.8	75	2000	0.51		0.29	0.25	<0.01
	Miracle Hot Spr.	27	72	2400			0.40	0.92	<0.01

(continued)

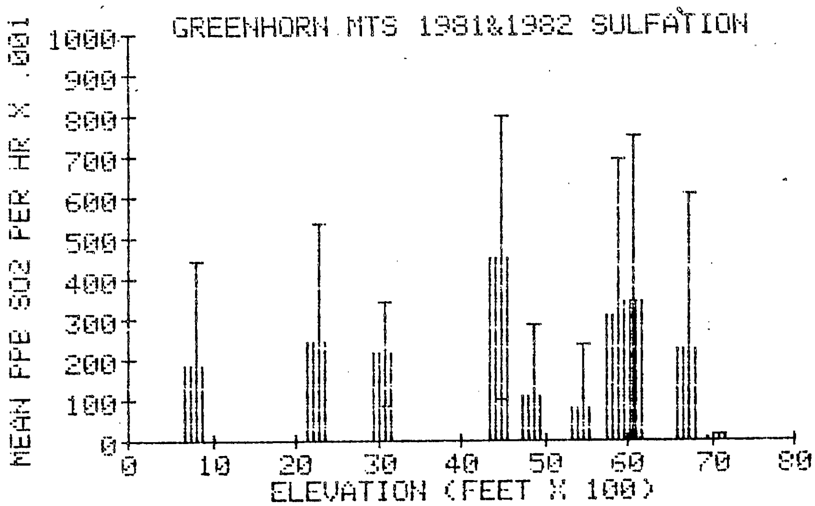
Table III-1 (continued) - 2

General Location	Plot	Distance and Elevation Direction from Oildale			Hourly Mean Sulfur Dioxide Concentration (ppb x 10^{-2})				
		Miles	Deg.	Ft.	6/30 to 7/30	7/13 to 8/21	7/29 to 9/4	8/21 to 10/6	9/25 to 10/28
Kern Canyon/ Caliente (continued)	Cal. Bod. Road	22.5	108	4500	0.38		0.30	0.04	
	Cal. Road	22.2	120	2000				0.37	0.46
					0.44 ± 0.09	0.65 ± 0.28	0.33 ± 0.06	0.47 ± 0.32	0.34 ± 0.34
Greenhorn Mountains	GH #6	8.8	93	2000				0.30	0.99
	GH #5	12.3	73	2800			0.23	0.81	0.27
	GH #4	14.6	65	4000			0.34	0.19	<0.01
	GH #3	16.9	68	4973	0.52		0.82	0.71	
	PR 6-6	24.4	62	6000				0.85	0.27
	GH #2	26.1	58	6250	0.50		0.70	1.0	
	GH #1	29.7	53	6520	0.50		0.81	1.05	
	GHS	31	50	6100	0.50		0.84	1.0	<0.01
	PR 6-11	32.4	49	7475				1.08	
					0.50 ± 0.01		0.62 ± 0.26	0.78 ± 0.33	0.31 ± 0.40
Breckenridge Mountain	BR #6	11.2	111	1850				0.31	0.58
	BR #1	13.8	97	2110		0.22		0.13	1.06
	BR #2	16	90	2930		0.22		0.70	<0.01
	BR #3	18.5	87	3915		0.02		0.25	
	PR 6-4	19.7	84	6020	0.28		0.59	0.71	0.04
	BR #5	22.4	90	7544	0.28		0.70	0.75	
					0.28 ± 0	0.15 ± 0.12	0.64 ± 0.08	0.48 ± 0.28	0.42 ± 0.50

Replicate plates exposed near Bakersfield where SO_2 hourly maxima sometimes reached 30-50 ppb (Table II-1) had less variation. Replicate plates exposed 7 hr day^{-1} to either 50 or 100 ppb SO_2 during fumigation of tree seedlings (Chapter VI) showed less between plate variation. Thus we have less reason to doubt the laboratory analysis process and more reason to suspect that plate-to-plate sulfation rates are quite variable when exposed to SO_2 concentrations $\lesssim$ 10 ppb.

The July-August 1981-82 and September-October 1981-82 data were studied as a function of elevation for the Greenhorn Mountain and Breckenridge Mountain transects and as a function of distance from Oildale for the Kern River Canyon transects (Figures III-3, III-4, III-5). The two mountain transects show no definite relationship of sulfation rate with elevation except for the July-August period of both years when sulfation appeared to be higher at 4500 feet on the Greenhorn Mountains (Figure III-3b) and at 7400 feet on Breckenridge Mountain (Figure III-4b). These trends are not significant, but do fit with the hypothesis that the greatest mass transfer from the San Joaquin Valley to the east is at ridgecrest elevations (Chapter II). The sulfation rates in the Bakersfield-Kern Canyon transect fit the general model of decreasing concentration with distance from the source area. The continuous air monitoring data (Table II-1) for SO_2 also supports this model. Furthermore, the mouth of the canyon is about seven to eight air miles from Oildale and the definite decrease of sulfation east of there (Figure III-5) is further support for the hypothesis that the narrow canyon may restrict the penetration of polluted air (Appendix 1). There were many missing plates in the data from the Sawmill Road transect and no trends were detectable.

a



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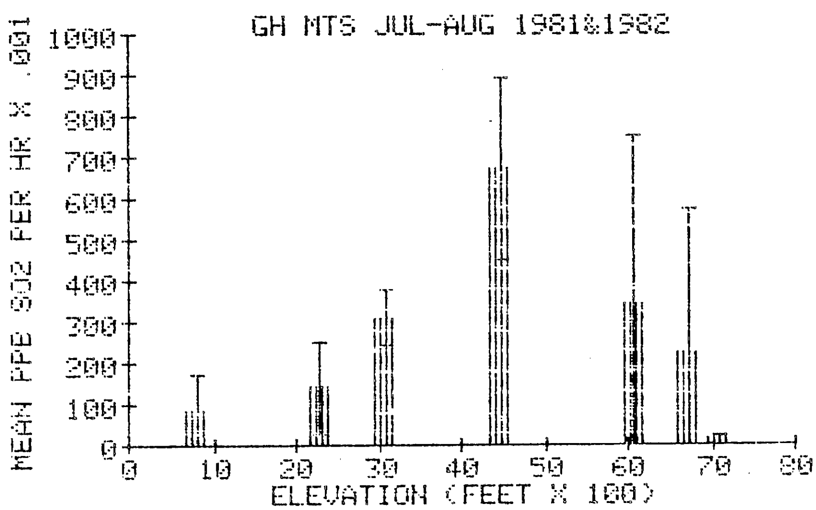

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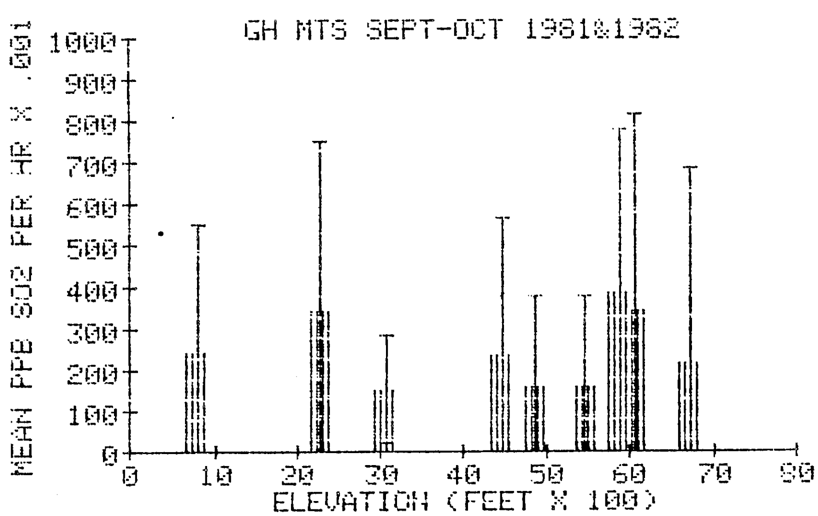


Figure III-3. Means and standard deviations of sulfation rates in an elevational transect on the Greenhorn Mountains. Sample periods include (a) July-October 1981 and 1982 combined, (b) July-August and (c) September-October 1981 and 1982.

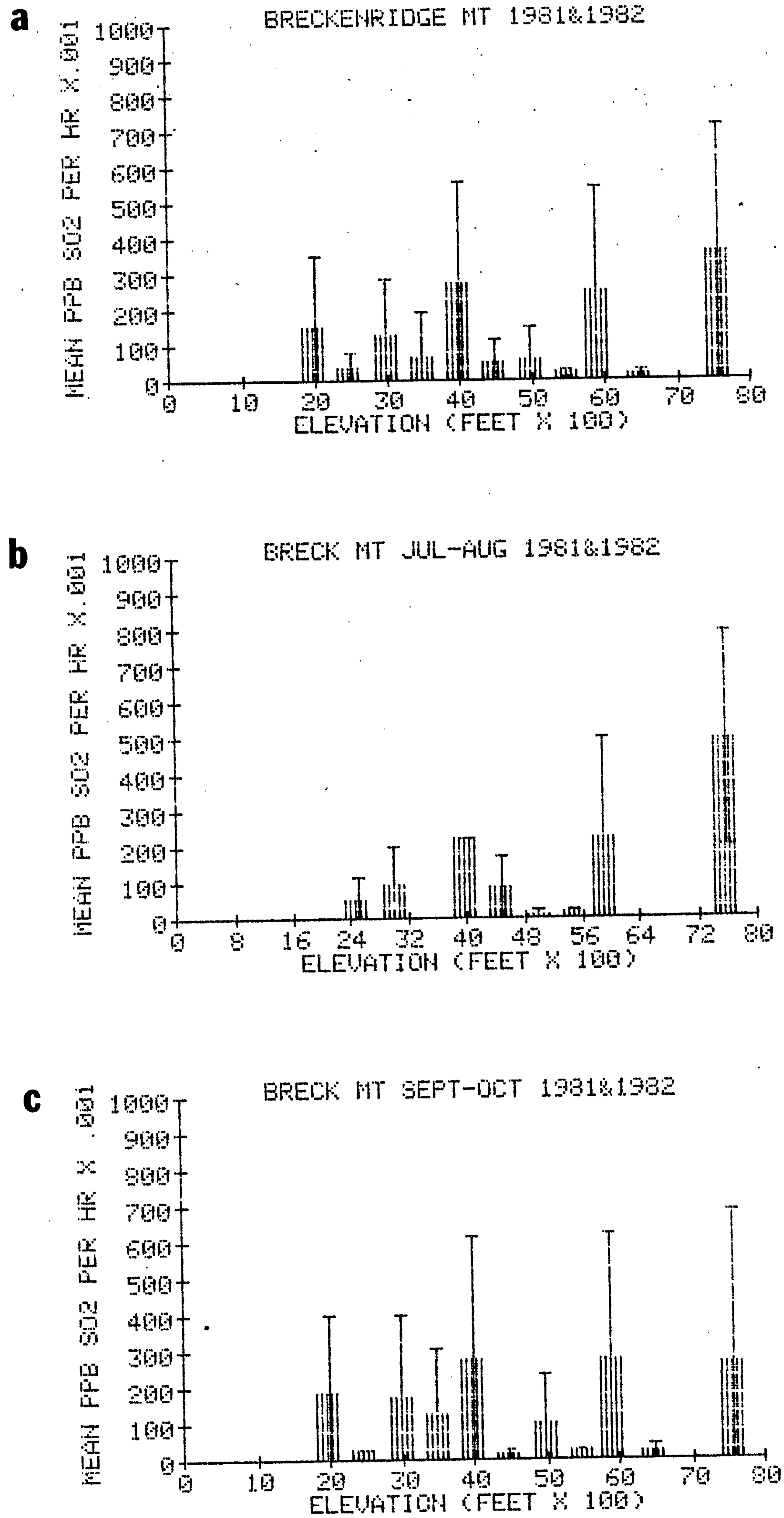


Figure III-4. Means and standard deviations of sulfation rates in an elevational transect on the southwest facing slopes of Breckenridge Mountain. Sample periods include (a) July-October, 1981 and 1982 combined, (b) July-August and (c) September-October 1981 and 1982.

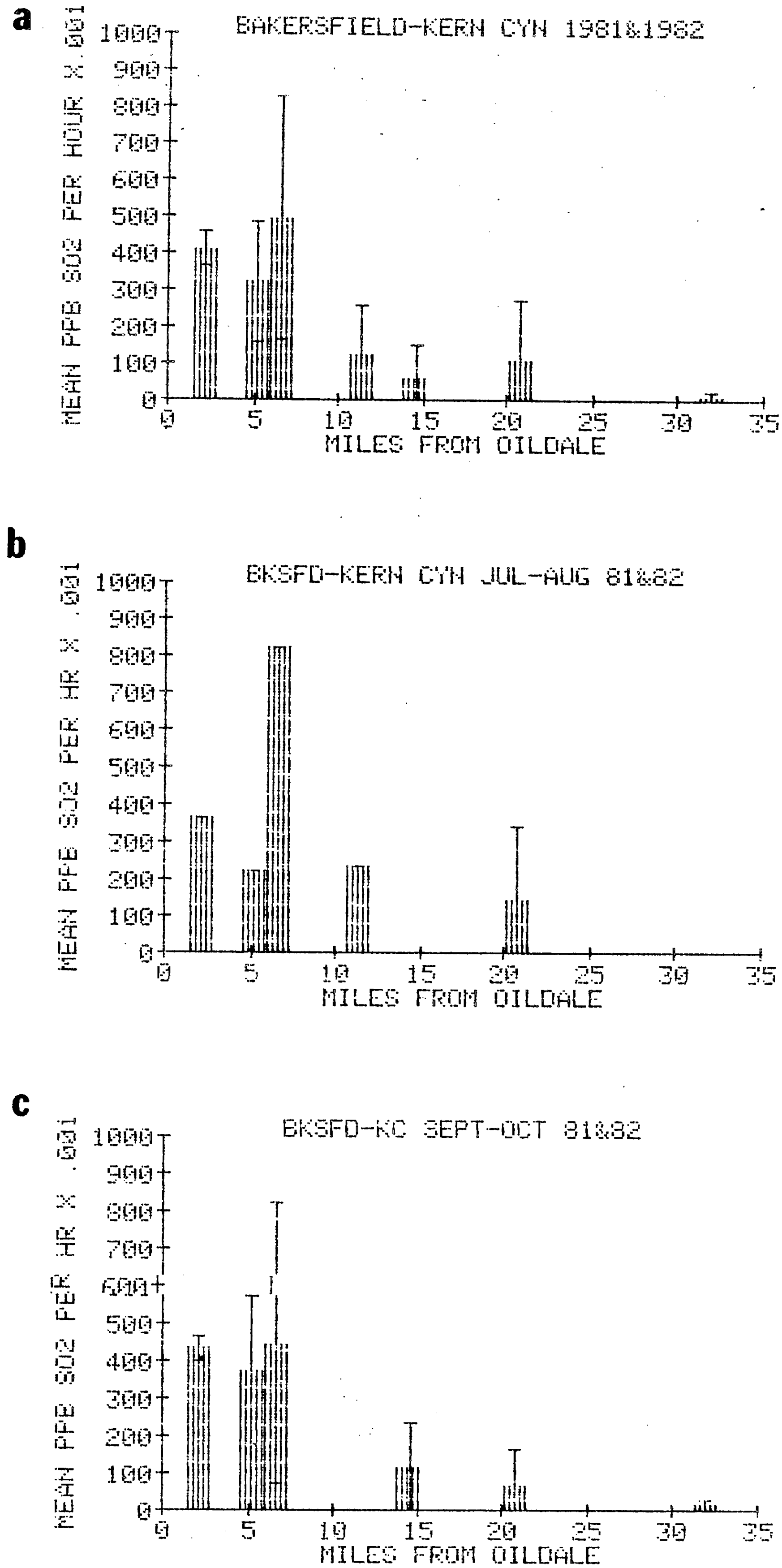


Figure III-5. Means and standard deviations of sulfation rates at intervals from Oildale to the mouth of the Kern River Canyon and eastward up the canyon to Lake Isabella. Sample periods include (a) July-October, 1981 and 1982 combined, (b) July-August and (c) September-October 1981 and 1982 combined.

IV. ANALYSIS OF SOIL AND FOLIAGE FOR SULFUR CONTENT

INTRODUCTION

Accumulation of sulfur in pine leaf tissue has been a useful indicator of sulfur dioxide pollution in the near vicinity of emission sources like smelters (Katz, 1949) and "sour gas" processing plants (Legge, 1980). Lichens are good indicators of sulfur dioxide pollution (Gilbert, 1969), particularly because their main source of nutrients is the atmosphere and not both the soil and atmosphere as with trees. Linzon et al. (1979) have provided valuable information on the various biological and physical factors that must be considered when interpreting the relative amounts of sulfur accumulated in plant tissue. These variables include geographical location, stage of plant growth, the relation of foliage injury (if present) to pollutant or biological causes, the sulfur content of soil and the sulfur dioxide emission data for the area.

The average background sulfur contents in foliage of 34 species collected in southern Ontario (Linzon, et al. 1979) ranged from 0.13 to 1.72% (dry weight basis). Low sulfur accumulators (0.13 to 0.15% S) include most of the conifers and high accumulators (> 0.26% S) include crop species, especially tomato (1.72%). In the same area, urban soils had 0.08% S and rural soils had 0.05% S in the surface layer (0-5 cm). Similar information on background levels of sulfur in foliage and soil is not available for the southern Sierra Nevada.

The purpose of this portion of the study was to determine the sulfur contents of soils, pine foliage and foliose lichens at plots located at increasing distances east (and elevations above) the Bakersfield-Oildale area.

PROCEDURES

Field Sampling

The locations where soils and pine needle tissue were collected in 1981 are indicated in Figure III-1. Sample locations used is 1982 for soils, needle tissue and foliose lichen tissue are indicated in Figure III-2. The major differences in sample locations between years were the exclusion of the remote Piute Mountain sites in 1982 and to have sites at 500 ft elevational intervals (an intensification of sampling) in the Greenhorn and Breckenridge Mountain areas.

One soil sample was collected at each of three depths, 0-5, 5-15 and 15-30 cm, from three locations within a 200 ft radius at each site. In 1982, additional samples were collected from the 70-100 cm depth at 1000 ft elevation intervals (for example, 1500, 2500, 3500, 4500, 5500, and 6500 ft).

Usually only one pine species was available at each sample site. The species most available in the Bakersfield area was Canary Island Pine (*Pinus canariensis*) at ~600 ft elevation. No pine species were available for sampling between 800 and 2000 ft. where open grasslands prevail. Digger pines (*Pinus sabiniana*) were sampled at elevations between 2400 and 5000 ft. Above 5000 ft. ponderosa pine (*P. ponderosa*), Jeffrey pine

(*P. jeffreyi*) or sugar pine (*P. lambertiana*) were sampled, usually only one species per site.

Two foliose lichen species were collected from the bark of pine species. *Letharia vulpina*, known for its prominent yellow-green thallus, was encountered at sampling sites above 4400 ft. *Hypogymnia enteromorpha*, with a less foliose, subtle gray thallus, was usually present as single or mixed cultures with *L. vulpina* at the same sites.

In 1981 foliage representing four years of growth, i.e., needles produced in 1980, 1979, 1978 and 1977, were collected from one tree at each site in July. At Oildale only 1980 and 1979 needles were present; at several Kern Canyon and Greenhorn Mountain sites the 1977 needles were not present on some Jeffrey pines. Ozone injury symptoms on the remaining needles at these sites suggested that the older needles (1978, 1977) had abscised because of ozone injury. In 1982 the procedure was to collect only the 1981 needles starting in late August. Five trees were sampled within a 600 ft. radius at each site.

Soil samples were dried gradually in a greenhouse and passed through several sieves to remove rocks and organic matter. Leaf and lichen tissue were dried in an oven at 70°C and ground to a fine powder in a Wiley mill. Sample preparation, soil extraction, tissue digestion and sulfate analyses were carried out by the Department of Soil and Environmental Sciences, University of California, Riverside.

Extraction, Digestion and Analysis

Soil samples collected in 1981 were extracted with monocalcium phosphate according to Wall et al. (1980). Five g of soil were extracted with 25 ml of $Ca(H_2PO_4)_2 \cdot H_2O$ solution (500 ug $P \cdot ml^{-1}$) with 0.1 g charcoal added. Samples were shaken for 15 min., centrifuged at 3000 rpm and filtered through Whatman #4 filter paper. In 1982, the extraction procedure was simplified by using a 1:1 water extraction.

Plant samples were digested on a block digestor (Technicon BD-40 or Tecam DG-1) in a mixture of HNO_3 and $HClO_4$. Four ml of concentrated nitric acid were added to 0.400 g of ground plant tissue and allowed to stand overnight. Then 2 ml of 70% of $HClO_4$ were added and the solutions were heated at 120°C until the liquid became clear. The time necessary for this step varied from 24 to 96 hours.

The procedure used for sulfate analysis was an adaptation of a method developed by Wall et al. (1980). Basically it is a turbidimetric method adapted for use on a Technicon Autoanalyzer II. The Autoanalyzer was equipped with a modified Sampler IV (40+40 option) which allowed side-by-side aspiration of sample and $BaCl_2$ reagent. The method presented by Wall et al. (1980) was modified by using two reagents rather than four. The $BaCl_2$ reagent and diluent were prepared as follows: (1) $BaCl_2$ reagent--Gum Arabic/Acacia was dissolved in heated deionized water in the amount of 5 g/l. After filtering (Whatman #541) 12.5 g of $BaCl_2$ were dissolved in 500 ml of the gum arabic solution; and (2) Diluent: 40 ml of concentrated HCl were added to one liter of deionized water. The reagent and sample reacted in deionized water unless samples had a matrix that was not sufficiently acidic. Insufficient acidity prevented complete washing out of the $BaSO_4$ precipitate. If that was the case, the reagent wash used was 2 N HCl. Sulfur data for plant tissue are reported as sulfate-sulfur (SO_4-S); whereas, soil extract data are reported as sulfate (SO_4).

RESULTS

Soil Sulfate

The sulfate content of the 0-5, 5-15 and 15-30 cm layers were determined in 1981 at 15 of the sites indicated in Figure III-1 (Table IV-1). The sites above 2000 ft. elevation generally exhibited a decreasing sulfate concentration with depth. Below 2000 ft., in the Oildale area the sulfate concentrations were generally higher in all layers. Increases of sulfate with depth at these sites may have been due to native deposits of gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum may not be present in the subsoils of higher elevation sites thus accounting for the decrease of sulfate with depth. This small data set did not permit us to conclude whether gypsum or deposition of sulfate from the atmosphere was responsible for higher concentrations in the surface (0-5 cm) layer at sites above 2000 ft. elevation.

In 1982 a second set of samples was obtained from the sites indicated in Figure III-2. During this collection, to further investigate the presence of gypsum, samples were obtained from depths between 70 and 100 cm. The mean sulfate contents of the four soil layers were compared in all possible combinations. Means were separated with the t-test (Table IV-2).

Table IV-1. Sulfate Content of Upper Soil Layers Collected at Increasing Distances from Oildale in 1981.

General Location	Name of Plot	Elevation Feet	Miles from Oildale (Oil Center)	Direction (degrees)	Sulfate Concentration ($\mu g \cdot g^{-1}$) Sample Depth (cm) 0-5	5-15	15-30
					Means and Standard Deviations		
Oildale	Ant Hill	800	6.2	100	102 ± 17	76 ± 26	86 ± 28
	Round Mtn. Road #1	1000	5.5	85	1740 ± 10	4704 ±960	6255 ±157
	Round Mtn. Road #2	700	6.7	67	324 ± 402	38 ± 17	68 ± 62
	Comanche Road	1000	9.2	110	52 ± 5	48 ± 22	108 ± 17
Kern Riv. Canyon	Democrat Springs	2000	20.8	75	41 ± 12	44 ± 4	38 ± 6
	Miracle Hot Springs	2400	27.0	72	84 ± 4	43 ± 27	27 ± 30
Greenhorn Mountains	GH #4	4000	14.6	65	55 ± 6	48 ± 5	46 ± 7
	GH #3	4973	16.9	68	14 ± 5	8 ± 3	3 ± 0
	GH #2	6250	26.1	58	30 ± 4	20 ± 9	18 ± 0
	GH #1	6520	29.7	53	16 ± 16	14 ± 9	6 ± 4
Breckenridge Mountain	Br #2	2930	16.0	90	30 ± 11	19 ± 4	18 ± 0
	Br #3	3915	18.5	87	34 ± 16	28 ± 7	24 ± 0
	Prono 6-4	6020	19.7	84	21 ± 15	13 ± 5	12 ± 8
Piute Mountains	Havila	3000	24.9	82	12 ± 4	10 ± 6	6 ± 4
	Prono 7-1	6600	32.9	80	11 ± 6	9 ± 7	6 ± 4

In the Breckenridge Mountain and Sawmill Road transects there were significantly higher sulfate contents in the surface (0-5 cm) layer compared to the 5-15 amd 15-30 cm layers. In the Greenhorn Mountain transect the 0-5 cm layer had significantly higher sulfate than the 15-30 cm layer but not the 5-15 cm layer. These results support the hypothesis that sulfate may have been added to the surface layers from the atmosphere. However, the hypothesis is weakened by the relatively high subsoil (70-100 cm) sulfate content in the Greenhorn Mountain transect. In an attempt to clarify this point, the functional relationship between surface soil sulfate and elevation (and distance away from Oildale) was examined.

Regression analysis of soil sulfate against elevation for each soil layer along the Greenhorn Mountain transect did not show significant slopes for any layer (Figure IV-1). However, the 0-5 cm layer of the Breckenridge Mountain transect did show a significant ($p < 0.01$) decrease with increasing elevation but none of the other layers showed significant slopes (Figure IV-2). All soil layers of the Sawmill Road transect showed decreasing sulfate concentrations with decreasing elevation (Figure IV-3). This transect descends from the 6000 ft level on the Greenhorn Ridge in a west to east direction. At the lower end of Sawmill Road, soils and vegetation could receive atmospheric sulfur transported up the lower Kern River Canyon, however, a paradoxical situation was revealed. While all soil layers decreased in sulfate content, the vegetation sulfate content increased significantly with decreasing elevation. The soil sulfate trend with elevation is not consistent with the other transects but the vegetation sulfur trend is similar to that of the other transects.

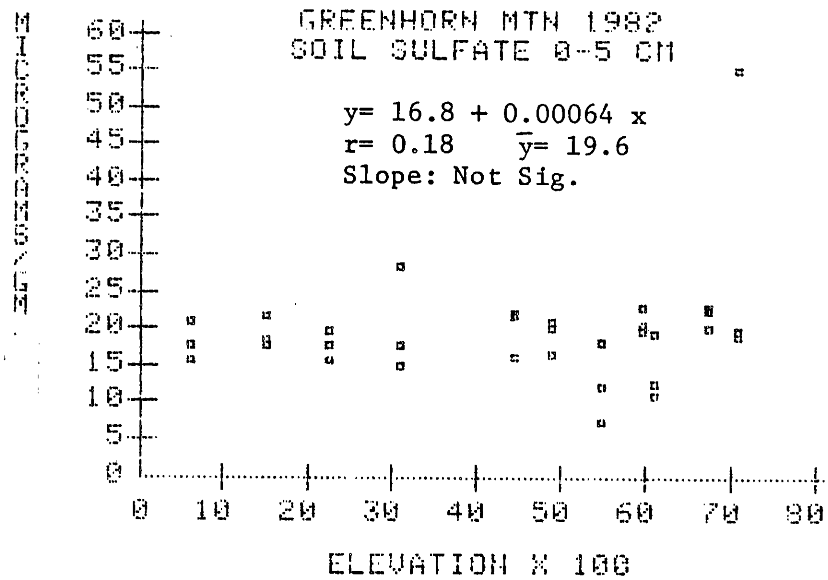
Table IV-2. Comparison of sulfate concentrations at four depths on three transects east of Bakersfield.

Sites	Depth of Soil Layers Compared cm	Mean Sulfate Concentrations $\mu g \cdot g^{-1}$	Differences between Layers Compared
Breckenridge Mountain	0- 5 and 5- 15	18.76 - 12.49	6.27**[1/]
	0- 5 and 15- 30	18.76 - 8.57	10.19**
	0- 5 and 30-100	18.76 - 9.95	8.81*[2/]
	5-15 and 15- 30	12.49 - 8.57	3.92**
	15-30 and 30-100	8.57 - 9.95	1.38 N.S.[3/]
	5-15 and 30-100	12.49 - 9.95	2.54 N.S.
Greenhorn Mountains	0- 5 and 5- 15	19.57 - 16.07	3.50 N.S.
	0- 5 and 15- 30	19.57 - 12.51	7.06**
	0- 5 and 30-100	19.57 - 18.59	0.98 N.S.
	5-15 and 15- 30	16.07 - 12.51	3.56 N.S.
	15-30 and 30-100	12.51 - 18.59	6.08 N.S.
	5-15 and 30-100	16.07 - 18.59	2.52 N.S.
Sawmill Road	0- 5 and 5- 15	13.79 - 9.08	4.71*
	0- 5 and 15- 30	13.79 - 5.62	8.17**
	0- 5 and 30-100	13.79 - 5.50	8.29 N.S.
	5-15 and 15- 30	9.08 - 5.62	3.46*
	15-30 and 30-100	5.62 - 5.50	0.12 N.S.
	5-15 and 30-100	9.08 - 5.50	3.58 N.S.

[1/] t = 0.01

[2/] t = 0.05

[3/] Not significant



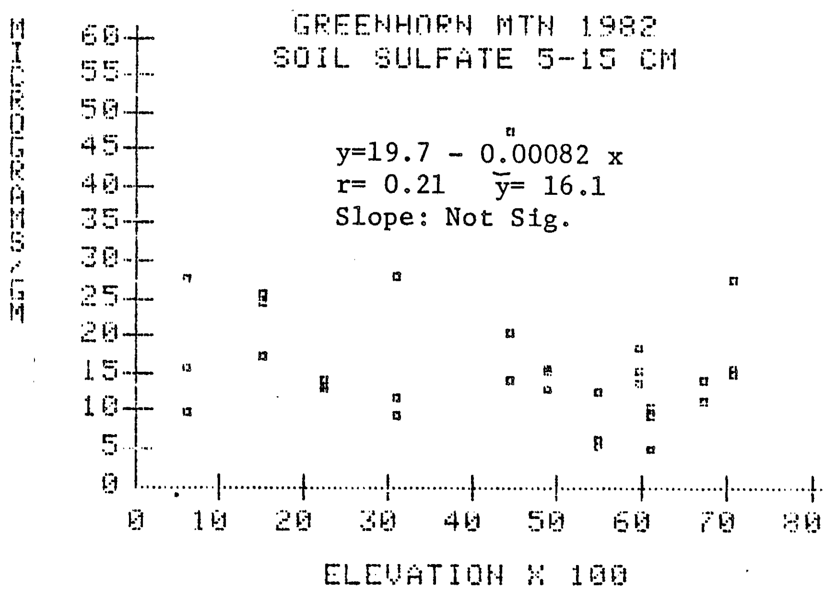
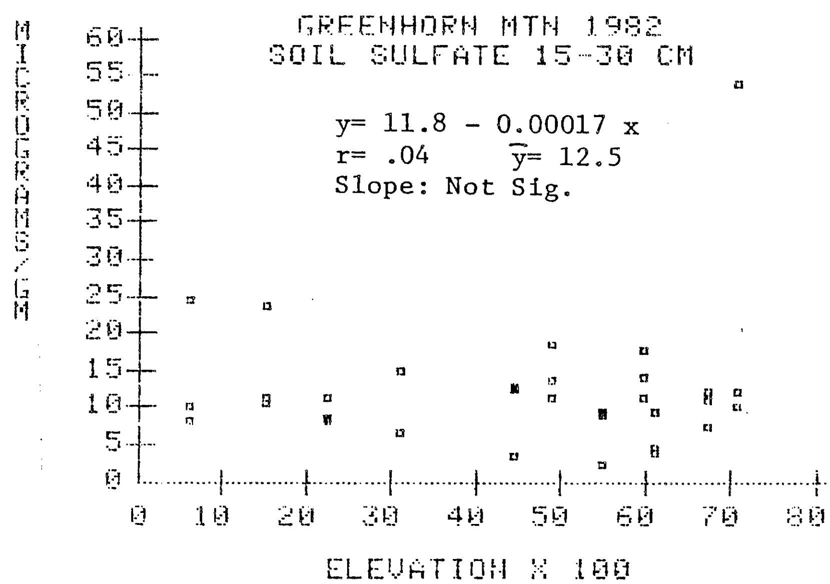


Figure IV-1. Sulfate concentrations in surface and subsoil layers at sites (see Figure III-2) located on a gradient of increasing elevation in the Greenhorn Mountains east of Bakersfield



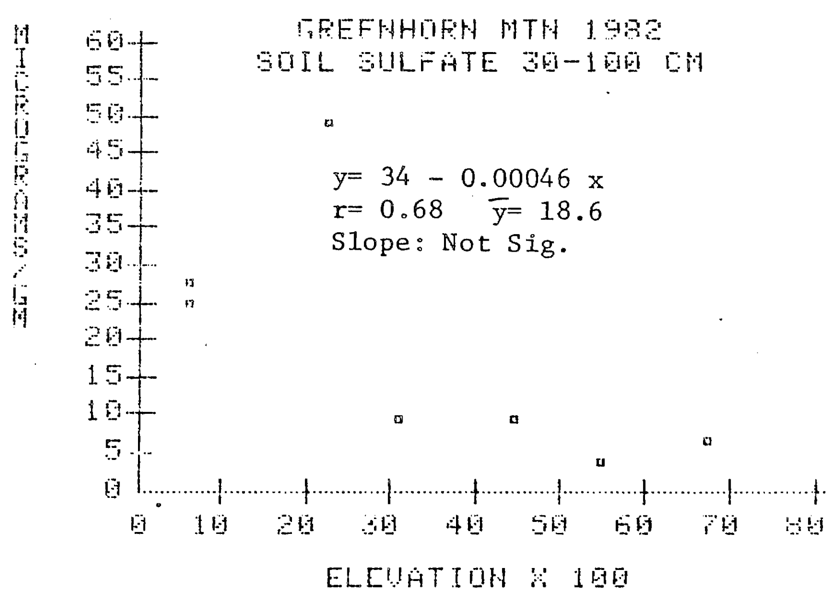


Figure IV-1. (Continued)

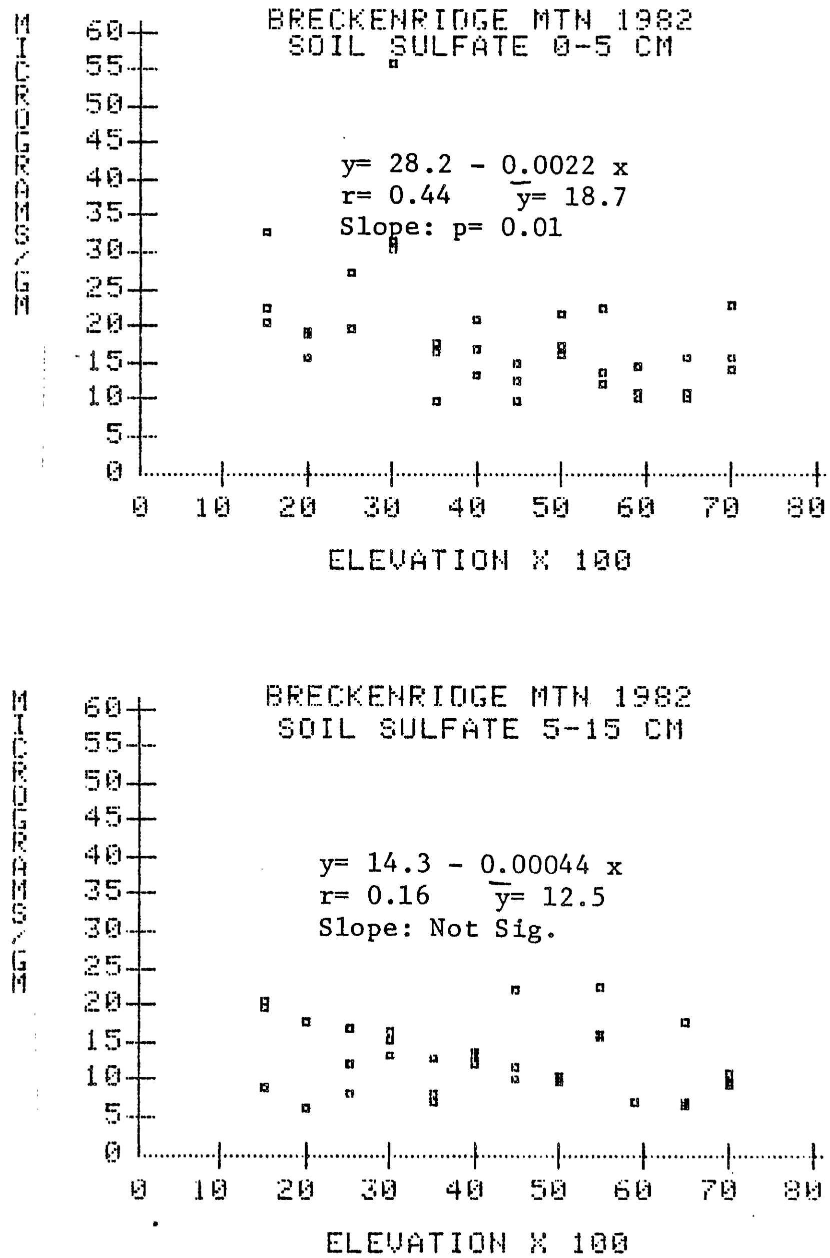
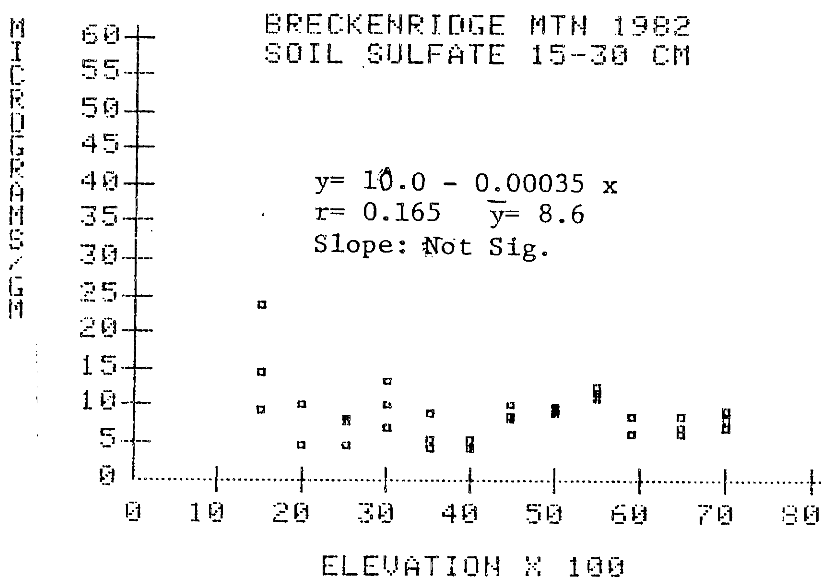
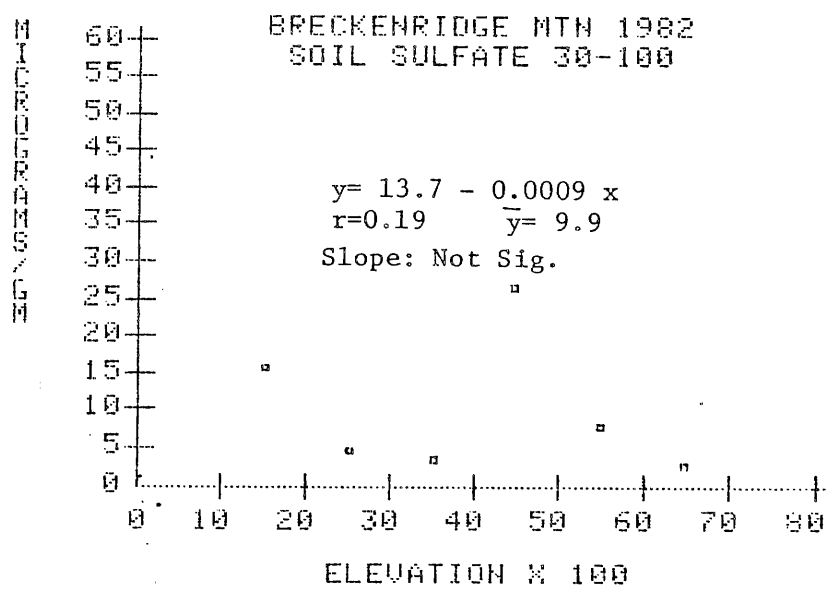


Figure IV-2. Sulfate concentrations in surface and subsoil layers at sites (see Figure III-2) located on a gradient of increasing elevation in the west slope of Breckenridge Mountain





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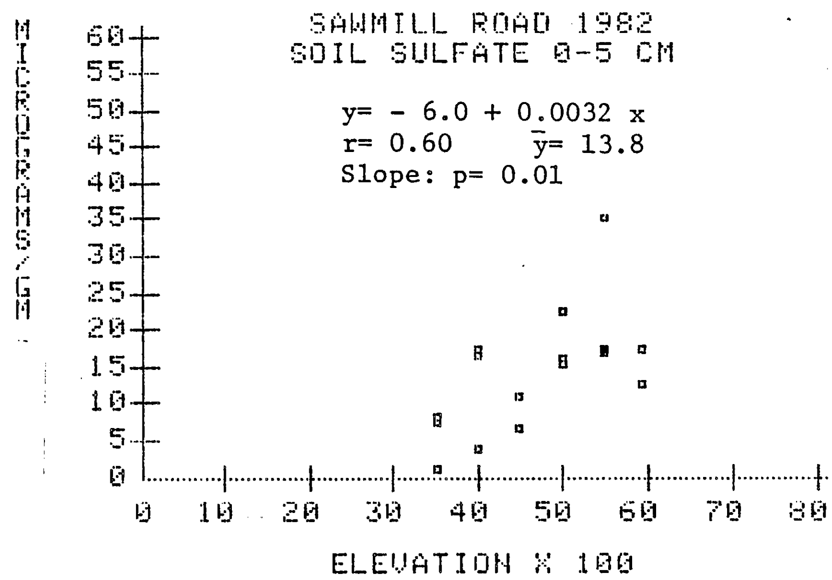


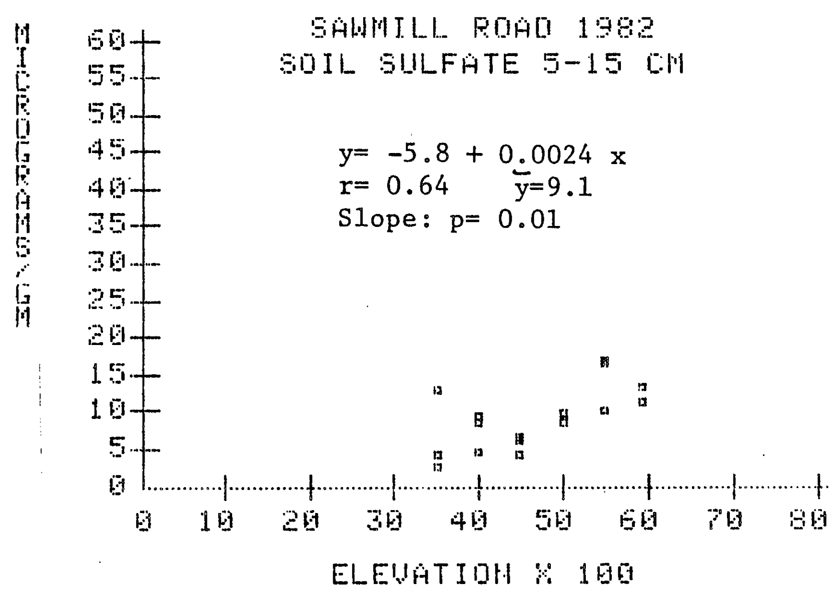
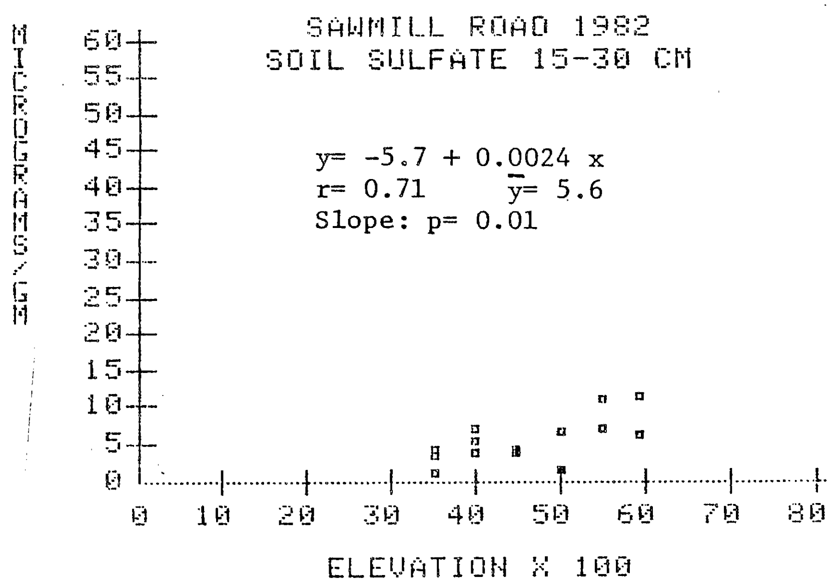


Figure IV-3. Sulfate concentrations of surface and subsoil layers at sites located on elevational gradient along Sawmill Road which starts on the Greenhorn Ridge at 6,000 feet, leads down in an easterly direction and terminates at Highway 155 on the west shore of Lake Isabella. See Figures III-1 and III-2.



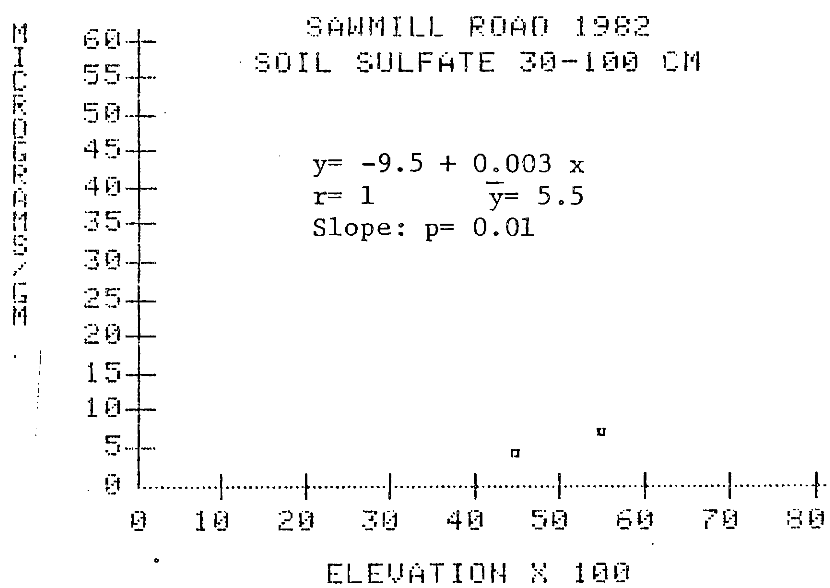


Figure IV-3. (Continued)

Pine Needle and Lichen Sulfate

The sulfur content of individual needle whorls and the averages of all whorls from *Pinus canariensis*, *P. sabiniana* and *P. jeffreyi* collected in 1981 are shown in Table IV-3. For single whorls the concentration ranged from 860 to 2020 $\mu g \cdot g^{-1}$. The grand averages of all needle whorls combined (e.g. one- (current year), two-, three-, and four-year-old) ranged from 1281 $\pm$ 160 to 1661 $\pm$ 425 $\mu g \cdot g^{-1}$. These data suggested trends but because of the relatively small number of samples and large standard deviations, it was necessary to do additional sampling. Two preliminary interpretations could be advanced. First, the Canary Island pine (*P. canariensis*) needles from trees very close (1-5 miles) to Oildale had slightly higher but not significantly different sulfur concentrations compared to other pine species at more distant sites. Second, the youngest needles of digger pine (*P. sabiniana*) and jeffrey pine (*P. jeffreyi*) at some remote sites had slightly less but not significantly different sulfur concentrations compared to older needles. We concluded from these data that only one-year-old needles (1980 needles in Table IV-3) would be collected in the future because there was not much difference between their sulfur content and that of older needles. Furthermore, 5 trees were to be sampled at each site.

The trend of sulfur concentrations with elevation determined from samples collected in 1982 at sites in the Greenhorn Mountains, Breckenridge Mountain and along the Sawmill Road transect are shown in Figure IV-4. In this analysis, to have a larger span of elevation, digger, ponderosa and Jeffrey data were grouped. There was no data to suggest that background sulfur levels in needles of the 3 species would be significantly different; conifers as a class are low accumulators of soil sulfur (Linzon et al., 1979).

Table IV-3. Sulfur Content of Leaf Tissue for Different Age Needles and for Different Plots in 1981.

Species	General Location	Plot	Elevation Feet	Distance and Direction from Oildale Miles	Degrees	Needle Age and $ug \cdot g^{-1}$ S 1981	1980	1979	1978	$\overline{X}$ and s.d. per site
Pinus sabiniana	Kern Canyon	DHS	2000	20.8	75	1240	1540	1350		1377 ± 152
		MHS	2400	27.0	72	1380		1610		1495 ± 163
	Greenhorn Mts.	GH4	4000	14.6	65	1280	1390	1540		1403 ± 131
		GH3	4973	16.9	68	1160	1240	1160		1187 ± 46
	Breckenridge Mts.	BR2	2930	16.0	90		1390	1390	1160	1313 ± 133
		BR3	3915	18.5	87	1200	1390	1390	940	1230 ± 213
	Piute Mts.	HAV	3000	24.9	82	1090	1350	1350	1390	1295 ± 138
			1/ r=-.68	2/ r=0.44		1225±100	1383±96	1399±145	1163±225	1315 ± 157 3/
Pinus jeffreyi	Greenhorn Mts.	Prono 6-6	6000	24.4	62	860	940	1500		1100 ± 349
		GH2	6250	26.1	58	1160	1280	1500		1313 ± 172
		GH1	6520	29.7	53	1370	1540	1470	1840	1555 ± 202
		Prono 6-11	7475	32.4	49	940	1390	1050	940	1080 ± 213
	Breckenridge Mts.	Prono 6-4	6020	19.7	84	1560	1560	1670	1620	1620 ± 70
		BR5	7544	22.4	90	1050	980	1050	1160	1060 ± 74
	Piute Mts.	Prono 7-1	6600	32.9	80	1280	1390	1050	1090	1205 ± 160
			1/ r=-0.57	2/ r=-0.26		1174±248	1297±250	1327±267	1344±396	1281 ± 160 3/
Pinus canariensis	Oildale	Pan. Park(N)	600	1.8	180	1280	1350			1315 ± 50
		Pan. Park(S)	600	1.8	180	1280	1390			1335 ± 78
		Kern Park	500	5.3	85	2210	2020	2100		2110 ± 95
						1590±537	1587±376			1661 ± 425 3/

1/ Correlation coefficient for regression of $\overline{X}$ $ug \cdot g^{-1}$ $SO_4^=$ per site on elevation above sea level

2/ Correlation coefficient for regression of $\overline{X}$ $ug \cdot g^{-1}$ $SO_4^=$ per site on distance from Oildale

3/ Grand $\overline{X}$ $ug \cdot g^{-1}$ $SO_4^=$ for all age needles of a species

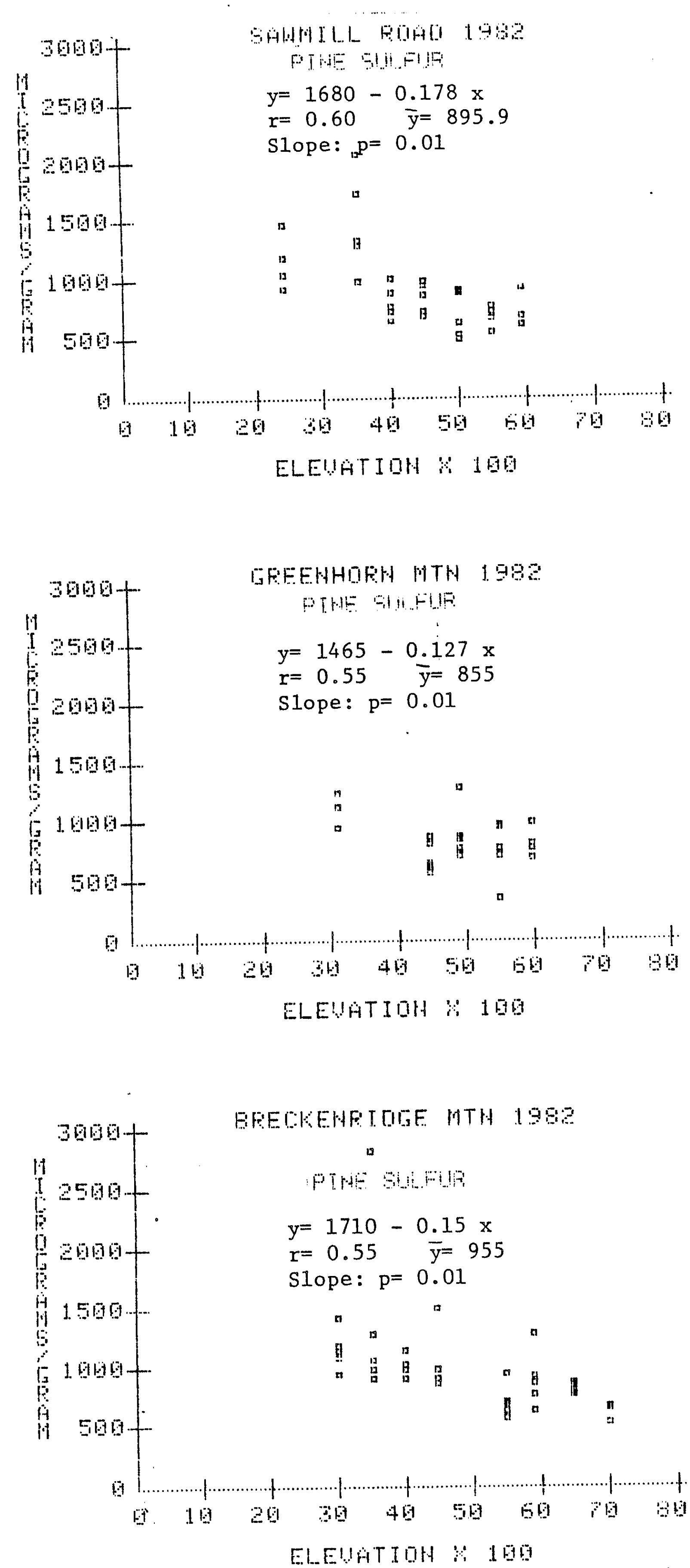


Figure IV-4. Sulfur concentrations in one-year-old needles (1981) of three pine species sampled in 1982 along gradients of increasing elevations in the Greenhorn and Breckenridge Mountain areas.

The slopes of all three regression lines are significant ($p < 0.01$) suggesting a decrease in foliage sulfate content with increasing elevation above or distance east of Bakersfield. The tissue sulfur for 1982 and the combination of 1981 and 1982 samples of digger pines from all three transects shows significant negative slopes ($p < 0.01$) with increasing elevation (Figure IV-5) but the separate slopes for Jeffrey, ponderosa and sugar pine (P. lambertiana)were not significant.

Digger, ponderosa and Jeffrey pines have similar needle lengths and each have three needles per fasicle. The density of foliage ranges from sparse to moderately dense. In 1982, the mean sulfur content of ponderosa pine needles from all 3 transects was 801 $ug \cdot g^{-1}$ and that for Jeffrey pine foliage was 705 $ug \cdot g^{-1}$. These means are not significantly different, however, the lower mean for Jeffrey pine is probably because it is found at the highest elevations. Sugar pine growing at the same elevation as Jeffrey pine had a mean sulfur content of 1237 $\mu g \cdot g^{-1}$ (Figure IV-6). Sugar pine has relatively short needles and five per fasicle. The density of the foliage ranges from moderate to very dense. It would appear that the flux of sulfur compounds to sugar pine is larger because deposition may be a function of the larger surface area of sugar pine foliage. It is also possible that sugar pine accumulates more sulfur from the soil than the Jeffrey pine.

A comparison of the sulfur contents of the two lichen species in the Greenhorn Mountains and Breckenridge Mountain transects (Figure IV-7) show means that are higher than any of the pine species. Sulfur contents of Letharia vulpina were 2033 and 2136 $\mu g \cdot g^{-1}$ for Greenhorn and Breckenridge, respectively. The corresponding values for Hypogymia enteromorpha were

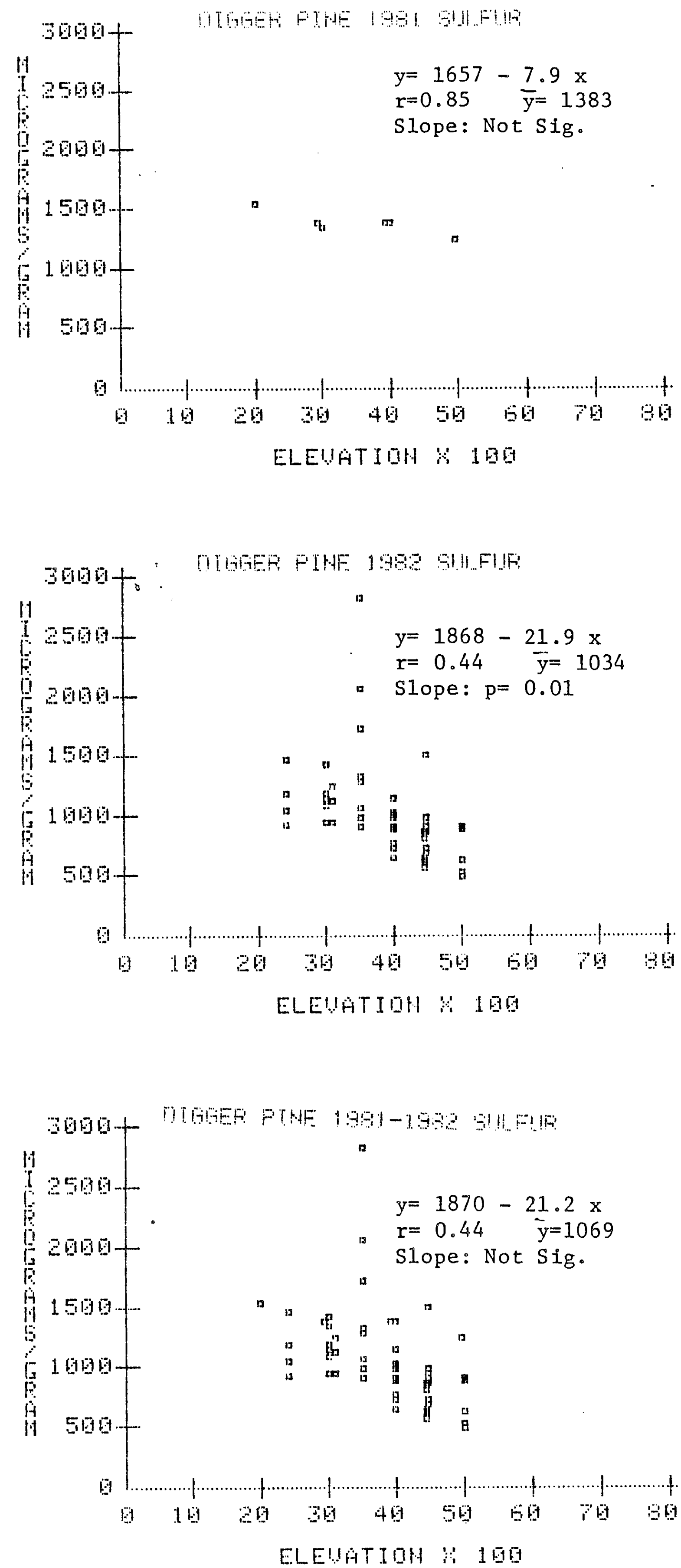
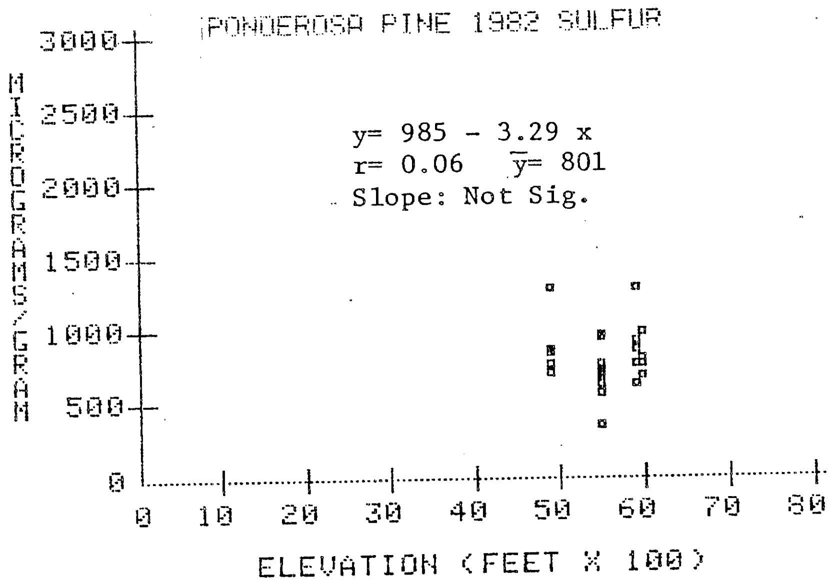
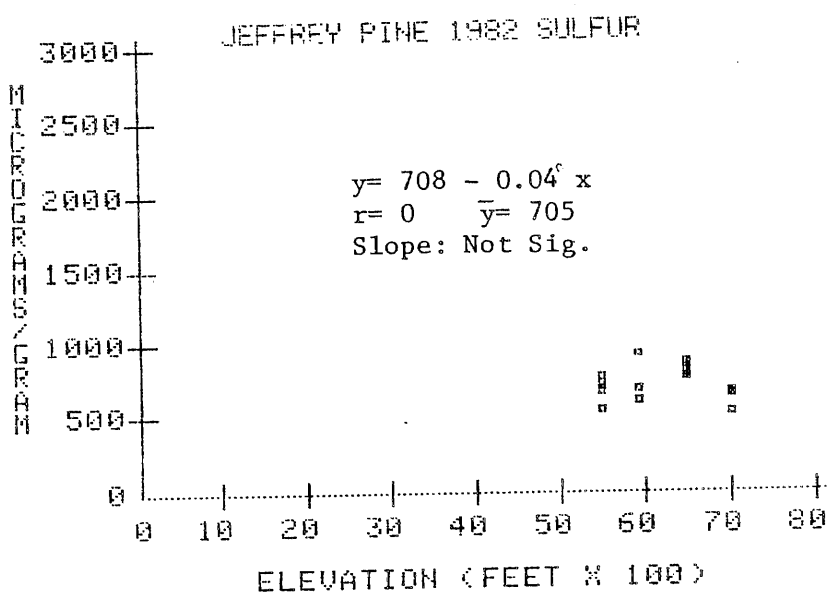


Figure IV-5. Sulfur concentrations in one-year-old needles of digger pine (P. sabiniana) sampled in 1981 and 1982 along gradients of increasing elevations in the Greenhorn and Breckenridge Mountain areas.





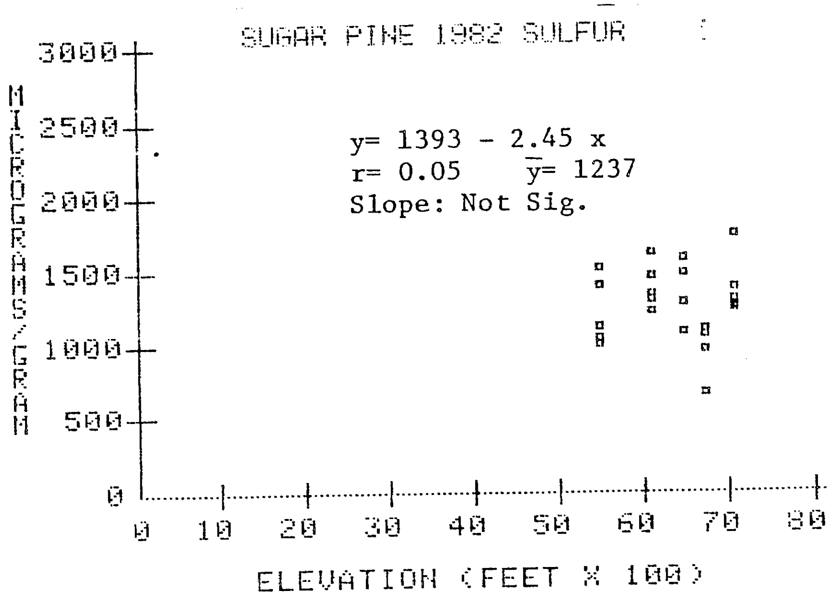


Figure IV-6. Sulfur concentrations in one-year-old foliage of <u>Pinus ponderosa</u>, <u>P</u>. <u>Jeffreyi</u> and <u>P</u>. <u>lambertiana</u>.

1611 and 1438 $ug \cdot g^{-1}$. _L. vulpina_ is the most foliose of the two species and probably has a greater surface area. Both lichen sulfur concentrations are appreciably higher than sugar pine and since lichens are epiphylic, they must be accumulating sulfur from the atmosphere only. These higher concentrations in lichens are probably related to more efficient absorption of sulfur compounds and exposure times that exceed the life span of pine needles (> 4 years). None of the slopes for sulfur content of lichens versus increasing elevation were significant but were negative in three of the four cases (Figure IV-7).

DISCUSSION

The surface soil layers appear to be enriched in sulfate. The 0-5 cm layers decrease significantly in sulfate concentration with increasing distances (and elevation above) from Bakersfield in the direction of Breckenridge Mountain. Pine needle sulfur concentrations also show a significant decrease with increasing elevation for the Breckenridge Mountain transect and the other major transect in the Greenhorn Mountains. Soil sulfate trends in the Greenhorns do not follow the Breckenridge model, namely there was no trend of decreasing concentration with elevation increase. Another difference was that high sulfate concentrations appear in the 70-100 cm layer at 2 sites below 3000 ft. Otherwise, the concentration in this layer at other sites above 3000 ft are lower than the layers between 0 and 70 cm, and the 15-30 cm layer in particular has significantly less sulfate than the 0-5 cm layer.

The reasons for opposite trends for soil sulfate in all layers and pine needle and lichen sulfur content in the Sawmill Road transect remains

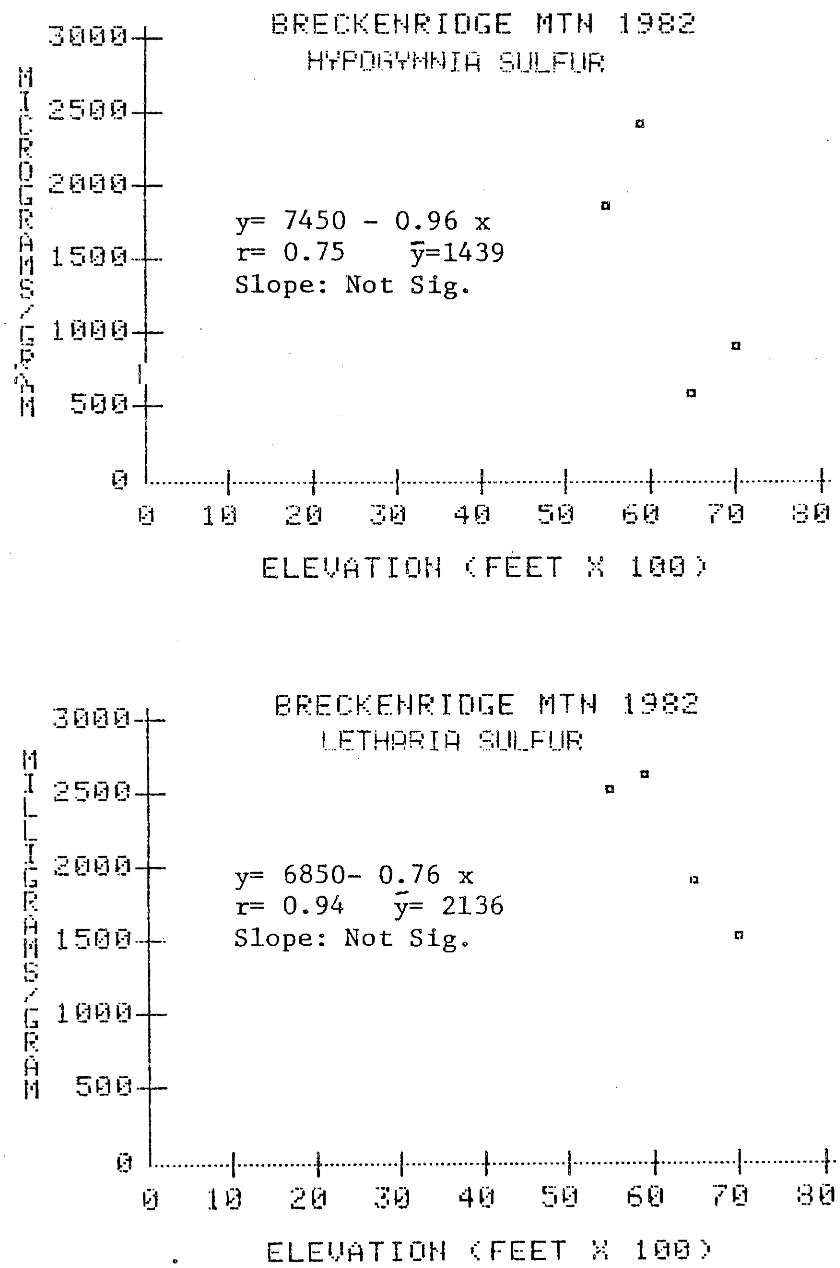
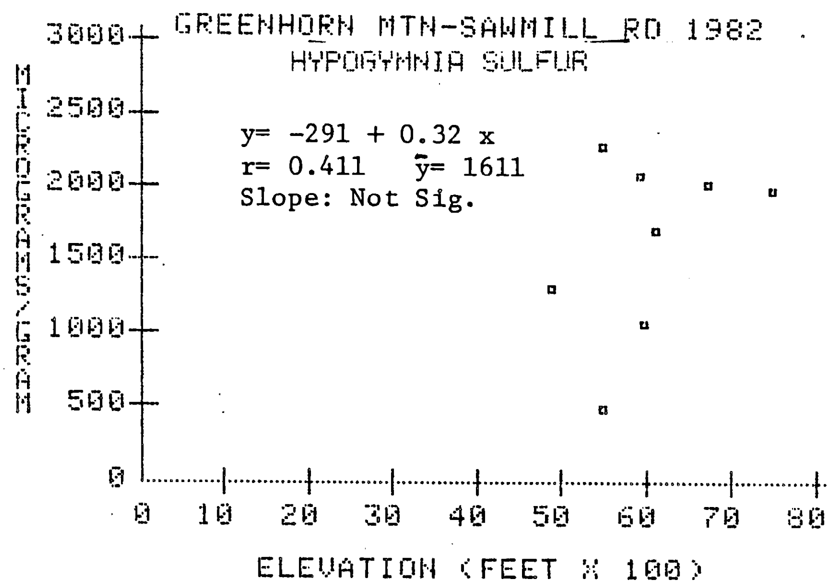


Figure IV-7. Two lichen species, Letharia vulpina and Hypogymnia enteromorpha, collected at the same sites as pine needle tissue (Figure IV-6), had generally higher mean concentration of sulfur, but differences between lichens and pines were not significant.



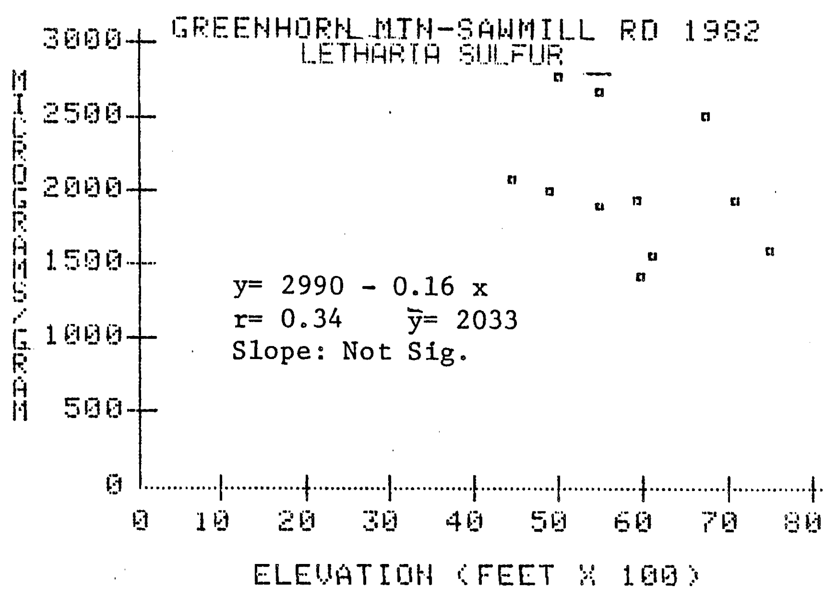


Figure IV-7. (Continued)

unexplained. If atmospheric deposition is the cause for foliar sulfur increases at lower elevations then surface soil layers should show the same trend. The west end of this transect is 24 miles east of Oildale and it extends only 7 miles eastward. The Greenhorn and Breckenridge transects begin near Oildale and extend eastward for 32 and 23 miles, respectively. Therefore, they should give the best representation of regional trends.

It is difficult to determine the background sulfur concentration above which the excess may be attributable to atmospheric sources. Linzon et al. (1979) determined that conifers were low sulfur accumulators with respect to that accumulated from the soil. Typical concentrations ranged from 1300 to 1500 $ug \cdot g^{-1}$ sulfur as measured by the X-ray fluorescence method with dry, pelletized tissue. Our sulfur concentrations were similar to those reported by Linzon et al. (1979).

SUMMARY

Soil and plant tissue concentrations of sulfur decrease with increasing distance along east and northeast transects extending to higher elevations in the Breckenridge and Greenhorn Mountain areas. Plant tissue concentrations are not high enough to cause visible injury symptoms but they do generally resemble the typical downwind transport and deposition patterns of sulfur pollutants.

V. SULFUR ISOTOPE ABUNDANCES OF AIR, SOIL AND PLANT TISSUE SAMPLES

INTRODUCTION

Isotopes of an element differ in their masses and consequently their abundances are altered in nature by mass dependent processes. Sulfur isotope abundances can be used to effectively evaluate contributions of sulfur to the environment from air pollution sources provided that the sources vary in their isotopic composition from the prepollution background (Krouse, 1980). Of the four stable isotopes of sulfur, ^{32}S and ^{34}S are usually examined. Their abundances are expressed on a $\delta^{34}S$ scale defined as

$$\delta^{34}S = \frac{[^{34}S/^{32}S]_{\text{sample}}}{[^{34}S/^{32}S]_{\text{meteorite standard}}} - 1 \times 10^3$$

The technique has been effectively applied to environments in the Province of Alberta, Canada (Krouse, 1980). There, the emissions from the sour gas industry are considerably enriched in ^{34}S compared to the preindustrial surroundings. This isotopic "leverage" is not always available for environmental assessment.

In this study, the technique was used in the conventional manner to determine the relationship of the sulfur isotopic composition of sulfur oxide emissions in the Bakersfield-Oildale area to that of the same soil and plant tissue samples described in Chapter IV.

PROCEDURES

Sampling Sources of Atmospheric Sulfur and Fuel Oil at Oildale

In the summers of 1981 and 1983, high volume sampling was done at the Oildale, Manor Street Monitoring Station employing a special filter pack. Sampling was done for 4- or 6-hour periods, day and night. The filter pack consisted of a quartz filter to remove larger particulate and aerosol fractions followed by two K_2CO_3-glycerine impregnated filter papers for absorbing SO_2. The filter papers (Schleicher and Schuell, Inc., SS 2W) were treated and sealed in a polyethylene bag according to the latest method used by the Brookhaven National Laboratory (Dan Leahy, Personal Communication).

A clean oil sample representative of that burned to generate steam was obtained through the courtesy of Mr. Craig Jackson, Environmental Analyst, Getty Oil Company, Bakersfield. A sample of elemental sulfur was obtained from an outdoor storage pile north of Bakersfield, courtesy of the Wilbur Ellis Company. Because of the widespread use of sulfur by agriculture, we considered it necessary to evaluate the effect that the isotope ratio of this source might possibly have on the soils and plant tissue at our sample sites east of Bakersfield.

Sampling Soils, Foliage of Pine and Lichens at Increasing Distances East and Southeast of Oildale

The locations where soil or foliage and soil were collected have been described in Figure III-1 for 1981 and Figure III-2 for 1982. Subsamples of the collection for each year were used for sulfur isotope analysis. The sulfate contents of these samples are reported in Chapter IV. By the means of two successive research agreements with Dr. H. R. Krouse, Department of Physics, University of Calgary, it was possible to have the sulfur isotope ratios of hundreds of samples determined by his laboratory which is highly experienced in this analytical technique. The development of a continuing dialogue with Dr. Krouse regarding data interpretation was an important aspect of the agreements.

Analytical Methods

In preparation for $^{34}S/^{32}S$ analysis, $SO_4^{\ 2-}$ was extracted from a few ground vegetation samples using LiCl solution and ultrasonic agitation. For total analysis, samples were combusted in a Parr bomb at 20 atm O_2 pressure to convert all sulfur compounds to $SO_4^{\ 2-}$.

Solutions were filtered and $SO_4^{\ 2-}$ precipitated with Ba^{++}. SO_2 was prepared for stable isotope analyses by the following reaction sequence:

$$BaSO_4 \xrightarrow{H_3PO_2\text{-}HI\text{-}HCl} H_2S \xrightarrow[\text{sol}]{\text{CdAc}} \underset{\text{ppte}}{CdS} \xrightarrow[\text{sol}]{\text{Hot } AgNO_3} \underset{\text{ppte}}{Ag_2S} \xrightarrow[900^{\circ}C]{Cu_2O} SO_2$$

The mass spectrometer used for stable isotope analyses was built up around Micromass 602 components.

RESULTS

Source Area Sampling

The analyses of atmospheric sulfur and sulfur from fuel oil and other sources are reported in Table V-1. For the most part, the sulfur isotope ratio of atmospheric samples, fuel oil, and agricultural sulfur were in the range from -1.5 to +7.5 with a mean of +2.9. The mean would be +4.4 without the three negative values obtained from SS-2W filters during the 1983 hivol sampling. There is no definite explanation for the negative values.

Table V-1. Sulfur Isotope Composition of Atmospheric Samples and Other Sulfur Sources.

Category of Sample	Sample Description	$\delta^{34}S$ ‰
Hivol. Oildale 8-20-81	Particles, 40 cfm	+3.8
Hivol. Oildale 8-20-81	Particles, 30 cfm	+4.1
	SS-2W, First Filter	+4.3
Hivol, Oildale 9-6-83		
9-6-83	Particles	+3.1
1415-1800	Particles	+6.2
1805-2400	SS-2W, First Filter	-1.0
Hivol, Oildale 9-7-83		
0500-0800	Particles	+7.4
	SS-2W, First Filter	-1.4
0805-1200	Particles	+3.9
	SS-2W, First Filter	-0.8
Fuel Oil, Getty Oil 1981	Sample A	+4.2
	Sample B	+2.8
Elemental sulfur 1983		+4.5

Sampling of Soils and Vegetation Downwind from Bakersfield in 1981 and 1982

The locations where soils or both vegetation and soils were sampled are shown in Figures III-1 and III-2 for 1981 and 1982 respectively. Appendix 3 includes all of the data from each year. The trends of $\delta^{34}S$ with elevation for both soils and vegetation were examined for both years combined for sample transects extending into the Greenhorn and Breckenridge Mountain areas. For elevations ranging from 800 to 7000 ft along both transects, the $\delta^{34}S$ became more positive for all three soil layers and pine needle tissue. The slopes of calculated regression lines were significant ($p < 0.05$) in all cases (Figures V-1 and V-2). $\delta^{34}S$ values in the 0-5 cm layer were always more positive than in the 5-15 cm layer which in turn were higher than in the 15-30 cm layer on both transects. A few $\delta^{34}S$ values at 70 or 100 cm depth were slightly more positive than in the 15-30 cm layer, i.e., minima in $\delta^{34}S$ tended to occur in the 15-30 cm depth range. The differences among means for all layers on the Greenhorn transect were not significant ($p < 0.05$) but for the Breckenridge transect, the 0-5 cm layer was more positive than the 5-15 cm ($p = 0.03$) and the 15-30 cm ($p = 0.02$) layers.

The $\delta^{34}S$ of pine needle tissue on both transects showed positive slopes ($p < 0.01$) with increasing elevation (Figure V-3). The means for pine tissue were higher than the soil layers in all cases except the Greenhorn Mountain 0-5 cm layer, however, none of the differences were significant ($p < 0.05$).

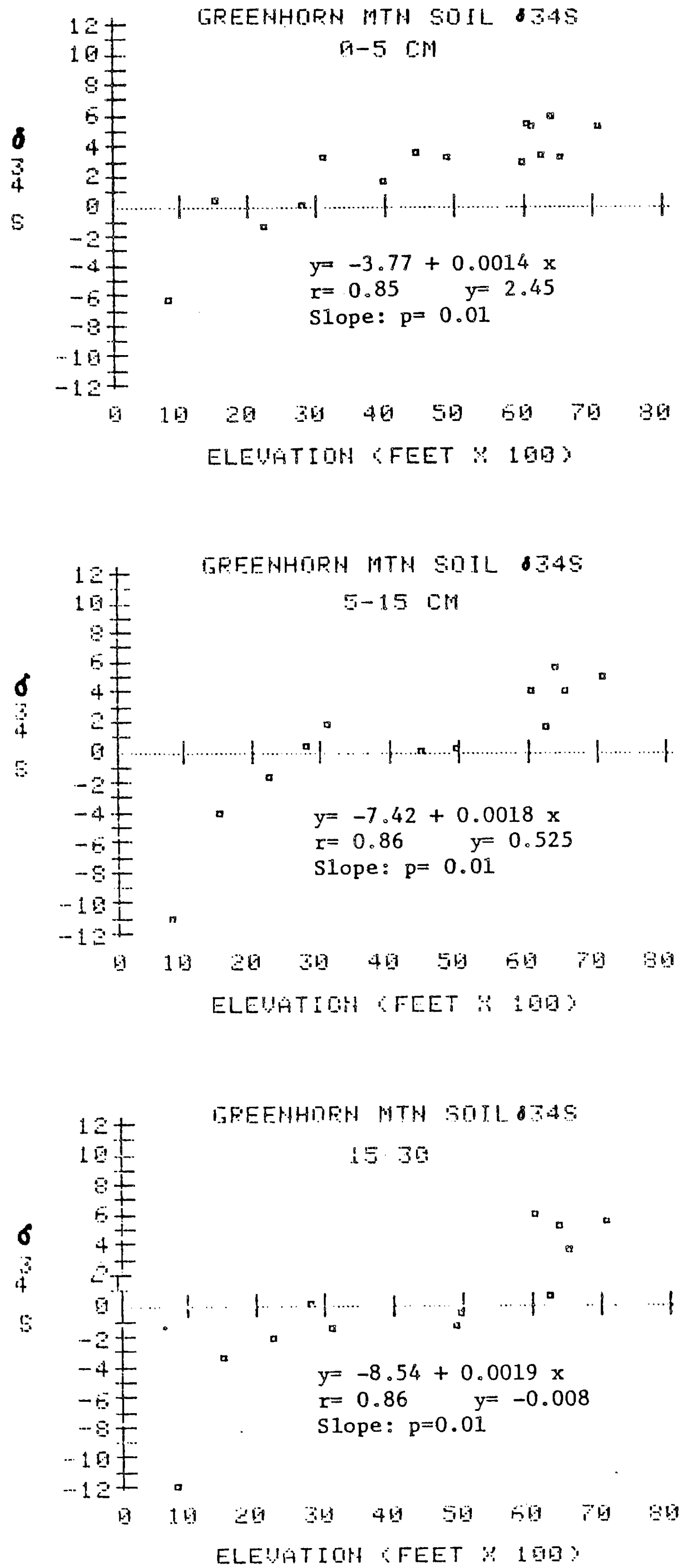


Figure V-1. $\delta^{34}S$ values of surface and subsoil layers collected in 1981 and 1982 at sites on a gradient of increasing elevation in the Greenhorn Mountain area.

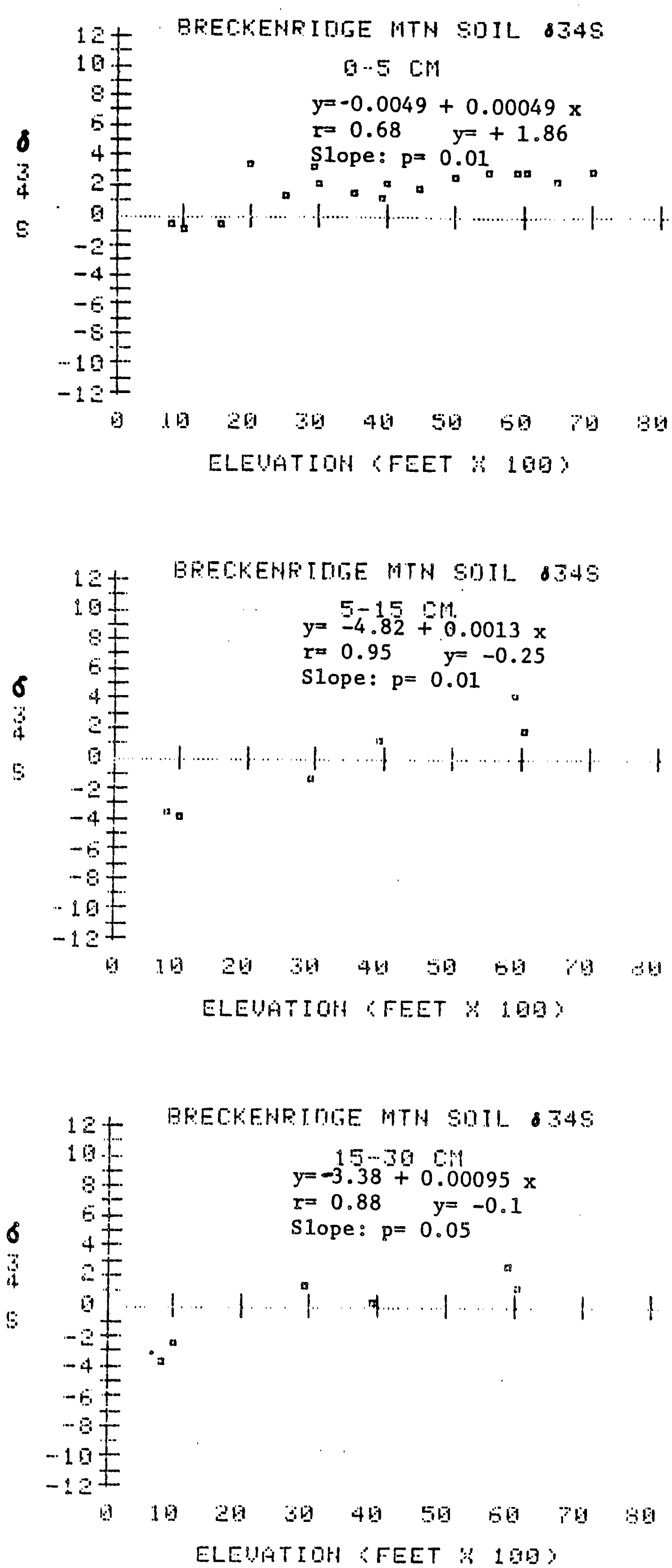
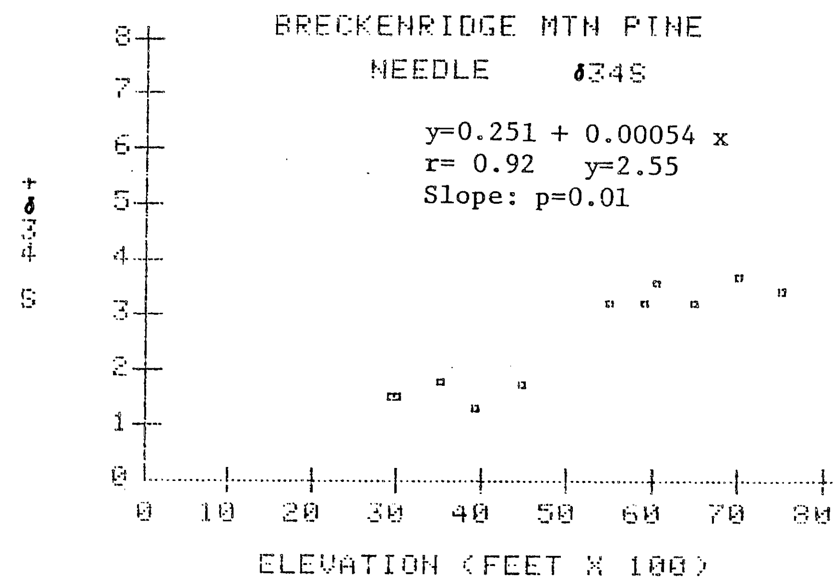


Figure V-2. $\delta^{34}S$ values of surface and subsoil layers collected in 1981 and 1982 at sites on a gradient of increasing elevation in the Breckenridge Mountain area.



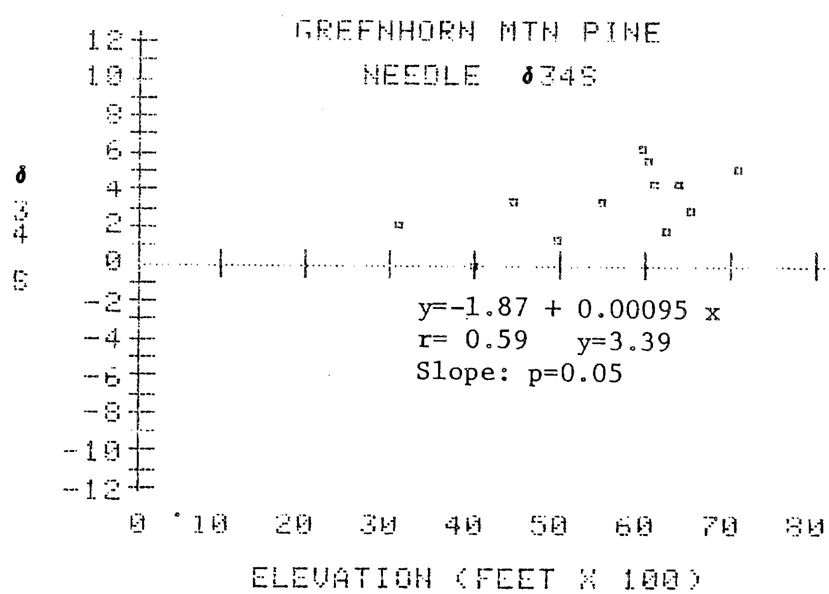


Figure V-3. $\delta^{34}S$ values of needle tissue from several pine species collected in 1981 and 1982 at sites on a gradient of increasing elevation in the Breckenridge and Greenhorn Mountain areas.

Greenhorn Mountain pine tissue had a more positive $\delta^{34}S$ than at Breckenridge Mountain but the difference between means (3.2 versus 2.6) was not significant. Along both transects, pine foliage sulfur was more positive than soil layers but differences were not significant ($p < 0.05$). At comparable sites, both lichens had higher mean $\delta^{34}S$ values than pine needles. For example, *Letharia vulpina* was +4.2 and *Hypogymnia enteromorpha* was +4.7 compared to +4.0 for pine tissue; these differences were not significant ($p < 0.05$). In addition to these data from the two major transects (Greenhorn and Breckenridge Mountain areas) soil or pine needle tissue samples were obtained at sites closer to Bakersfield and at greater distances as well in both years.

The soil samples from Mount Mountain (6.7 miles east of Oildale) were extremely negative (-25 to -28) in all three layers (Table V-2). At Lene Place (8 miles east of Bakersfield) all soil layers ranged between -1.2 and -1.9 (Table V-3). Other sites below 3000 ft elevation show negative values in all three soil layers (Figures V-1 and V-2). Similarly, negative $\delta^{34}S$ values have been found in water and soils in the Peace River area of Alberta, Canada. They have been specifically related to small localized subsurface sulfate mineral deposits (Hitchon and Krouse, 1972; Krouse and Case, 1981). Primary sulfate minerals are generally enriched in $\delta^{34}S$ whereas negative $\delta^{34}S$ values tend to be characteristic of secondary sulfates formed by oxidation of reduced sulfur species. In the Peace River area, Cretaceous shales are the likely sources of these reduced species.

The $\delta^{34}S$ of all soil layers above 3000 ft were positive (Figures V-1 and V-2). The soil data from the Sawmill Road transect (Table V-3) show consistently positive values for all layers. The soils here are derived from granitic parent materials and are poorly developed. Sulfate mineralization may be generally absent from this area.

DISCUSSION

Sulfur isotope analysis is helpful for evaluating the proportions of sulfur from different sources in a sample. In studies of air pollution effects on vegetation, the evaluation of the source of accumulated sulfur in foliage can be accomplished where there is generally only one source which emits sulfur with a $\delta^{34}S$ value distinctly different from sulfur available in the surface soils and rocks in which the plants are rooted (Krouse, 1980). Situations where the "isotopic leverage" was sufficient to distinguish between pollution source and soil sulfur have been reported recently (Krouse, 1977; Winner et al., 1978; Case and Krouse, 1980; Taylor and Bell, 1983).

Our data do not permit a definite interpretation of the proportions of sulfur from different sources in either soil or vegetation samples for several reasons. Although we cannot dismiss these reasons, there is still a hint that some accretion of atmospheric sulfur may be taking place in both surface soils and vegetation.

The trends of sulfate concentration of both surface soil and pine leaf tissue tend to decrease with distance away and elevation above Bakersfield. Significant negative slopes, $p < 0.01$, were seen for 0-5 cm soils on the Breckenridge transect (Figure IV-2) and pine needle sulfate on the Breckenridge and Greenhorn Mountain transects (Figure IV-4). Sulfate concentration decreases with distance from a source area are expected. On the other hand, the reason for this observed trend could be due to decreasing abundance of the sulfate minerals in soils at higher elevations along with decreasing accretion from atmospheric sources. However, the significantly higher levels of sulfate in the 0-5 cm layer compared to deeper layers on the Breckenridge Mountain transect and to a lesser extent for the Greenhorn Mountain transect (Table IV-2) argues in favor of accretion of sulfur form atmospheric sources.

The significant trends toward more positive $\delta^{34}S$ values at higher elevations for both soils and vegetation (Figures V-1, 2, and 3), cannot be interpreted in a straightforward manner. In the current study, the natural background isotopic variations (-30 to 7 $^{o}/oo$) are larger than the difference in isotopic composition between the atmospheric sulfur and that in receptors. The wide variations in S concentrations with location further compound the problem. For example, a soil with a high sulfate mineral concentration and a very negative $\delta^{34}S$ value could have acquired significant amounts of atmospheric sulfur and still possess a negative $\delta^{34}S$ value. In contrast, a granitic soil with a low natural sulfur content may have a $\delta^{34}S$ value close to that of the atmosphere even with low deposition rates. Thus the southern Sierra situation contrasts to Alberta, Canada where atmospheric emissions from the sour gas industry are very enriched in ^{34}S in comparison to the surroundings. In Alberta studies, increased sulfur concentrations are invariably associated with more positive $\delta^{34}S$ values which in turn attest to higher proportions of industrial sulfur in the environment. This does not mean that sulfur isotope data are incapable of assessing the amount of industrial sulfur in the southern Sierra Nevada. Rather, many more data are required in this region to overcome the problems associated with the natural variations in $\delta^{34}S$ values and sulfur concentrations. A promising line of evidence for the relative importance of atmospheric contributions is provided by the comparison of lichens, which obtain most of their nutrients from the atmosphere, to pine needles. The mean $\delta^{34}S$ values of both lichens species were higher than pine needles although the difference was not significant.

Finally, the hypothesis advanced in Chapter II that the greatest mass transfer from the San Joaquin Valley to the east occurs over ridgetops and not through drainages is not contradicted. That is, the more positive $\delta^{34}S$ values observed in foliage a higher elevations may indicate the deposition of sulfur from a mixture of industrial and urban areas where petroleum combustion is the dominant source of sulfur pollution.