PROFILE MEASUREMENTS OF SULFUR DIOXIDE, NITROGEN OXIDES, AND NITRIC ACID DEPOSITION VELOCITIES IN CALIFORNIA'S SOUTH COAST AIR BASIN

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EXECUTIVE SUMMARY

1.0 BACKGROUND PERSPECTIVE

The Kapiloff Acid Deposition Act of 1982 requires the California Air Resources Board (CARB) to "design and operate a comprehensive research program to determine the nature, extent, and potential effects of acid deposition in California." The CARB is further required to give priority, in its research programs, to the South Coast Air Basin (SoCAB) of California. Although a monitoring program to measure wet (i.e., ocurring in conjunction with fog or precipitation) deposition had been established prior to the present research, some estimates indicated that dry deposition in California could be 5 to 15 times more important than the wet processes. This contrast was especially expected in the SoCAB, with its dry climate and numerous sources of acidic and acid precursor species such as oxides of nitrogen and sulfur gases.

Prior to 1986, however, data documenting the nature and extent of dry acid deposition, in the SoCAB or elsewhere in California, were scarce. Particularly, there were essentially no measurements of the rates with which acidic species deposited to the surface of the SoCAB in dry conditions. This situation arose partly because these "flux" measurements are in their research and development stages. The present research is intended to assist the CARB in its efforts to quantify dry versus wet acid deposition in the SoCAB, by directly quantifying the dry "deposition velocities" of five acidic species, which in turn allows quantification of their deposition fluxes.

2.0 FIELD SITE AND MEASUREMENT PROGRAM

A three week measurement program designed to quantify the dry deposition of SO_2, NO, NO_x, and HNO_3 gases, and sulfate aerosol, was conducted at a field site on the campus of California State University, Dominguez Hills, near Carson, CA.

In addition to the basic dry deposition velocity measurements, the objectives of this research are:

1. To develop and apply a practical measurement process, quantifying deposition velocities in a less-than-ideal urban environment;
2. To develop and apply validation criteria which identify excessive deviations from measurement method assumptions.

The field site was chosen after examination of twelve options in the highly urbanized SoCAB. A flat field offering 350 m of fetch on the E-W axis, covered with closely mown grass, was selected. The measurement approach was adjusted to be appropriate to the available fetch distance.

After consideration of three options, the gradient, or profile, method was chosen as offering the best approach to estimation of the rate of transport to the surface of the five species studied. The gradient method allows estimation of the species deposition velocities, based on careful measurement of their gradients on a 5 m tower. The acidic species were measured at three levels on the tower, together with three-axis wind measurements, temperature and dewpoint. The required measurement precision was of order 1 ppb for 30 min averages, and this precision was shown to be achieved in the field program, as measured by the standard errors of 30-minute averages of the SO_2, NO, and NO_x data. The precision of the HNO_3 measurements is uncertain because the response times of the two-channel measurement method may have differed. The sulfate aerosol data always indicated very low concentrations, and was attributed to aerosol particle losses in the sampling tubing.

3.0 RESULTS

The SO_2, NO, NO_x, and HNO_3 data were screened according to selection criteria including elimination of sampling periods when interfering activities took place, elimination of wind directions outside the acceptable fetch sector, selection of species concentrations above minimum thresholds, selection of "stationary" conditions as defined by species standard deviations less than maximum thresholds, and elimination of cases where wind speeds were below the proper operating thresholds of the anemometers.

The data were stratified according to day/night sampling periods, but only the SO_2 deposition velocities showed a difference approaching a significant value. The average nighttime SO_2 deposition velocity exceeded the daytime value, and it is speculated that this effect may be due to reduction of surface resistance by surface moisture (dew). Table 1 summarizes the estimated deposition velocities and their uncertainties.

These deposition velocity estimates are similar to published values for the same species with the exception of the low HNO_3 values and the negative daytime SO_2 value. Published data rarely indicate that the HNO_3 deposition velocity is as low as zero and usually this species is thought to deposit very effectively, "sticking" to almost any surface.

4.0 RECOMMENDATIONS

1. This project included only short periods of continuous monitoring of any species at one level. In a future project, continuous monitoring at each level would determine whether or not fluctuations

were occuring on a shorter time scale than the sampling and averaging time for each level.

2. Although the horizontal wind speeds usually conformed to the expected logarithmic profiles, the 1.25 meter (lowest) sampling level may have been too close to the surface; it should be raised in future experiments. Fetch requirements may always be a limiting factor, however.

3. The anemometer data acquisition rate was hardware-limited to 1 Hz; in future efforts, 2 to 5 Hz is desirable.

4. The proximity of the instrument trailer to the instrumented tower resulted in part from the requirement of minimizing the gas species travel times. This distance should be increased in future studies if at all possible.

5. Separate, electrically-conducting tubing with enhanced flows should be employed for sulfate aerosol measurements in the future; this would most likely reduce aerosol particle losses to acceptable levels.

6. The two-channel HNO_3 detection system needs more research and development to attain both static and dynamic balance of the two channels. A field HNO_3 calibration standard also needs to be developed for field performance tests.

7. The current data base should be re-analyzed to determine the optimal averaging time for which the uncertainty due to non-stationary conditions equals the uncertainty due to instrument repeatability. Non-stationarity is the major contributor to the standard error of the 30 minute averages, not the instrument repeatability.

Table 1

Summary of Estimated Deposition Velocities and their Uncertainties

Gas	Estimated Deposition Velocity (cm/s)		Progagated Uncertainty (cm/s)
SO_2 (day)	-2.1	+-	1.8
SO_2 (night)	2.6	+-	1.2
NO(day)	-0.2	+-	3.3
NO (night)	0.3	+-	0.1
NO_x (day)	-0.3	+-	1.0
NO_x (night)	0.0	+-	0.3
HNO_3 (day)	-0.8	+-	1.7
HNO_3 (night)	-0.1	+-	0.7

ABSTRACT

A three-week dry deposition measurement field program in the South Coast Air Basin of California is described, the objectives of which were to quantify the deposition velocities, and their associated uncertainties, for sulfur dioxide, sulfate aerosol, nitrogen oxides, and nitric acid. The measurements took place in May and June, 1986, on a flat, grass-covered surface near Carson, CA. Deposition velocities were estimated by the profile method, based on gas concentration gradient measurements and associated wind and temperature data acquired on a 5 meter tower, using a sampling frequency of 1 Hz. The estimated nighttime sulfur dioxide deposition velocity was 2.6 cm/s, exceeding the daytime value of -2.1 cm/s. The nitrogen oxides deposition velocities were estimated to be very close to zero, regardless of time of day. The estimated nitric acid deposition velocities were slightly negative (indicating no deposition). Insufficient data were obtained to estimate sulfate aerosol deposition velocities. The estimated deposition velocity measurement uncertainties ranged from 0.1 cm/s to 3.3 cm/s.

ACKNOWLEDGEMENTS

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We are grateful to several individuals at California State University, Dominquez Hills, particularly Mr. Gary Levine, who arranged permission for use of the field site, and Dr. Jim Lyle and his staff of the Chemistry Department who provided laboratory facilities and other assistance. We are also grateful to Mr. Ed Avol of Rancho Los Amigos Hospital for his help in the site search.

An essential part of the program was the loan of gas analyzers and calibrators, arranged by the courtesy of Mr. Richard Egami at DRI. Mr. Clarence Fought, Mr. Eric Broten, and Mr. Tom Swafford of DRI prepared the analyzers and calibrators for field use. Heavy logistics and erection of the tower were capably handled by Mr. Dave Nielson. Mrs. Debbie Cox and Mrs. Beverly Brooks patiently typed the several drafts of the final report.

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gas 2 g (ppb)	gas concentration at level 2, best fit to 30 minute averages, 30 minute average
hws 2m (m/s)	horizontal wind speed (vector sum of u and v) at level 2, 30 minute average
Kh (cm^2/s)	eddy diffusivity of heat
Km (cm^2/s)	eddy diffusivity of momentum
mxsdgs (ppb)	maximum standard deviation of gas concentration in a 30 minute averaging period stability parameter, defined as in Businger(1971)
u (m/s)	horizontal wind speed, E-W component
unvd (cm/s)	propagated uncertainty in V_d
v (m/s)	horizontal wind speed, N-S component
V_d (cm/s)	deposition velocity
w (m/s)	vertical wind speed
$\overline{w}$ (m/s)	average vertical wind speed
X_t (m)	fetch distance
Z (m)	measurement height
Z_o (cm)	roughness length
σ	standard deviation
$\sigma s/\sqrt{N}$	standard deviation of mean

1.0 INTRODUCTION

The South Coast Air Basin (SoCAB) includes a geographical area of about 12,000 km^2. Low mountain ranges to the north and east, and the Pacific Ocean coastline on the west, are boundaries and interfaces of relevance to studies in the atmospheric boundary layer. Important point and area sources of acid precursors are found in the extensively urbanized interior of the SoCAB. Air trajectories are at times difficult to specify, as when stagnant conditions predominate. Gases or aerosols generated within the SoCAB, even in precipitation-free periods, may be "processed" by encounters with extensive fog, or by sluggish circulation out over the Pacific Ocean, and back into the SoCAB. Measurements by Hudson and Rogers (1984) at 765 meters elevation at the northern boundary of the SoCAB furthermore showed that at times the water-soluble component of the submicron aerosol is remarkably constant (in concentration) with time; such a result suggests that, in the absence of major storms or air circulation, the SoCAB might exhibit some of the characteristics of a stirred plenum and micrometeorological measurements of dry deposition fluxes can be made.

In view of the dearth of information relevant to dry acid deposition, and the possibility that the major deposition mechanisms in the SoCAB involve dry pathways rather then wet processes (South Coast Air Quality Management District, 1984), the California Air Resources Board (ARB) has conducted a dry acid deposition measurement program. This program consists of two components. The first component involves long-term monitoring (one year) of acidic atmospheric constituents at several sites throughout the SoCAB. These concentrations can be multiplied by assumed deposition velocities to estimate dry deposition fluxes. The second component consists of short-term measurements of these deposition velocities to verify the assumed values. This report addresses the second component.

The objectives of this deposition velocity measurement project are:

- To develop and apply a practical measurement process, using the gradient method, quantifying deposition velocities in a less-than-ideal urban environment.
- To develop and apply validation criteria which identify excessive deviations from measurement method assumptions.
- To estimate deposition velocities for sulfur dioxide, sulfate aerosol, nitrogen oxides, and nitric acid in California's South Coast Air Basin with specified validity and precision.

The quantification of dry deposition fluxes is far from trivial, even under the most ideal circumstances when classical criteria for stationary concentrations, fetch, and atmospheric stability need to be met. A greater challenge is present in an urban area such as the SoCAB. These measurements push the assumptions of previous "classical" studies performed in more ideal locations (e.g. flat grassland in Illinois including 1 km of fetch without local sources) to their limits. In fact, even though those limits are largely unknown, liberal estimates for their values are unlikely to be met in the SoCAB.

The South Coast Air Quality Management District (1984) observes that the dry deposition of acidic species in the SoCAB may exceed that of wet deposition by a factor of ten or more. There is, however, a paucity of published gas and particle deposition data for the SoCAB when compared to other regions of comparable interest and importance. For example, John et al. (1984) report measurements at three California sites outside the SoCAB; these data required the application of assumed values of the relevant deposition velocities (V_d). Comparatively speaking, there is a profusion of data from other states and regions, such as Illinois (Katen and Hubbe, 1983; Wesely, et al., 1977 and 1983), Ohio (Hicks et al., 1983), North Carolina and Texas (Wesley et al., 1983), Colorado (Sievering, 1983), including direct measurement of V_d's. These values may or may not be applicable to the SoCAB without introducing large uncertainties. These uncertainties in V_d are largely undefined by most monitoring projects.

Existing data from other locations allow some preliminary estimates to be made of the magnitudes of measurement uncertainties. At best, the uncertainty in V_d measurements seems to be ± 25% (Durham and Ellestad, 1984). Wesely et al. (1977) measured V_d for particulate deposition to a partially-vegetated surface in Illinois, and estimated the accuracy of their measurements to be about ± 40%. Sehmel (1980) summarizes gas and aerosol V_d values; variations in V_d of one or more orders of magnitude are common, although clearly these variations are reduced if the data are stratified by surface type and by day/night vegetative surface resistance (Hicks et al., 1983).

In order to properly use these measurements for estimating the amount of dry acid deposition, it is not enough to obtain values for V_d; quantitative estimates must also be made of the random uncertainty intervals surrounding those V_d estimates.

This introductory section has established the need for dry deposition measurements in the South Coast Air Basin, stated the objectives of this monitoring project, and has identified the difficulty of making these measurements. Section 2 identifies the measurement alternatives and the rationale for selecting the profile measurement method for this project. Since sampler siting is so critical to the success or failure of this measurement method, and since the highly urbanized Los Angeles area has so few sites which can meet dry deposition measurement criteria, an intensive search was conducted for a sampling site. Section 3 documents the results of that search. The dry deposition measurement system is described in Section 4 while Section 5 documents the intensive measurement period of May 15 through June 1, 1986. The results of the experiment are reported in Section 6, and the conclusions and recommendations are presented in Section 7.

2.0 GENERAL METHODS AND ASSUMPTIONS

The central problem in estimating the transfer of acidic and acid precursor species to the earth's surface is to measure or infer the flux of the given species. The "deposition velocity", V_d, is a convenient index of the rate of deposition, being the flux divided by the concentration of the species, referenced to a given height above the surface. Businger (1986) describes seven approaches to the field measurements necessary to estimate gas or aerosol particle fluxes. Of these methods, only three are capable of addressing the objectives of this project: 1) the eddy correlation method; 2) the chamber method; and 3) the gradient method. Careful analysis of these methods is given by Businger (1986). For this project, methods 1 and 2 were rejected, after some consideration, for a number of reasons.

The eddy correlation method is a direct flux measurement based on the simultaneous, fast-response measurement of species concentrations and turbulent vertical velocities. Gas concentrations need to be measured at a frequency of 1 Hz or better, but the commonly available gas analyzers have response times on the order of several to ten seconds. Stocker et al. (1987) report eddy correlation measurements of NO_2 taken in the Mohave Valley in June 1986 using experimental fast-response instruments collocated with the commercial instruments used in this project. These data will soon be analyzed to determine the potential for these experimental devices.

The chamber method utilizes an artifical "control volume" located at the surface to be studied, such as a Teflon hemisphere sealed to a soil surface. The rate of uptake of a tracer species allows estimation of the surface resistance. This approach can provide information specific to the vegetation and soil at a specific site, i.e., the surface resistance. It is possible, however, that additional "aerodynamic" resistances contribute to the deposition velocities and no data of this type results from application of the chamber method.

The gradient or profile method is described by Businger (1986) and has been applied in a number of deposition studies, including Droppo et al. (1983) and Davis and Wright (1985). This method assumes: 1) accurate measurements of concentration differences in the vertical, so that gradients can be derived; 2) a flat, homogeneous site with acceptable fetch distances; and 3) "stationary" meteorological conditions and species distributions over a typical 15-30 minute averaging period. The gradient method is the most practical of the three methods.

Compliance with Assumption 1 is assessed in Section 5; gas concentration differences on the order of 1 ppb were attained in this program. Compliance with Assumption 2 is discussed in Section 3; this requirement was met in the context of a careful matching of measurement heights and fetch distances, and a careful limitation of the acceptable fetch sector. Compliance with Assumption 3 was evaluated by specifying a data selection criterion, to exclude those data with gas concentrations varying by more than given amounts. An important aspect of this work involves a quantification of the extent to which deviations from these assumptions can be tolerated before other measurement uncertainties are exceeded.

3.0 MONITORING SITE SELECTION

3.1 Site Criteria

Siting criteria for the SoCAB follow those defined by Businger (1986) and are similar to those adopted in previous studies (e.g., Droppo et al., 1983).

- Uniform fetch (X_t) of 1 kilometer along the prevailing westerly or southwesterly wind direction.
- Roughness length Z_o no greater than a few centimeters, allowing the lowest measurement level to be 100 Z_o, or no more than a few meters.

In addition, the maximum height, Z, of measurements above the surface should be limited to $100Z < X_t$ (Businger, 1986).

Significant obstacles upwind from the area of desirable fetch are also to be avoided. In stable conditions, the flow can be perturbed by upwind obstacles located at greater distances than under neutral or unstable conditions (Businger, 1986). Sources or sinks close to the measurement area also need to be documented. This criterion led to rejection of a site that otherwise seemed to meet the above criteria.

3.2 Sampling Site Alternatives

Table 3-1 presents the site candidates within the South Coast Air Basin (SoCAB) that were considered and rejected as not complying with the criteria.

In the case of Rancho Jurupa Park, rejection was based on the proximity of upwind sources (ammonia from stockyards), and previous findings that particulate matter measurements taken near this site are often the highest within the SoCAB, indicating a non-representative situation. It was also surmised that the acid precursor gases emitted from the major source regions

Table 3-1

Sampling Sites which were Considered and Rejected

SITE CANDIDATE CONSIDERED	REASON FOR REJECTION
1. Santa Fe Flood Control Basin	No flat area with short vegetation
2. SCAQMD site at Anaheim	Inadequate fetch
3. SCAQMD site at Rubidoux	Inadequate fetch
4. Rancho Jurupa Park, Riverside Co.	Not respresentative of greater SoCAB
5. Various locations near Upland	Inadequate fetch, possible impending construction
6. Field South of Chaffee College	Proximity to hill, tall brush
7. Lewis Homes site Ettiwanda Airport	Lack of permission, no power
8. Claremont, property of "Mr. Alex"	Narrow sector of fetch; lack of permission
9. Brackett Field Airport	Proximity to mountains.
10. Whittier Narrows Park	Lack of fetch; no power; security in doubt
11. El Monte Airport	Narrow concrete strip on N-S axis

within the SoCAB would experience an atypically long aging and reaction time before reaching Rancho Jurupa.

Two other site candidates were tentatively accepted. First, a county-owned field near Rancho Los Amigos Hospital (RLAH), in Downey, was found to have about 320 m fetch on an E - W axis. Second, a field on the campus of California State University, Dominguez Hills (CSUDH), was found to offer a wider sector of acceptable fetch than that at the RLAH site, ranging from about 600 m on the SW - NE axis, 350 m on the W - E axis, and 500 m on the NW - SE axis (see map, Figure 3-1). The roughness length was estimated to be 1 cm or less. (Later estimates based on neutral wind profiles ranged from 1 to about 3 cm.) Two 20 amp circuits were available at the west end of the CSUDH Velodrome.

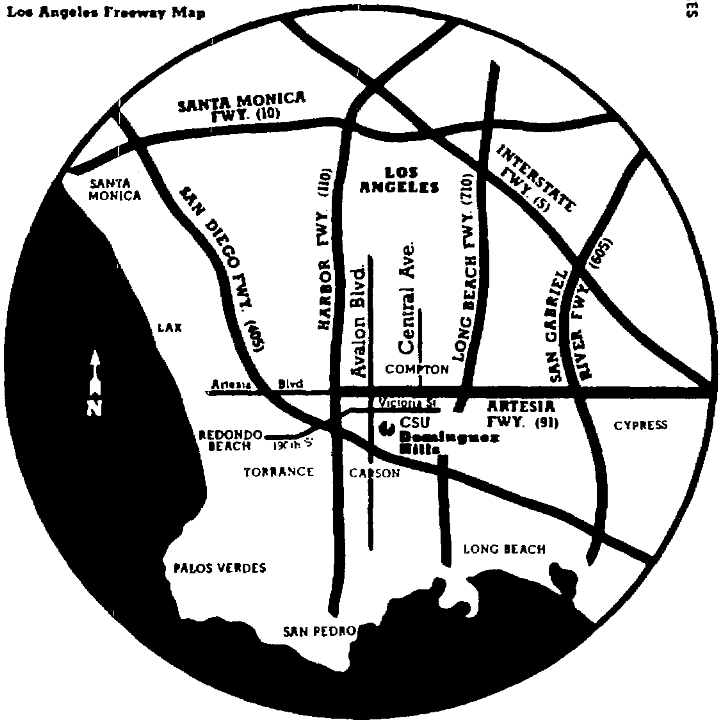
It was clear that site criterion #1, one kilometer of fetch, was unlikely to be found within the SoCAB. A fetch length of roughly one-half this amount, as provided at CSUDH, was deemed acceptable as long as the additional site criteria were carefully met (Businger, 1986a).

Sources near CSUDH are mainly limited to oil refineries south of the site, toward Long Beach. This direction is excluded from the sector of acceptable fetch, which is roughly 260° to 360° compass bearing, measured at the tower location.

3.3 California State University, Dominguez Hills Site Description

The CSUDH site was chosen over the RLAH site owing to its greater sector of acceptable fetch and to the proximity of a light industrial area at the upwind edge of the RLAH fetch. A site use agreement was negotiated between CSUDH and DRI and upgrading of the two Velodrome 20 amp circuits was arranged and financed by DRI.

Los Angeles Freeway Map



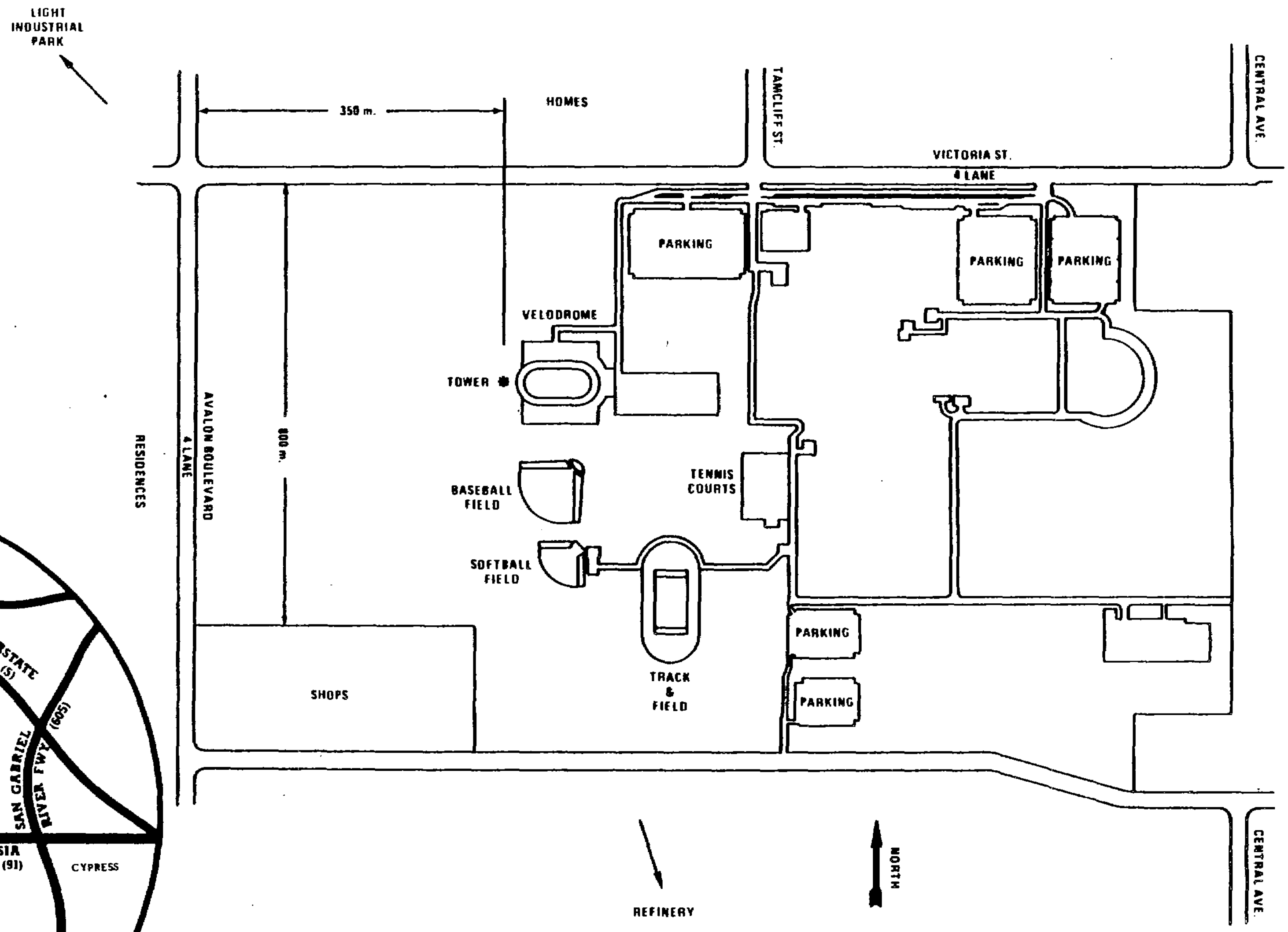


Figure 3-1 CSUDH FIELD SITE

A closely-mown grass field covered the acceptable fetch sector. The field is very nearly flat, except for an estimated 5% downward slope in the SW direction. The surface is composed of dry earth and grass usually mown to a height of 10 cm or less. The grass in the SW quadrant was mown early in the measurement program.

Activity in the fetch area was limited; approximately two vehicles per day used a dirt road on the east side of the tower, and joggers were occasionally seen circling the perimeter of the area. Model airplane hobbyists used the extreme northern area, but they almost never penetrated into the 260°-360° sector.

Powerlines suspended from tall pylons were aligned along Avalon Boulevard on the upwind edge of the acceptable fetch. The power cables did not appear to create a significant perturbation but two of the pylons were within the acceptable fetch sector. Small residences, warehouses, and very light industries were located within 1 km E of the site. Automotive traffic along Avalon Boulevard (4 lanes) was heavy. Traffic along Victoria street, on the north boundary of the CSUDH field, was less than that of Avalon Boulevard. Oil refineries were located S and SE of the CSUDH field, at a distance on the order of 10 km. These sources were outside of the acceptable fetch sector (260°-360°).

The sloping terrain in the SW quadrant of the CSUDH field limits the acceptable fetch sector. Drainage flows could arise in this quadrant due to buoyancy forces. These concerns are accommodated by limiting the fetch sector for valid data to the 260°-360° interval.

The lowest measurement level was 1.25 m, which was estimated to be at least 100 Z_0, where Z_0 was the estimated roughness length. The top measurement level was 5.00 m, slightly greater than the due-westerly fetch distance, 350 m, divided by 100. The instrument trailer was 3.1 m high and 6.5 m long and was located 7.5 m in the NE direction from the tower in order to provide minimum disturbance to the air flow at the tower. The separation distance was limited by the length of the Teflon gas sampling tubing. Concerns have been expressed that the trailer was close enough to the tower to cause spurious air flow accelerations. (Businger, 1986a.)

3.4 Assessment of Deviations from Classical Siting Criteria

The most important deviation from the siting criteria is with respect to the fetch length. The fetch length criterion was originally 1000 m; the CSUDH fetch length in the 260°-360° sector varies from 350 m to about 490 m. It is possible that the air motions, temperatures, and gas concentrations measured at the 5 m level on the tower have not fully "adjusted" to the surface, except when the wind is along the 315° axis. Longer fetch lengths were not available at other practical sites within the SoCAB. The literature does not suggest a means of quantifying the random uncertainty or systematic bias which might be introduced by allowing the top measurement level to be 0.0143 times the fetch distance X_t, rather than 0.0100 X_t. Businger (1986) reports measurements taken by Garland and Cox (1982) and Garland (1983), where the top measurement level was 0.0133 X_t. In this case, the error due to this deviation was judged to be negligible. In spite of these uncertainties, this site was deemed to be the best available candidate in the SoCAB.

4.0 MEASUREMENT SYSTEM

4.1 System Overview

The profile, or gradient, method described by Businger et al. (1971), Hicks (1979) and Droppo et al. (1983) was used in this study to estimate deposition velocities for gaseous SO_2, NO, NO_x, HNO_3, and sulfate particulate. This method samples each species in order to measure its vertical gradient. Concentration resolution is recommended to be ± 5% or better (Hicks, 1979), with an averaging time of 15 min or more and a sampling frequency of 2 Hz (Kaimal, 1975). The recommended precision of mean horizontal wind speed and mean temperatures and dew points are + 5 cm/sec and + 0.1 °C, respectively.

As shown in Figure 4-1, measurements of SO_2, sulfate aerosol, NO, NO_x, HNO_3, wind speed, temperature and dew point were made at three levels on a 5 m tower. Three identical gas sampling lines of approximately 17 m length were connected to the tower at 1.27 m, 2.48 m and 4.94 m. Each 5/16 inch FEP Teflon line led to a PFA Teflon solenoid valve which determined the level being sampled. The sampling level was chosen by software control of three solenoid valves. Time-of-travel through the tubes, assuming plug flow, was about 34 seconds. The network of valves and PFA Teflon tees was connected to the four gas analyzers for measuring the ambient concentration of the various species.

Horizontal wind measurements were made using R.M. Young uvw Gill anemometers, with the u-v planes mounted at 0.89 m, 2.13 m, and 4.60 m and the w propellors at the nominal 1.25, 2.50, and 5.00 m levels. R.M. Young temperature and dew point probes with appropriate aspirated housings were mounted with inlets at 1.25 m, 2.50 m and 4.98 m.

Data from the gas analyzers and meteorological sensors were collected on an IBM PC/XT with 10 megabyte hard disk through a Tecmar Labmaster A/D interface.

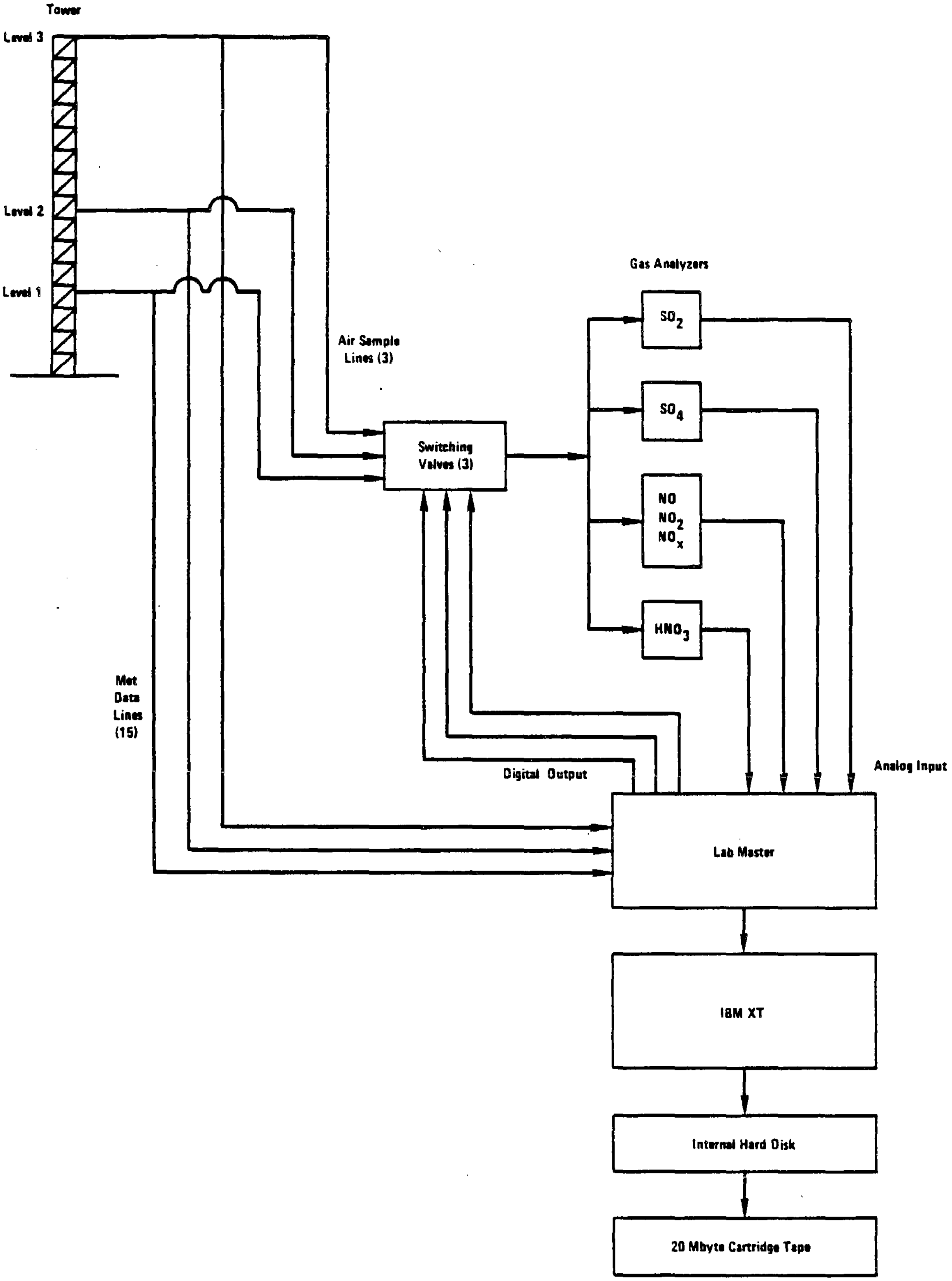


Figure 4-1

SCHEMATIC OF GRADIENT FLUX MEASUREMENT SYSTEM

Data were transferred from the IBM PC/XT hard disk to a magnetic tape unit at about 12 hour intervals. Each data cassette had a maximum storage capacity of 25 megabytes. Table 4-1 presents a summary of all measurements and their specifications.

4.2 Instrument Description

4.2.1 Meloy SA-285: SO_2 and Sulfate Aerosol

The Meloy SA-285 flame-photometric sulfur analyzer operating on the 0-500 ppb scale was used for the measurement of SO_2 and sulfate aerosol. In its standard configuration, the instrument measures total sulfur, which in this case was assumed to be predominately SO_2. A lead acetate SO_2 denuder was attached to the inlet of a second instrument for the sulfate measurements. The instrument response was then assumed to be due to particulate sulfur, i.e., sulfate aerosol.

The flame photometric principle used in the Meloy SA-285 instrument involves the conversion of sulfur-containing species (SO_2, H_2S, CS_2, $SO_4^=$, etc.) to S_2 in a hydrogen flame. The hydrogen and hydroxyl radicals also produced in the flame react with S_2 to yield an excited S_2 molecule, S_2*, which relaxes to ground state S_2 by emitting photons at 394 nm. The intensity of the emitted radiation is proportional to the number of S_2 molecules. For SO_2, the instrument response is proportional to the square of the number of molecules, since two SO_2 molecules are required to produce one S_2 molecule. The proportionality factor is determined through calibration using dilutions of certified gas cylinders created by a calibration system.

The lead acetate SO_2 denuder consisted of a 22 cm long by 0.8 cm id FEP Teflon tube lined with lead acetate-saturated Whatman 41 filter paper. This

Table 4-1

Summary of Measurements

Measurement	Measurement Method	Lower Quantifiable Limit	Response Time(s)	Acquisition Rate	Data Averaging Time	Period of Operation
SO_2	Meloy SA 285	≤ 1 ppb	3-10	1 Hz	30 min	5/13 - 5/31
Sulfate Aerosol	Meloy SA 285 w/lead acetate denuder	≤ 1 ppb	3-10	1 Hz	30 min	5/15 - 5/31
NO, NO_x NO_2	CSI 1600	≤ 1 ppb	1-20	1 Hz	30 min	5/13 - 5/31
HNO_3	ML 8440E with dual converters and Nylon filter	≤ 1 ppb	1-20	1 Hz	30 min	5/14 - 5/21, 5/26 - 5/31
Temperature	Gill 43382	0.5°C	15	1 Hz	30 min	5/13 - 6/1 Dew
Point	Gill 43382 LiCl dew point cell	0.9°C	15	1 Hz	30 min	5/13 - 6/1
Wind	Gill anemometer	0.02 m/s threshold	<1	1 Hz	30 min	5/14 - 6/1

denuder removed 200 ppb SO_2 from simulated air samples with near 100% efficiency, when tested prior to field monitoring.

4.2.2 CSI 1600 Oxides of Nitrogen Analyzer: NO, NO_2, NO_x

The CSI 1600 analyzer operating on the 0 to 500 ppb scale measured NO, NO_x, and NO_2. The flameless reaction of NO with O_3 produces excited NO_2, NO_2*, which decays to ground state NO_2 with the emission of infrared light detected by a photomultiplier. When the O_3 concentration is in excess of the NO concentration, the number of photons emitted is proportional to the amount of NO. By passing the sample over a thermal converter which reduces all NO_x (NO_2, HNO_3, PAN, N_2O_5, etc.) species to NO, total NO_x is measured. In the CSI 1600, a single reaction chamber and photomultiplier is used to quantify both NO and NO_x by alternately sampling directly or through the converter. Assuming NO_2 is equal to NO_x minus NO, the NO_2 concentration is calculated by difference. In the SoCAB where HNO_3, PAN and N_2O_5 concentrations may be appreciable, this assumption is not necessarily valid.

4.2.3 ML 8440E Nitrogen Oxides Analyzer: HNO_3

The ML 8440E is a chemiluminescent nitrogen oxides monitor similar to the CSI 1600. The ML 8440E contains two reaction chambers and photo-multipliers which simultaneously measure NO and NO_x. NO_2 (and other NO_x species) are converted to NO by passing the airstream over molybdenum at 300 to 350°C. As with the CSI 1600, NO_2 is calculated by difference. The ML 8440E was modified as described by Spicer et al. (1982) to quantify HNO_3. As shown in Figure 4-2, a molybdenum convertor was added to the NO path to reduce all oxidized nitrogen species, including HNO_3, to NO prior to chemiluminescent reaction. A nylon

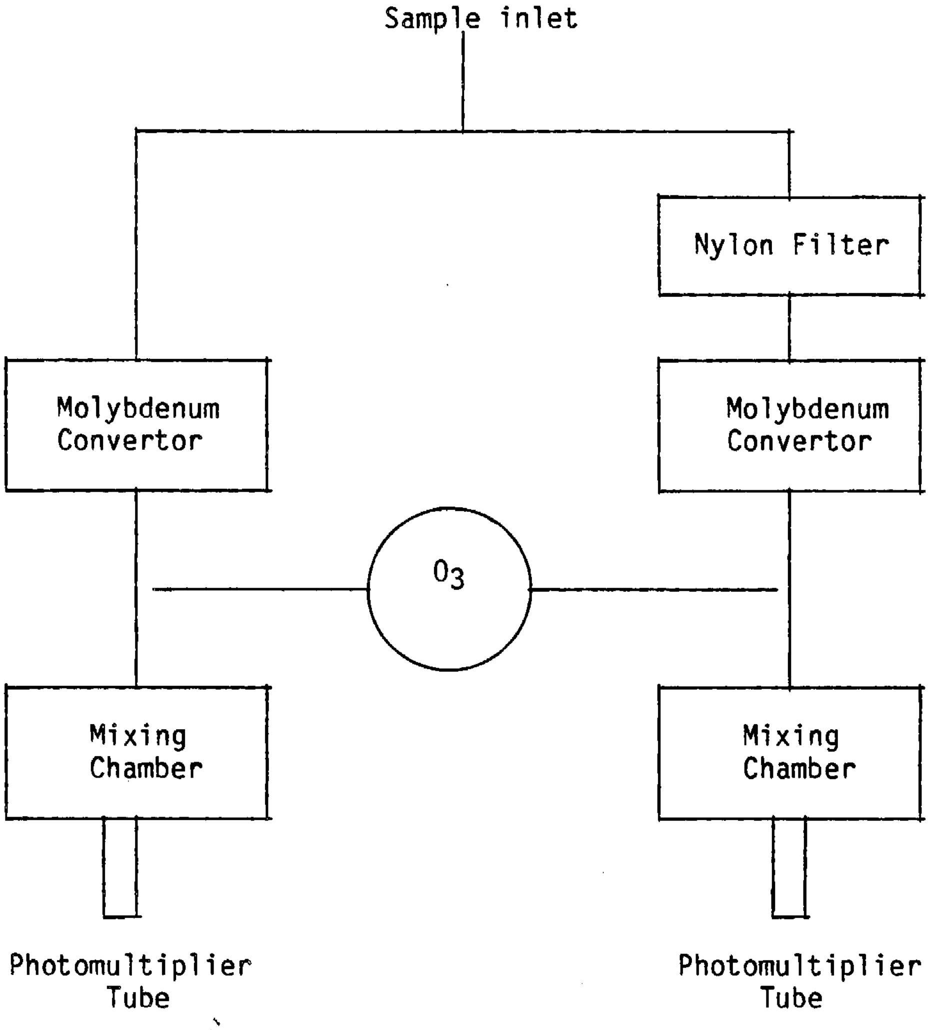


Figure 4-2

SCHEMATIC DIAGRAM OF NITRIC ACID DETECTION METHOD filter removed HNO_3 in one of the two channels, thereby allowing HNO_3 to be estimated as the difference between the two channels.

Both HNO_3 and PAN may be absorbed on Nylon filters. The efficiency of PAN collection on Nylon is unknown and in the SoCAB PAN may be a significant fraction of the total NO_x. If this were the case during this measurement period then the quantity measured as HNO_3 is really HNO_3 plus some fraction of the PAN present at the time of sampling. The location of the CSUDH sampling on the upwind end of typical SoCAB wind trajectories minimized the PAN interference. Since PAN is the product of photochemical reactions, it is expected to reach significant levels only at downwind locations, such as Riverside or Pasadena.

4.2.4 Gill uvw Anemometer - Wind Speed and Wind Direction.

The R.M. Young (R.M. Young, Inc., Traverse City, MI) Gill uvw anemometer measures wind velocities in three orthogonal directions: an along wind component, u; an across wind component, v; and a vertical wind component, w. These orthogonal velocities define the magnitude and direction of the wind vector.

Three Gill 27005 helecoid propellers were mounted at right angles to each other (except for the level 2 w propeller) on a common mast with sufficient separation to minimize the effects of one propeller. The midlevel w propeller was mounted off axis in order to include a little of the horizontal component to avoid the instrument dead-zone. Data were later corrected to provide a true w component. The propellers were molded styrofoam with a 19 cm diameter and a 30° pitch.

The sign convention was selected so that wind flow toward the u and v anemometers results in a positive velocity and a downdraft in the w direction results in a negative velocity. Gill anemometers have a dead zone at wind speeds of less than 20 cm/s and require correction for speeds up to 50 cm/s. The anemometer generators were calibrated with a constant rpm motor in both the clockwise and counter-clockwise directions.

4.2.5 R.M. Young Temperature/Dewpoint Indicating System

A R.M. Young 43342 Pt temperature sensor and a 43382 LiCl dewpoint sensor were located in aspirated radiation shields. The temperature sensor is a 1000 ohm Pt resistance thermometer with a range of -50.0 to +50.0 °C. The nonlinear output of this thermometer is compensated electronically.

The dewpoint (T_d) sensor consists of a thermistor composite surrounded by a LiCl impregnated fiberglass wick. The conductivity of the wick varies in relation to the amount of moisture absorbed from the air. Current passing through electrodes wound on the wick generates heat in proportion to the conductivity. Moisture evaporates from the wick until an equilibrium temperature, proportional to the dewpoint, is reached. The measurable range for T_d is -10.7 to +30.0 °C.

4.3 Data Acquisition and Processing

4.3.1 Data Acquisition Hardware

The data acquisition hardware consisted of a Scientific Solutions (Tecmar) Labmaster card installed in an IBM/XT along with a Metrabyte EXP-16 multiplexer board. This provides a capacity of 31 A/D channels. Twenty of these channels were used for the five meteorological observables at three levels plus the five gas measurements. The Labmaster board also provided for digital/analog output which was used in conjunction with solid state relays to control the valves which selected the level for gas sampling.

The output of each monitor was read once per second and the data were temporarily stored in digital form on the computer's hard disk. These data were manually transferred to permanent storage provided by a Cipher 5210 tape cartridge backup unit. The one second data were also processed on the IBM/XT to produce thirty minute averages and standard deviations in physical units for the 20 primary measurements. The wind direction was derived from the three orthogonal components at each level. The thirty minute averages and standard deviations were transferred to a VAX 780 for final processing and calculation of deposition velocities.

4.3.2 Data Processing

Wind speed averages were adjusted in the u and v directions for the non-cosine response of the Gill anemometers (Horst, 1973). The wind speed averages in the w direction were not adjusted since they were not used in the subsequent calculations. The standard deviations of the u and v velocity components were not adjusted since; 1) the non-cosine response adjustment in this case is not accurate owing to the squared values used in standard deviations for averages; and 2) standard deviations are used only in uncertainty calculations where adjustments of a few percent are not significant.

Horizontal wind speed averages were calculated at the three levels by vector addition of the wind speed averages in the u and v directions. These wind speed averages are of the average horizontal wind vector and they differ from the more common meteorological use of the average of the magnitudes of the horizontal wind vectors. They differ by at most a few percent and there is some reason to prefer the vector average treatment over the average speed method (Businger et al., 1971). These averages were reduced by a factor of 10% to adjust for overspeeding of the Gill propellers (Businger et al., 1971).

Horizontal wind speed averages were fit to the horizontal wind speed profile given in Businger et al. (1971). This profile is a logarithmic profile for neutral stability with extensions to non-neutral stability given by empirical functions of the stability. This fit to the data determines the stability, which in turn determines the coefficient of eddy diffusivity for momentum, K_m. The coefficient of eddy diffusivity for heat, K_h, is then determined by empirical functions in Businger et al. (1971), giving the ratio of K_h to K_m. This fitting was extended to the temperature and gas measurements using empirical functions from Businger et al. (1971) for heat, with stability determined by the horizontal wind speed fit. Since gas concentrations and temperatures are scalar quantities, the assumption is that the same transport properties pertain for heat and gas concentrations. Gradients and mean concentrations used in subsequent calculations were determined by the data fits and not from the individual measurements. Derived V_d estimates pertain to the 2.5 level, since the gas species gradients are calculated at this level.

Uncertainties associated with calculated quantities were determined using first order error propagation formulae derived for functions of the averages (Bevington, 1969). Standard errors were calculated to represent the uncertainties associated with each average. For the average gas concentration uncertainty, either the standard error of the average or the deviation of the average from the fitted curve was chosen, whichever was larger. A more complete discussion of calculations and their assumptions is presented in Appendix A.

5.0 MEASUREMENT PROGRAM

5.1 Sampling Periods

With the exception of the level SO_2 (2.5 meter) relative humidity probe, all instruments were operational as of 1640 PST, 15 May 1986. Thereafter, except for those times when calibration gas was being supplied to the gas analyzers, or when instruments were off-line for maintenance or adjustments, the full complement of data were taken continuously, and were recorded at one-second intervals. Table 5-1 indicates periods when instruments were off-line, or when data were invalid, for reasons other than routine calibrations; other relevant conditions are also shown in Table 5-1. The validated deposition velocity data base excludes all calibration periods, and all periods of invalid data as noted in Table 5-1. Due to the gradient method assumptions of fetch and stationary concentrations, deposition velocity calculations were limited to those sampling periods when the wind was from the 260° to 360° sector, and when the ambient gas concentrations varied by less than specified amounts, as will be discussed.

The period May 15, 1986 through June 1, 1986 was favorable in terms of weather conditions. Synoptically, the period was characterized by westerly flow aloft, no precipitation, and on most days, domination of the afternoon surface winds by the westerly sea breeze. Morning winds were usually light, variable, and unpredictable. A weak front passed on May 22, with no effect on the measurements. The daily maximum temperatures were in the low 70's (F), and minimum temperatures were in the 50's. Relative humidities ranged from about 60% during most days to near 100% several evenings.

Table 5-1

Significant Events During the CSUDH Monitoring Program

Date	Times		Events
	Start	End	
86/5/13	1901		SO_2: level 2 continuous monitoring
86/5/14	0824		
86/5/14	1910		All analyzers: level 2 continuous monitoring, HNO_3 on chart recorder
86/5/15	1640 PST		Started full operation
86/5/16	1700	2100	Shelter temperature above 80°F computer crash
86/5/17	1200	1400	Car rally on campus
86/5/18	2100		Checked SO_2 denuder on Meloy #2
86/5/19	0700		Fog
86/5/19	0900		Mowing SW quadrant
86/5/19	1030	1115	High SO_2 episode
86/5/19	0947	1130	Wrong NGASI and NAVG settings
86/5/19	1138		Shelter temperature above 80°F
86/5/19	1400		First gas calibrator returned to Las Vegas
86/5/19	1450		Solenoid valve power off briefly
86/5/19	1650	1720	Readjusted orientations and heights of all u, v, w units
86/5/19	1927		Fog approaching
86/5/20	0845	0959	Computer crash
86/5/20	1200	1300	Installed calibration gas line to tower
86/5/20	1400		Replacement gas calibrator arrived

Table 5-1 (continued)

Significant Events During the CSUDH Monitoring Program

Date	Times		Events
	Start	End	
86/5/21	1100	1650	Working on tower, installing J. Horrocks' equipment, and calibrations
86/5/22	0815		Finished installation of Horrocks' equipment
86/5/22	0952	1130	HNO_3, NO, and NO_x analyzers off-line
86/5/22	1400	1600	Visit of L. Ashbaugh and activities near tower
86/5/23	0700		Mowing SW quadrant
86/5/23	0950		J. Horrocks working on tower
86/5/23	1300		HNO_3 analyzer off-line until 86/5/26
86/5/26	1000		HNO_3 analyzer back on-line with replacement converter on HNO_3 side
86/5/27	0700		Fog
86/5/27	0945		Visit of J. Horrocks
86/5/27	1850		Return of first gas calibrator
86/5/27	1858		File #51 at 120 seconds rather than 240 seconds
86/5/28	0952		Replaced SO_2 denuder on SO_4 analyzer
86/5/29	0700		High SO_4
86/5/29	0800		Fog
86/5/29	1058		Visit of J. Businger
86/5/30	0915		Visit of R. Farber

Table 5-1 (continued)

Significant Events During the CSUDH Monitoring Program

Date	Times		Events
	Start	End	
86/5/30	1410		Started collecting data at 180 seconds per level rather than 240 seconds
86/5/31	1713		Started collecting data at 180 seconds per level rather than 240 seconds
86/6/1	0700		Started collecting data at 120 seconds per level
86/6/1	1212		End

5.2 Procedures

The routine operating procedure included the following activities:

- Arrive at site each morning, check instrument condition and record any anomalies in the field logbook.
- Transfer data from the IBM/XT hard disk to the tape cartridges.
- Perform gas analyzer performance tests: SO_2 and NO on alternate days, 100 ppb, 50 ppb, and zero gas air.
- Perform instrument maintenance, such as replacement of desiccant in the NO-NO_x analyzers, and in the gas calibrator.
- Examine the half-hour data averages and note changes in meteorological conditions.
- Before leaving site at night, again transfer data from the IBM/XT hard disk to the tape cartridge.

5.3 Anomalies

Table 5-1 summarizes events which might be anomalous or significant. The periods when the gas analyzers were sampling calibration gas are not shown in Table 5-1, though these periods were included in the deposition velocity data analysis. Significant events included:

- High instrument trailer temperatures; in one case this caused a computer failure.
- The SO_2 denuder on the $SO_4^=$ aerosol detection system may have been experiencing breakthrough in the few days preceding 86/5/28.
- The HNO_3 detector (Monitor Labs 8440) was off-line from 1300 on 86/5/3 until 1000 on 86/5/26 due to an electrical short circuit; its absence reduced the gas sampling flow rate from about 1500 cm^3/min to about 1000 cm^3/min, which increased the time needed to obtain a valid gas sample after each solenoid valve switch.
- HNO_3 analyzer data prior to 1300 on 86/5/23 are unreliable due to the uncertain date of failure of one of its molybdenum converters.
- On 86/5/27, 30, 31, and 86/6/1, some data were taken with reduced gas sampling times at each level (i.e., 120, and 180 seconds instead of 240 seconds) for comparison purposes.

5.4 Performance Testing and Calibration Methods

The gas analyzers and meteorological sensors used in this program were subjected to accuracy and precision evaluations. The following discussion will address accuracy and precision, first for the gas analyzers, and then for the temperature and wind sensors. The gas analyzer section will include the evaluation of the sulfate aerosol detection method, using an SO_2 gas analyzer. The discussion will include data obtained in the laboratory before and after the field program, and at both the CSUDH (Los Angeles) and Mohave Valley field sites.

5.4.1 Gas Analyzers: Laboratory Studies

The species of interest in this study, SO_2, $SO_4^=$, NO, NO_x and HNO_3, have been reported by earlier researchers to have deposition velocities in the range of 0.1 cm/s to several cm/s. If ambient concentrations are in the range of 50 to 100 parts per billion (ppb), the expected differences in concentrations of these gases, measured at two levels on a 5 meter tower, are approximately 1 ppb (see for example, Hicks, 1979). It is, therefore, important to apply frequent calibration and performance tests to the gas analyzers in order to detect any drifts or biases, and to accumulate enough data to quantify their measurement precision.

The Meloy 285 sulfur dioxide analyzers (used for both sulfur dioxide and sulfate aerosol) and the CSI 1600 nitrogen oxides analyzer measurement precisions were quantified in the laboratory prior to field sampling using a portable gas calibrator which was also used in part of the field program. This calibrator creates clean dilution air at flow rates determined by mass flow controller/meters traceable to primary standards. NBS-traceable cylinders of known SO_2 and NO concentrations were connected to one input of the calibrator.

Pressurized, particle-free air was pumped through activated carbon and desiccant traps to provide a second input to the calibrator. The calibration gas and the "zero-gas" air passed through separate mass flowmeters before mixing. The flow of zero-gas air was several thousand cubic centimeters per minute, while the calibration gas flow was on the order of a few cubic centimeters per minute. The NBS-traceable cylinders of SO_2 and NO contained concentrations of 52 parts per million (ppm) certified to an accuracy of ± 2%. The calibrator output was in the range of about 50 parts per billion (ppb) at maximum dilution, to several hundred ppb.

Two types of issues are involved in calibrating and testing a gas analyzer with a calibration unit: accuracy and precision. With regard to accuracy, the requirements of this program are:

- To initially calibrate each gas analyzer and then to frequently challenge each analyzer with calibration gases of known concentrations in order to detect drifts or biases.
- To maintain overall gas detection accuracies of ± 10% or better, because the error in deduced deposition velocity is expected to be proportional to the error in the estimated ambient gas concentration.
- To ensure that observed gradients are due to given gas concentrations rather than a bias or attenuation in the sampling system.

The requirements with respect to precision are:

- To ensure that a given gas analyzer responds to a given gas concentration with an acceptable standard deviation of the differences between replicate measurements.
- To ensure that a given gas analyzer responds to a given gas concentration that has been sampled at one of the three inlet levels with an acceptable standard deviation of the differences between replicate measurements.
- To ensure that spurious gradients are not caused by unequal sampling lines leading from the three gas sampling levels; i.e., to ensure that if the sampling tubing and gas handling equipment involves any bias or attenuation with reference to ambient gas concentrations, then those biases or attenuations are equal to within the overall

measurement error, for all three gas sampling levels; this issue is particularly critical for species like HNO_3, which absorb and react readily.

SO_2 and NO calibration and performance tests were conducted both before and after field operations. Table 5-2 shows the results of an initial laboratory test of the Meloy 285 SO_2 analyzer, Serial Number 7C183, the analyzer used for SO_2 measurements in this program. Each concentration value is a 30-minute average. The two columns correspond to feeding the calibrator output through either the Level 1 (1.25 m) or the Level 2 (2.50 m) sampling lines. Arithmetic averages, standard deviations, and standard deviations of the averages (i.e., standard errors) were calculated for every ten data points. The differences between the two sampling levels are smaller, for each set of ten points, than the standard deviations of the replicate measurements at each level, which are about 0.2 ppb in each case.

Table 5-3 shows the results of laboratory performance tests of the CSI 1600 NO-NO_x analyzer used for NO-NO_x measurements. Each concentration value is a 30 minute average with the calibrator on a constant, 104 ppb NO setting. The two columns correspond to the NO and NO_x (total oxides of nitrogen) channels. Arithmetic averages, standard deviations, and standard errors follow each ten data points. Drift is apparent in the NO channel, but not in the NO_x channel. In another performance test of sampling calibration gas through the Level 1 and Level 2 sampling tubing, two half-hour averages were as follows:

	NO Channel	NO_x Channel
Level 1	108.68	123.81
Level 2	108.57	123.48

Table 5-2

Meloy 285 SO_2 Analyzer
Laboratory Performance Test 86/4/29
Response in ppb, 30 Minute Averages

	Test 1	
	Level 1	Level 2
	42.98	42.55
	42.76	42.73
	42.90	43.15
	43.13	43.02
	43.04	42.47
	42.56	42.82
	42.80	42.89
	42.72	42.98
	42.47	43.00
	42.80	42.42
Average =	42.82	42.80
σ =	0.21	0.25
$\sigma/\sqrt{N}$ =	0.07	0.08

	Test 2	
	42.66	42.34
	42.36	42.29
	42.24	42.46
	42.24	42.38
	42.15	42.27
	42.21	42.11
	42.33	41.77
	42.14	42.09
	42.28	42.10
	42.14	42.25
Average =	42.28	42.21
σ =	0.16	0.20
$\sigma/\sqrt{N}$ =	0.05	0.06

Table 5-3

CSI 1600 NO - NO_x Analyzer Serial No. 8857
Laboratory Performance Test, 86/4/19-86/4/20
Analyzer Performance in ppb, 30 Minute Averages

Test 1

NO	NO_x
94.80	109.50
97.46	109.64
95.81	108.81
96.85	108.68
96.91	108.12
97.08	107.60
97.24	108.04
97.08	108.12
98.58	108.66
98.41	108.73
Average = 97.02	Average = 108.59
σ = 1.11	σ = 0.64
$\sigma/\sqrt{N}$ = 0.35	$\sigma/\sqrt{N}$ = 0.20

Test 2

NO	NO_x
98.88	108.29
99.28	109.60
99.08	109.40
100.34	109.96
99.33	108.45
100.81	109.42
100.06	108.30
101.98	108.24
101.80	108.96
102.10	109.53
Average = 100.47	Average = 109.02
σ = 1.26	σ = 0.65
$\sigma/\sqrt{N}$ = 0.40	$\sigma/\sqrt{N}$ = 0.21

The differences between the two levels are less than the standard deviations reported in Table 5-3. The differences between the NO and NO_x channels are inconsequential in these experiments; slight readjustments to the span controls on the analyzer would have brought each channel to the nominal 104 ppb reading, but these adjustments would not change the precision estimates.

The largest standard deviation of replicate measurements of 30 minute averages was 1.3 ppb for the CSI 1600 NO channel, which is comparable to the desired 1 ppb or better measurement resolution. No biases due to different sample inlet tubing were detected. This large standard deviation does, however, contribute to an increased propagated uncertainty in the NO measurements.

5.4.2 Gas Analyzers: Field Measurements of Response 100 ppb and 50 ppb SO_2 and NO

Measurement precision obtained in a controlled laboratory environment is not necessarily the same as that which is found during field monitoring. The ambient temperature of the measurement environment, for example, is a major factor which cannot be as well controlled in a field shelter as in the laboratory. Particularly for the chemiluminescent reaction in the NO-NO_x analyzers, ambient temperature fluctuations cause variable analyzer response.

The calibration gases were introduced either directly to each analyzer or through the sampling lines. Figure 5-1 shows the results for field SO_2 performance tests of the Meloy 285 analyzer as a function of time. Data points for the 100 and 50 ppb concentrations are shown; the vertical axis is the deviation of the analyzer reading (usually, a 30-minute average) from the nominal calibrator output concentration.

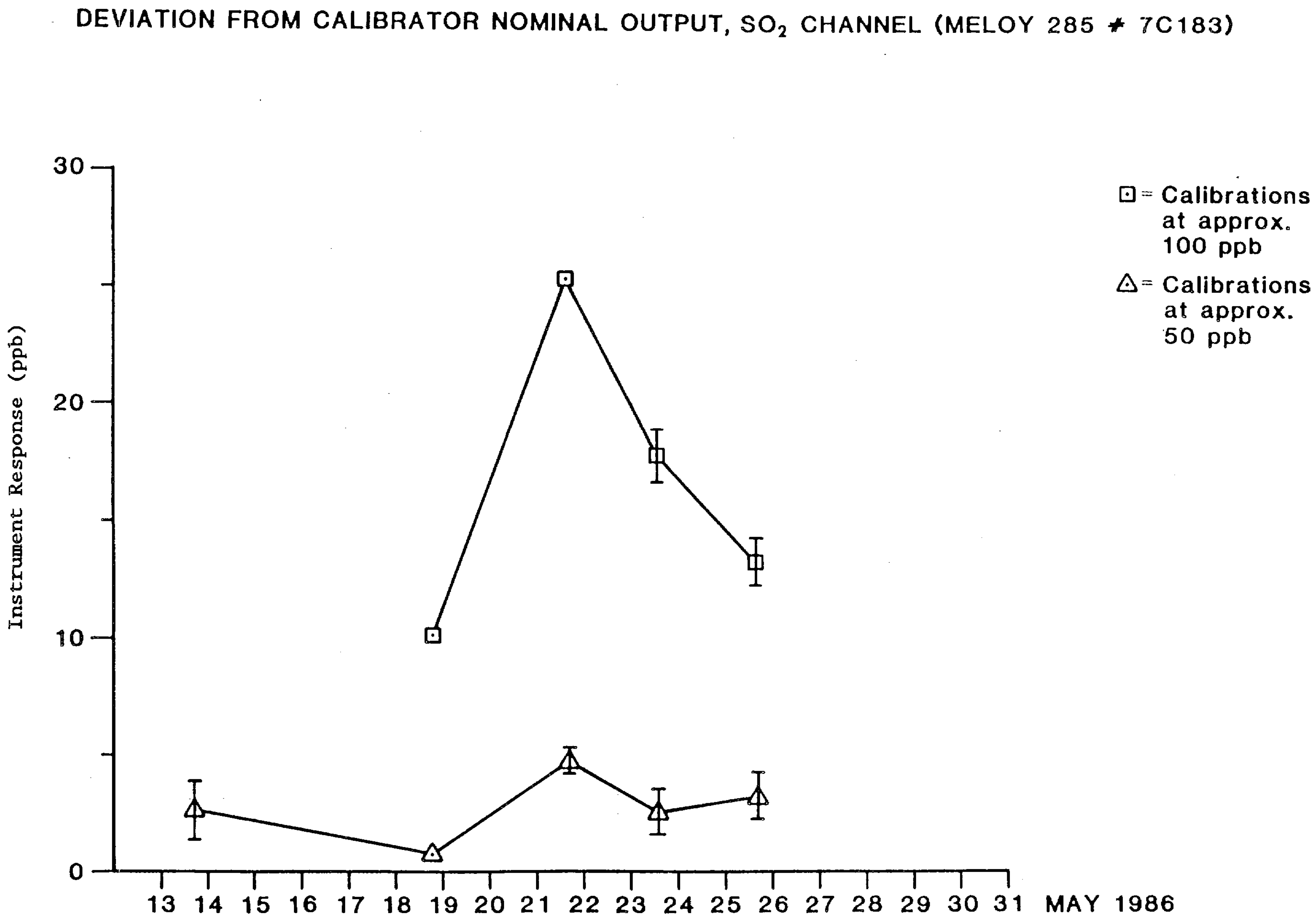


Figure 5-1 TIME SERIES OF RESULTS OF FIELD PERFORMANCE CHECKS. VERTICAL AXIS IS DEVIATION OF ANALYZER RESPONSE FROM NOMINAL CONCENTRATION OF CALIBRATION GAS. ERROR BARS ARE STANDARD DEVIATIONS OF ONE-SECOND DATA, WHERE AVAILABLE.

Figures 5-2 and 5-3 show similar time series for the field performance tests of the CSI 1600 NO-NO_x analyzer. Figure 5-2 shows the response of the NO channel to the NO standards, while Figure 5-3 shows the response of the NO_x channel to the NO standards.

The zero and span adjustments were not changed during sampling. The effect of long-term drifts in zero and span can be seen in these plots. The short-term variability is indicated by the uncertainty intervals in these plots, and it is this short-term variability which is relevant to the precision needed for measuring the differences between two sampling levels.

The data represented in Figures 5-1, 5-2, and 5-3 were analyzed to derive the average percentages of the indicated biases. In each case, the exact output of the gas calibrator was calculated, based on actual mass flowmeter readings taken in the field. The differences between the gas analyzer readings and the calibrator outputs were usually a positive amount. For the SO_2, NO, and NO_x readings, the average precentages are as shown in Table 5-4.

The standard deviations of the individual one-second data that made up each 30-minute average are presented in tabular form in Tables 5-5, 5-6, and 5-7. (It should be noted that the average consists of less than 1800 data points since the initial part of each sampling interval is rejected.) These standard deviations divided by the square root of the number of data points, or $\sigma/\sqrt{N}$, are estimates of the standard deviation of the mean (standard error of the mean). The standard error provides an estimate of the magnitudes of the differences to be expected if additional measurements of the same 30-minute average were made.

The average values of the σ and $\sigma/\sqrt{N}$ values are shown at the bottom of Tables 5-5, 5-6, and 5-7. As the laboratory calibrations in Tables 5-2 and 5-3 showed, the NO-NO_x measurements are less precise than the SO_2 measurements. The field measurements are also less precise than the laboratory measurements.

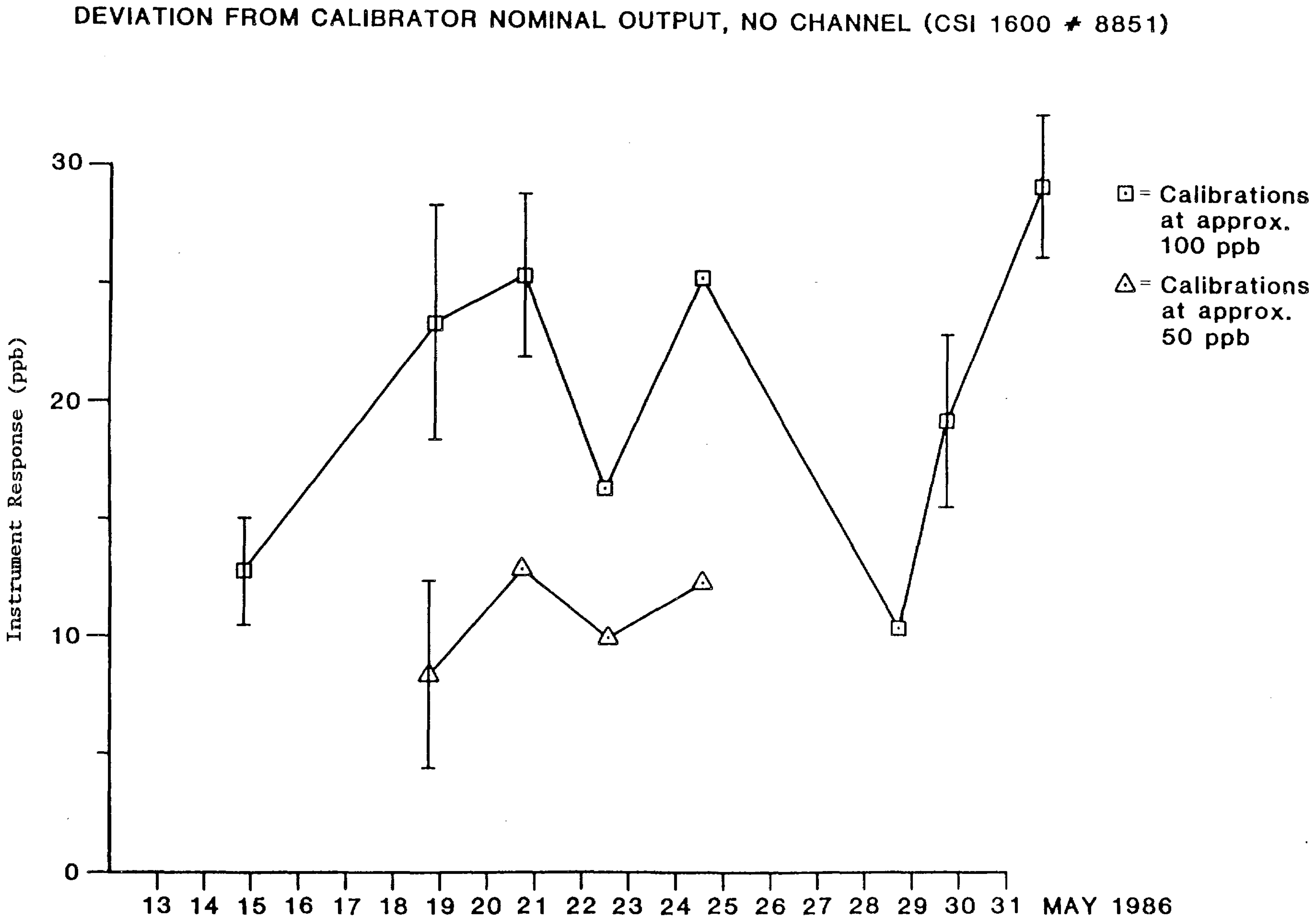


Figure 5-2 TIME SERIES OF RESULTS OF FIELD PERFORMANCE CHECKS. VERTICAL AXIS IS DEVIATION OF ANALYZER RESULT FROM NOMINAL CONCENTRATION OF CALIBRATION GAS. ERROR BARS ARE STANDARD DEVIATIONS OF ONE-SECOND DATA, WHERE AVAILABLE.

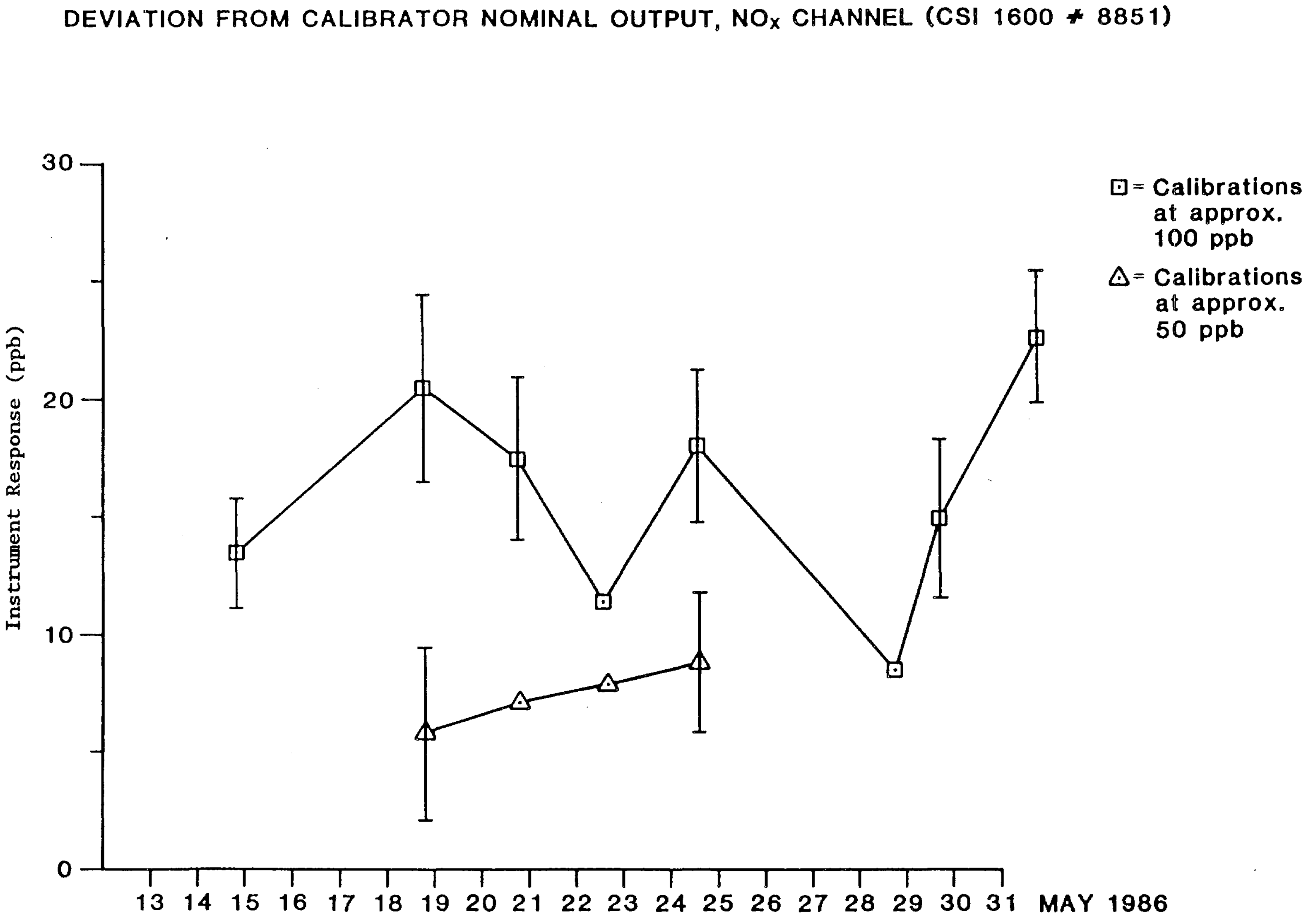


Figure 5-3 TIME SERIES OF RESULTS OF FIELD PERFORMANCE CHECKS. VERTICAL AXIS IS DEVIATION OF ANALYZER RESPONSE FROM NOMINAL CONCENTRATION OF CALIBRATION GAS. ERROR BARS ARE STANDARD DEVIATIONS OF ONE-SECOND DATA, WHERE AVAILABLE.

Table 5-4

Comparison of Gas Analyzer Responses to Gas Calibrator Output Concentrations for the Entire Sampling Period

Gas	Bias as Percentage of Calibration Output	Standard Deviation of Bias Percentage
SO_2	+ 11.7%	5.2%
NO	+ 21.3%	5.7%
NO_x	+ 15.9%	4.5%

Table 5-5

SO_2 Field Calibration Data

Date	Time	Gas Calibrator Output ppb	Response, ppb, 30 Minute Ave	σ (ppb)	$\sigma/\sqrt{N}$ (ppb)
86/5/13	1703	52.6	55.3	1.3	0.08
86/5/18	2053	102.5	112.7		
86/5/18	2128	52.6	53.4		
86/5/21	1408	95.4	120.8		
86/5/21	1650	47.2	52.0	0.5	0.03
86/5/23	1252	96.1	113.9	1.1	0.07
86/5/23	1357	47.2	49.8	1.0	0.06
86/5/25	1457	95.8	109.1	1.0	0.07
86/5/25	1602	46.6	49.9	1.0	0.05
			AVERAGE =	1.0	0.06

Table 5-6

NO Field Calibration Data

Date	Time	Gas Calibrator Output ppb	Response, ppb, 30 Minute Ave	σ (ppb)	$\sigma/\sqrt{N}$ (ppb)
86/5/14	1853	101.5	114.5	2.3	0.14
86/5/18	1724	101.5	125.0	4.9	0.30
86/5/18	1935	52.1	60.5	4.0	0.23
86/5/20	1701	95.1	120.6	3.5	0.20
86/5/20	1845	46.6	59.6		
86/5/22	1346	93.8	110.2		
86/5/22	1455	46.6	56.7		
86/5/24	1334	93.8	118.2	3.5	0.22
86/5/24	1440	46.6	59.0	3.3	0.21
86/5/28	1700	101.5	112.0		
86/5/29	1728	101.5	120.9	3.7	0.24
86/5/31	0832	52.1	62.7	3.1	0.16
86/5/31	1707	101.5	130.9	3.0	0.19
			AVERAGE =	3.5	0.21

Table 5-7

NO_x Field Calibration Data

Date	Time	Gas Calibrator Output ppb	Response, ppb, 30 Minute Ave	σ (ppb)	$\sigma/\sqrt{N}$ (ppb)
86/5/14	1853	101.5	115.0	2.3	0.13
86/5/18	1724	101.5	122.0	4.0	0.23
86/5/18	1935	52.1	57.9	3.7	0.22
86/5/20	1701	95.1	112.6	3.4	0.20
86/5/20	1845	46.6	53.7		
86/5/22	1346	93.8	105.2		
86/5/22	1455	46.6	54.5		
86/5/24	1334	93.8	111.8	3.3	0.21
86/5/24	1440	46.6	55.4	2.9	0.19
86/5/28	1700	101.5	110.0		
86/5/29	1728	101.5	116.4	3.4	0.22
86/5/31	0832	52.1	60.5	2.7	0.14
86/5/31	1707	101.5	124.1	2.8	0.18
				AVERAGE = 3.2	0.19

5.4.3 Gas Analyzers: Field Measurements of Response to 100 ppb and 50 ppb Calibration Concentrations, Supplied Through Two or More Levels of the Sampling Train.

An FEP Teflon line (3/8" tubing) was installed to carry calibration gas from the instrument trailer about 15 m to the sampling inlets on the tower. This line was used for the one-level performance checks shown in the time series in Figures 5-1, 5-2, and 5-3. It was also used to supply calibration gas to two or more levels at selected times; this procedure was quite time-consuming, and was not repeated frequently. Table 5-8 shows the dates and species of these checks, including those performed with a very similar configuration in June, 1986, in the Mohave Valley.

Table 5-9 displays the gas concentrations registered by the SO_2 analyzer, versus the level of the sampling train the calibration gas passed through. Table 5-10 is similar to Table 5-9, displaying the results for NO, registered by the NO channel of CSI 1600 analyzer.

In the case of each gas, there is one high outlier value of the average differences between sampling levels. Retaining these outliers, however, the average of the three SO_2 average differences between levels is 0.7 ppb; the average for NO is 0.9 ppb.

Figure 5-4 shows the SO_2 stripchart reading for 96 ppb SO_2 passing through levels 1 and SO_2 on 86/5/21. The first part of the trace from 1022 to 1113 occured when the calibration gas was supplied directly to the instrument's inlet. Figure 5-5 shows a similar result for NO. Again the first part of the trace was obtained with the calibration gas supplied directly to the instrument's inlet, bypassing the sampling lines. Figure 5-6 shows the reading from the NO channel and levels 1 and 2 with a mixture of NO and NO_2 passing through the sampling

Table 5-8

Dates of Gas Analyzer Performance Tests Through the Entire Sampling System

Observables	Date	Sampling Train Levels	Location
SO_2	86/4/28	1, 2	Reno Lab
SO_2	86/5/21	1, 2	CSUDH
NO	86/5/5	1, 2	Reno
NO	86/5/20	1, 2	CSUDH
NO	86/5/31	1, 2, 3	CSUDH
NO	86/6/18	1, 2	Mohave
NO, NO_2	86/6/19	1, 2	Mohave

Table 5-9

SO_2 Performance Tests at Different Sampling Levels

Date	Calibrator Output, ppb	Level	Result ppb	Average Difference Between Levels
86/4/28	52	1	42.82	
86/4/28	52	1	42.20	
86/4/28	52	2	42.80	
86/4/28	52	2	42.21	0.05 ppb
86/5/21	96.0	2	122.88	
86/5/21	95.0	1	120.82	(Allowing for drift in calibrator: 1.88 ppb)
86/5/21	47.1	1	52.20	
86/5/21	47.1	2	52.00	0.14

Table 5-10

NO Performance Tests at Different Sampling Levels

Date	Calibrator Output, ppb	Level	Result ppb	Average Difference Between Levels
86/5/5	104	1	108.68	
86/5/5	104	2	108.57	L2-L1 = 0.11 ppb
86/5/20	104	1	117.95	
86/5/20	104	2	118.09	L2-L1 = 0.14 ppb
86/5/31	104	1	130.67	
86/5/31	104	2	127.83	L3-L2 = 0.66 ppb
86/5/31	104	3	127.17	L2-L1 = 2.84 ppb
86/6/18	49.3	1	49.5	
86/6/18	49.3	2	49.8	L2-L1 = 0.3 ppb
86/6/19		1	184.5	
86/6/19		2	183.0	L2-L1 = 1.5 ppb

Figure 5-4

STRIPCHART RECORDING SO_2 PASSING THROUGH LEVELS 1 AND 2, AS REGISTERED BY MELOY 285 #7C183.

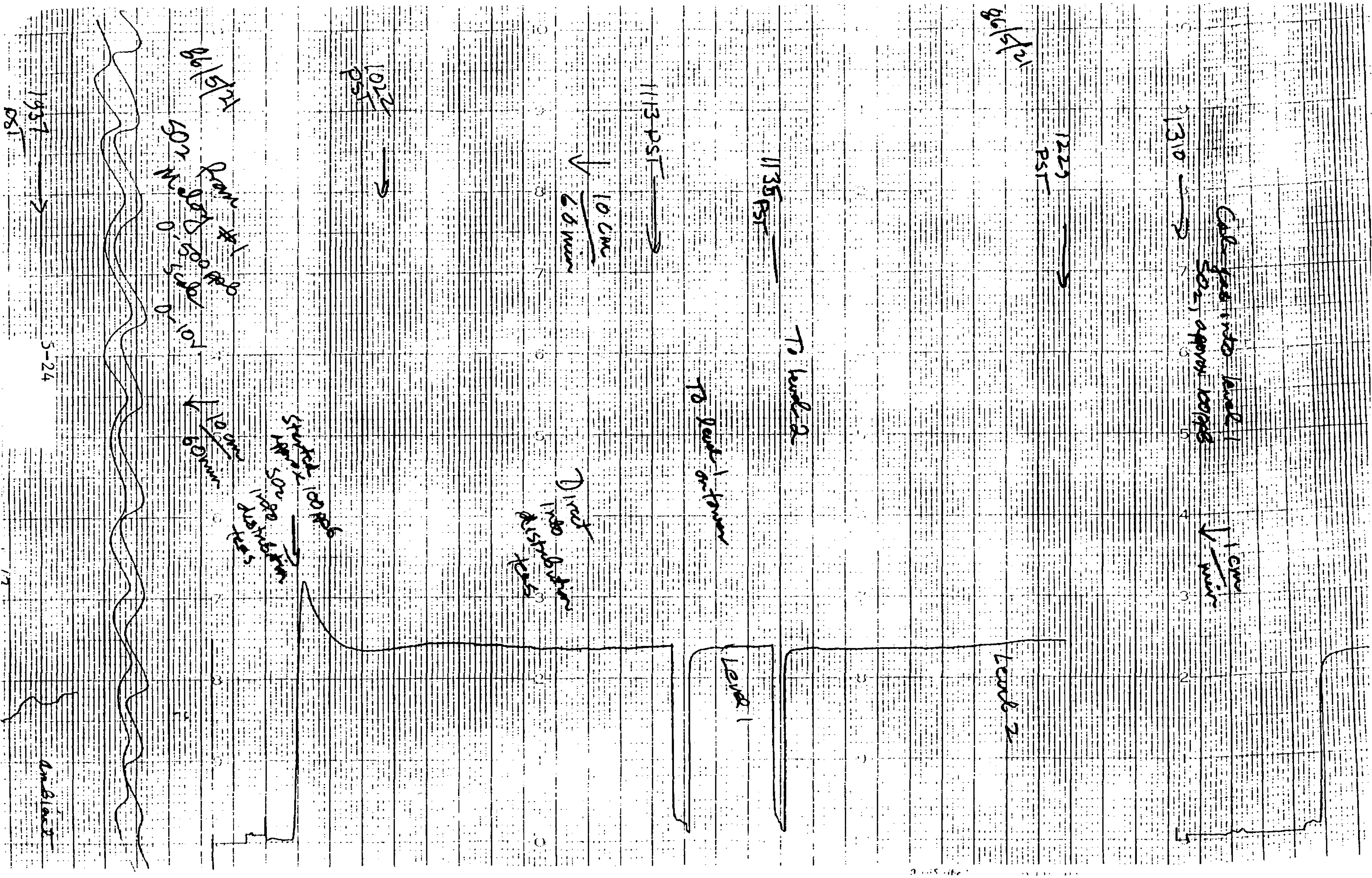


Figure 5-5

STRIPCHART RECORDING NO PASSING THROUGH LEVELS 1 AND 2, AS REGISTERED BY CSI 1600 #8851. GAS CONCENTRATION ABOUT 104 ppb.

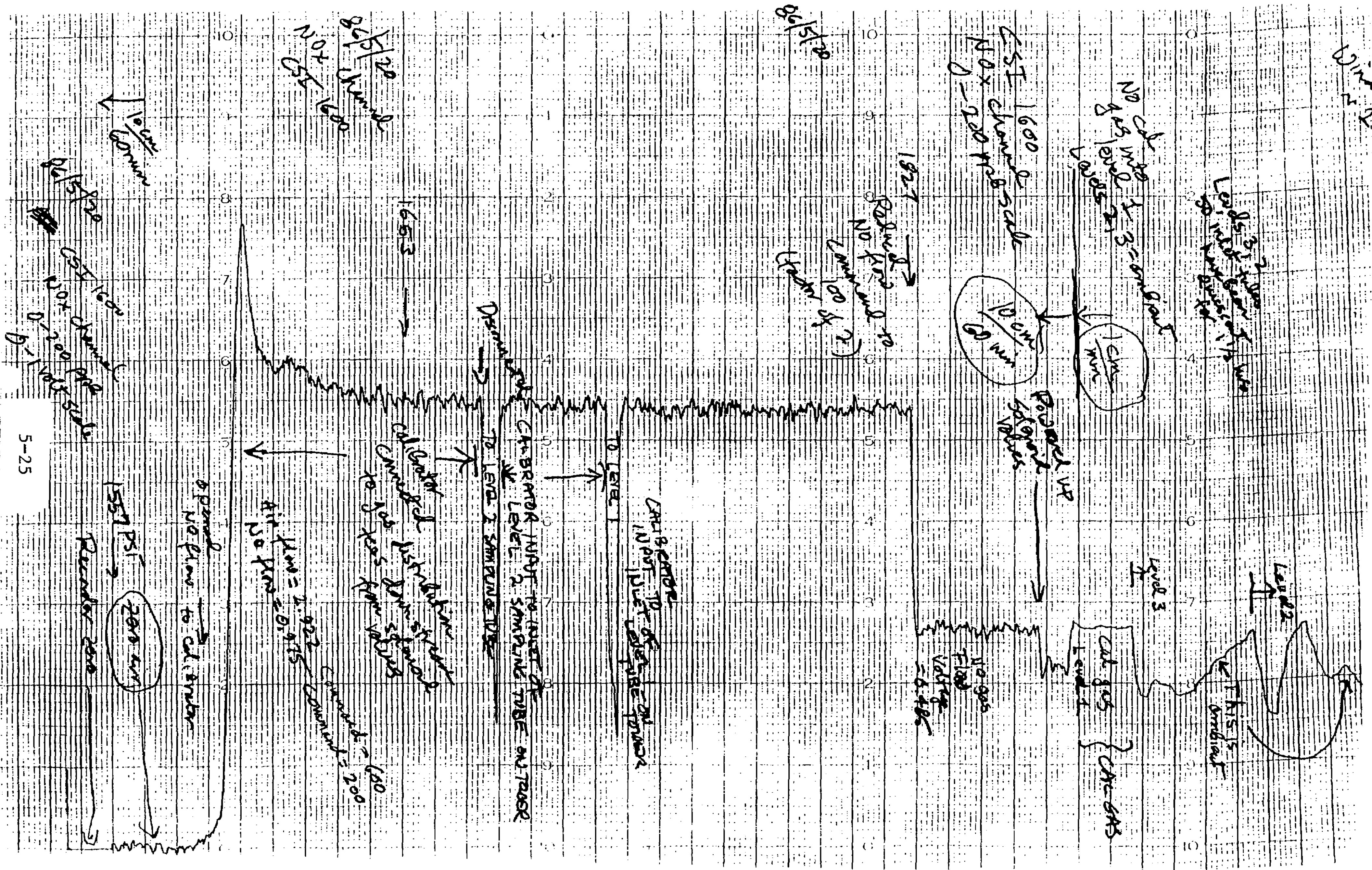
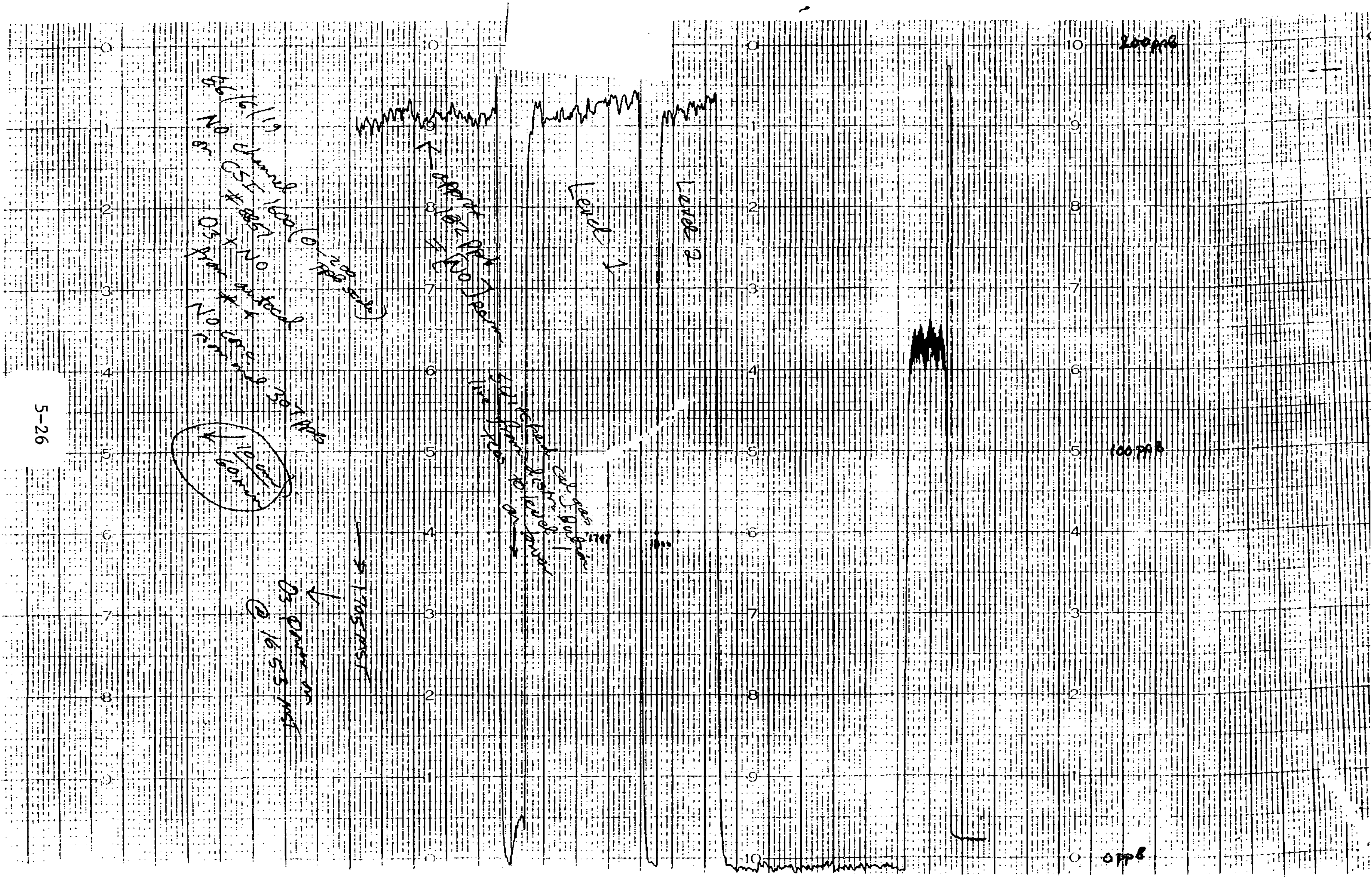


Figure 5-6

STRIPCHART RECORDING NO PASSING THROUGH LEVELS 1 AND 2, AS REGISTERED BY CSI 1600 #8851. GAS CONCENTRATION ABOUT 183 ppb.



train on 86/6/19. The trace is relatively noisy, and the average concentration values reflect this, as will be discussed shortly.

Figure 5-7 again shows the NO reading. This time the calibration gas was pure NO at a concentration of 49 ppb (86/6/18), and the instrument's NO_x channel was connected to the chart recorder. Levels 1 and 2 data are shown.

Figure 5-8 shows 5-minute samples from levels 1, 2, and 3 for NO at a concentration of 104 ppb (86/5/31). In between each calibration pulse, the instrument measured ambient NO through one of the other sampling levels.

Figure 5-9 shows the result with NO calibration gas at 52 ppb passing through the level 1 sampling line. The instrument monitored ambient air from the other two levels. Sampling took place at each level for four minutes in the normal operating mode. Figure 5-9 demonstrates monitoring reproducibility at the 50-ppb-level, the typical variability of ambient concentrations and the approximate one minute residence time in the sampling lines.

5.4.4 Sulfate Aerosol Measurement

Sulfate aerosol was measured using a Meloy 285 SO_2 analyzer (Serial No. OH180) drawing its sample through a lead acetate SO_2 and H_2S diffusion denuder. It was assumed that sulfate aerosol particles volatilize in the Meloy 285 hydrogen flame, and that their S emission lines are detected quantitatively the same as SO_2 gas (Hicks et al., 1983).

Table 5-11 shows the results from four performance tests at approximately 50 ppb SO_2 concentrations, with the SO_2 denuder removed. These data indicate that the analyzer responded consistently to known concentrations of gaseous sulfur. Routing the SO_2 test gas through the denuder yielded zero readings, within ± 2 ppb.

Figure 5-7

NO PASSING THROUGH LEVELS 1 AND 2, AS REGISTERED BY THE NO_x CHANNEL ON CSI 1600 #8851. GAS CONCENTRATION IS ABOUT 49 ppb.

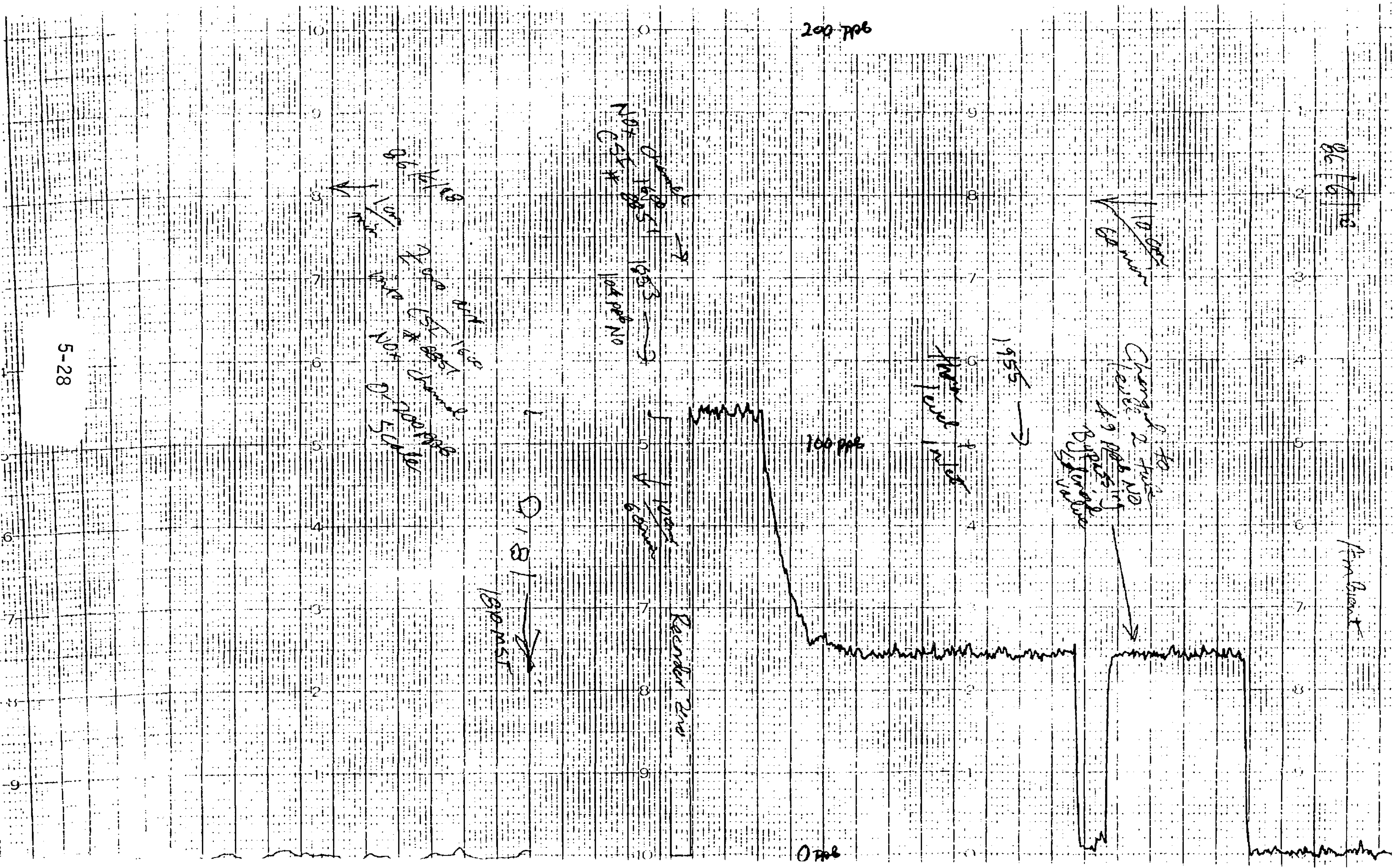


Figure 5-8

STRIPCHART RECORDING CALIBRATION NO PASSING THROUGH LEVELS 1, 2, AND 3, AS REGISTERED BY THE NO CHANNEL ON CSI 1600 #8851. GAS CONCENTRATION IS ABOUT 104 ppb.

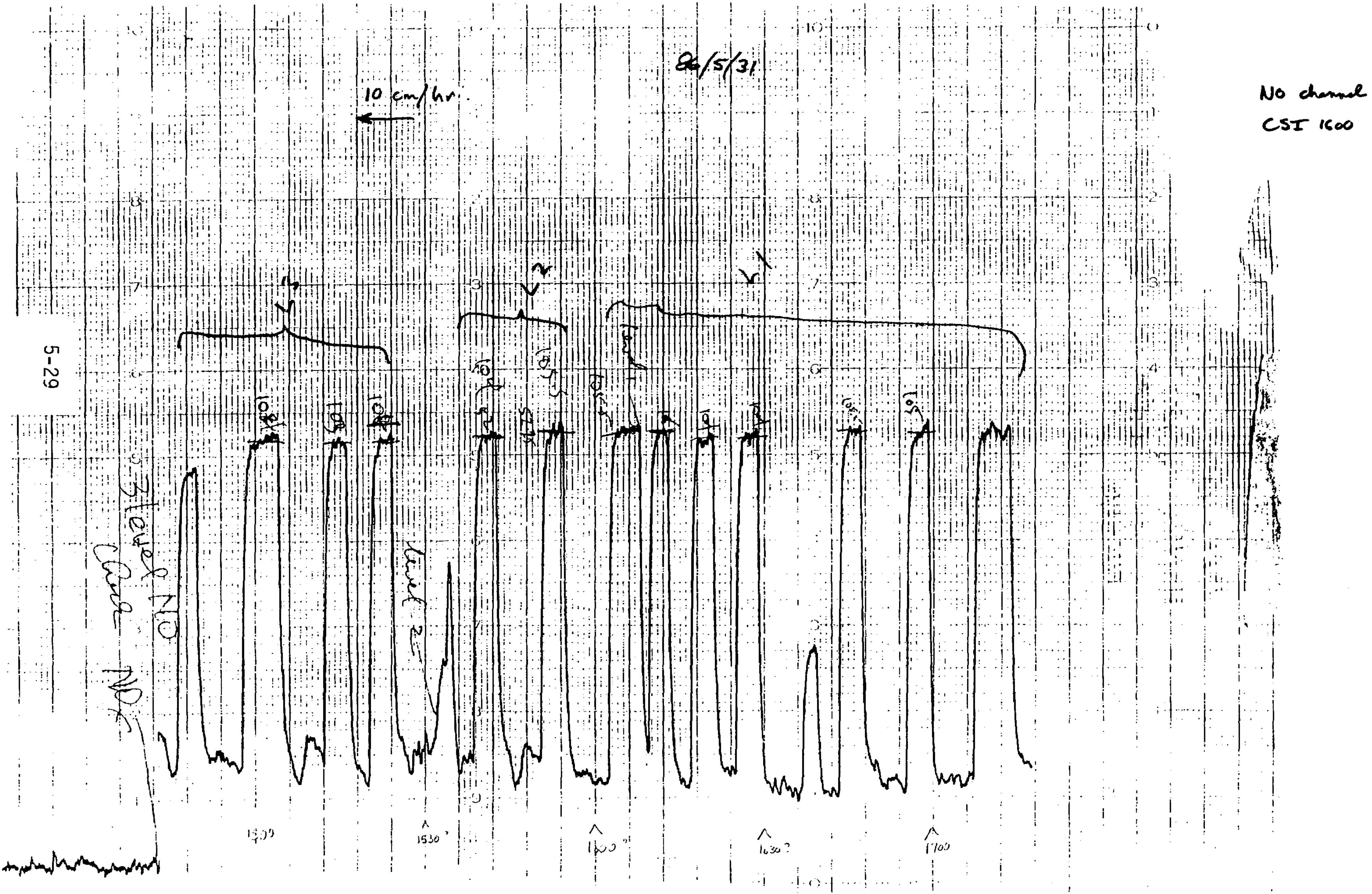


Figure 5-9

STRIPCHART RECORDING NO CALIBRATION GAS AT 52 ppb PASSING THROUGH THE LEVEL 1 SAMPLING TRAIN, AS DETECTED BY CSI 1600 #8851. SAMPLING SYSTEM IS PROVIDING 4 MINUTE MEASUREMENTS AT EACH LEVEL; AMBIENT AIR IS BEING SAMPLED AT LEVELS 2 AND 3.

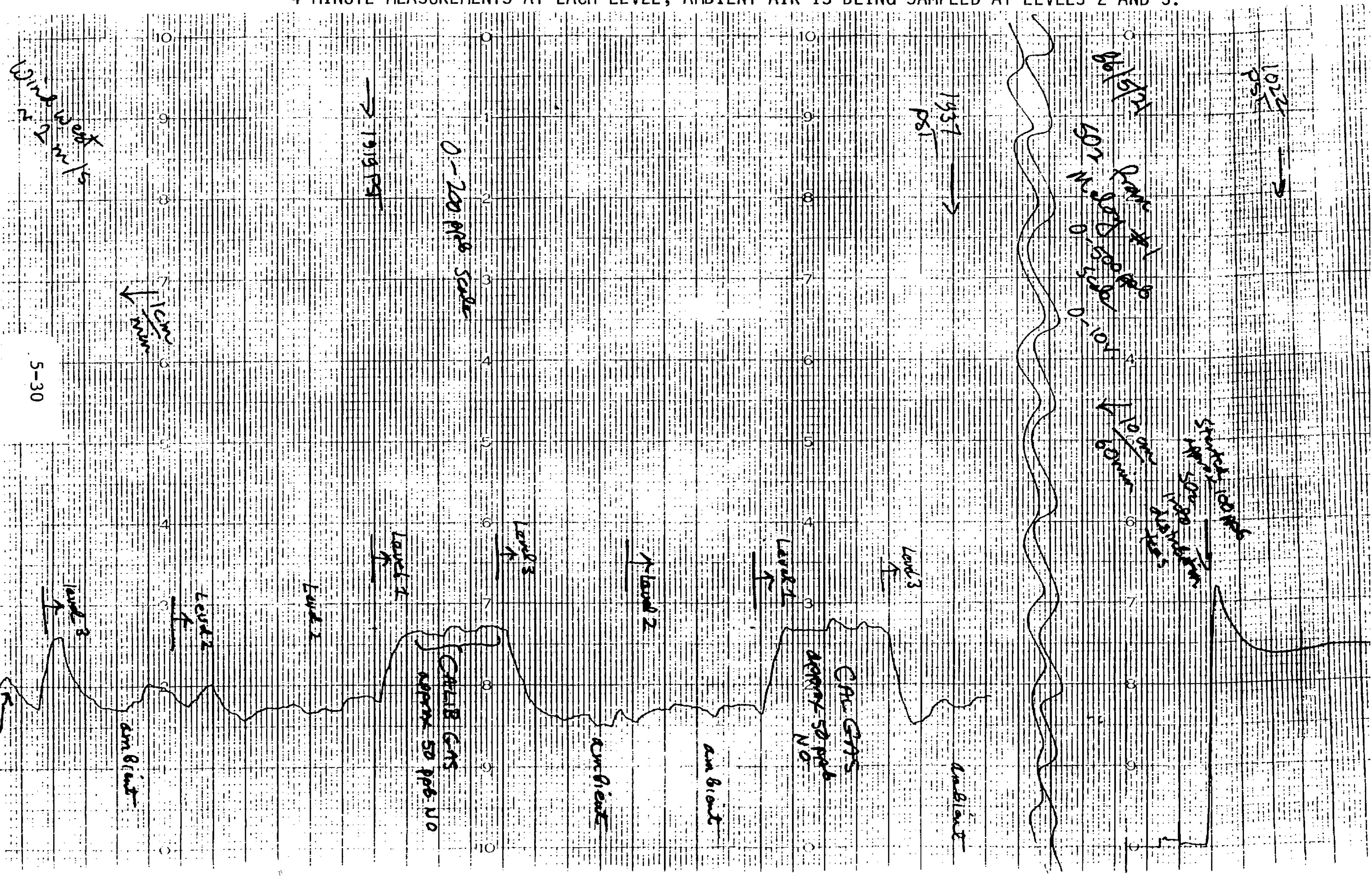


Table 5-11

SO_4 Field Calibrations: Response of SO_4 Analyzer to SO_2 Calibration Gas (Meloy 285 No. OH180)

Date	Time	Gas Calibrator Nominal Output ppb	Instrument Response ppb	σ (ppb)	$\sigma/\sqrt{N}$ (ppb)
86/5/12	1200	52.6	49.5		
86/5/12	1700	52.6	50.4		
86/5/13	1703	52.6	59.4	1.5	0.09
86/5/18	2105	52.6	55.4		
		AVERAGE =	53.7		

Sulfate aerosol calibration and performance test standards were not available for the field program. A major concern when sampling particles rather than gases is Brownian diffusion loss of particles to the walls of the sampling tubing. This type of loss can be estimated if the sample flow rate and the sampling inlet geometry are known (Fuchs, 1964). Table 5-12 summarizes the estimated losses for spherical particles of given size.

Table 5-12 shows that diffusion losses can exceed 10% for particles smaller than 0.05 μm equivalent diameter, with larger losses for smaller particle sizes. If Brownian diffusion were the only operative loss mechanism, these losses would be equal among the three sampling tubes. However, electric charge residing on the inner walls of the FEP Teflon sampling tubing might create a less uniform, less predictable, and more influential loss mechanism. To evaluate this possibility, a test, using monodisperse ammonium sulfate aerosols generated in the laboratory, was conducted after the field monitoring. A constant-output aerosol generation system provided 0.1 μm diameter ammonimum sulfate particles, with constant number concentrations (within ±5% over one hour). This test aerosol was passed through each of the three Teflon sampling tubes at a flow rate of 3.2 ℓ/min and relative humidity of 0% (field sampling involved a flow rate of 1.5 ℓ/min and much higher relative humidities). For the three tubes, the average transmitted concentration was 2.0%, but the individual transmitted percentages ranged from 0.7% for level 1 to 3.2% for the level 3 sample lines. Similar results, for PFA Teflon tubing, are reported by Bergin (1987). These results may not be directly relevant to the field data, where higher relative humidities may have alleviated electrostatic charge removal effects, but they do show the possibility that aerosol losses may have influenced the sulfate particle measurements. Since the field measurements of sulfate aerosol

Table 5-12

Estimated Aerosol Penetration Efficiencies[a]

Aerosol Particle Diameter, μm	Percent Transmitted
0.01	40%
0.05	87%
0.1	95%
1.0	100%

[a] Asssumes a flow rate of 25 cm^3/s in the main sampling lines and flow rate of 4 cm^3/s in the sample distribution system (Fuchs, 1964).

concentrations always indicated very low values, the validity of the sulfate concentration data is considered suspect at this time.

5.4.5 Nitric Acid Measurement

The responses of the nitric acid analyzer (Monitor Labs 8440 No. 812) to calibration gases are summarized in Table 5-13. The average response of the HNO_3 channel (difference between the instrument's two outputs) was about ±3 ppb for a wide range of HNO_3 - free gas inputs. Taken by itself, this result suggests that it was possible to balance the two ML8440 channels, so that they would consistently read near-zero when no HNO_3 was present, and then presumably read the contribution due to HNO_3 and other species collected on the nylon filter when those species were present.

In practice, it was found that the ML8440 demonstrated this ability to return to a "static" balance of the two channels, but that when ambient NO, NO_x, and other species were changing, there was a lack of "dynamic" balance, as though the two channels had significantly different response times. The results of Table 5-13 were achievable only when ambient detectable species were not changing in concentration which is obviously not the case for the field measurements. This problem leads to serious doubts regarding the validity of the HNO_3 measurements. Some additional validation of the HNO_3 concentration measurement method was obtained through five collocated diffusion denuder measurements carried out from May 28 through May 30, 1986, by Dr. J. Horrocks, of California Air Resources Board. These measurements are described in detail in Dr. Horrocks' report, in Appendix B. Comparison of the denuder measurements to simultaneous DRI data allowed the following conclusions:

Table 5-13

Response of ML8440 S/N 812 to NO Calibration Gas and Zero-Gas Air: Readings of Difference Between Two Channels, 5/86 - 6/86

Date	Time	Gas Calibrator Output ppb	Response, ppb, 30 Minute Ave	σ ppb
86/5/28	1700	101.5	+1.2	not available
86/5/28	1700	ADDED O_3	+2.4	not available
86/5/29	1728	101.5	+2.61	1.08
86/5/29	1622	0.0	+3.27	not available
86/5/31	0822	52.1	+3.23	1.36
86/5/31	1707	101.5	+2.72	1.38
86/5/31	1601	101.5	+3.26	1.24
		AVG	+2.67	
		σ	0.74	

- the two data sets were correlated with a coefficient of 0.85;
- the DRI concentration estimates were all at least 100% higher than the denuder measurements;
- the two data sets show a regression (slope) of 0.58, when the DRI data are plotted on the x-axis and the ARB denuder data are plotted on the y-axis; therefore, the two gas centration data sets tended to rise and fall together.

In addition, Dr. Horrocks suggested that the DRI HNO_3 measurements may be high due to the presence of other interfering gaseous species such as PAN, ethyl nitrate, ethyl nitrite, r-propyl nitrate and other nitrogeneous species which would be removed by the Nylasorb filter on the NO_x - HNO_3 channel but reduced to NO in the NO_x channel.

5.4.6 Meteorological Data: Temperature Probes

The platinum resistance thermometers were performance tested by: 1) immersion in a distilled water ice slurry; 2) comparison to each other, at ambient temperatures, with the three probes wrapped in an insulating blanket; and 3) comparison to a mercury thermometer, at about 0°C and 20°C.

Table 5-14 summarizes the results of these calibrations and performance tests; the resolution of the data acquisition system (A/D converter) is 0.05°.

Table 5-14 shows that the laboratory ice point performance test data are within 0.10°C of 0.00°C with the exception of T2 on 86/10/20, which was 0.14°C. The field ice point measurement made on 86/7/11 yielded similar results. The ice point measurement on 86/6/1, shows opposite signs and larger values for the T1 and T2 discrepancies. No reason for the increased descrepancies was uncovered.

Table 5-14

R. M. Young Temperature Sensors
Calibrations and Performance Checks
(A/D Resolution = 0.05°)

ICE BATH RESULTS (°C)

Date (1986)	T1	T2	T3	Mercury Calibration Thermometer #65432
5/5 (Reno Lab)	-0.05	0.00	0.00	
6/1 (CSUDH Field)	-0.63	+0.36	-0.01	
7/11 (Mohave)	-0.05	+0.16	+0.10	
10/20 (Reno Lab)	+0.03	+0.14	+0.10	+0.05

ISOTHERMAL COMPARISONS (°C)

Date (1986)	T1	T2	T3	Calibration Thermometer #47444
5/5 (Reno Lab)	24.10	24.05	24.10	
6/1 (CSUDH Field)	23.53	24.18	24.11	
7/11 (Mohave)	29.84 30.06	29.74 30.17	30.00 30.33	
10/20 (Reno Lab)	19.62 19.67 19.76	19.61 19.65 19.72	19.63 19.67 19.75	19.74 19.85 19.85

The "isothermal comparisons" of Table 5-14 were obtained by wrapping the three temperature probes together in an insulating, cotton blanket, allowing at least 30 minutes for equilibration. Again the laboratory results are consistent, with agreement among monitors which is better than or equal to the 0.05°C resolution. The laboratory results on 86/10/20 also agree with a mercury calibration thermometer to within 0.14°C. The field data on 86/7/11 show agreement among monitors within 0.27°C. The field data on 86/6/1 show agreement only within 0.6°C.

The average value of the probe-to-probe differences lumped together for both the ice point and the isothermal comparisons, is 0.11°C if the data of 86/6/1 are excluded, and it is 0.23°C if they are not. It is probably conservative to assign a precision in the range 0.1°C to 0.2°C based on these measurements. If the ice point data of 86/6/1, which show significant positive and negative differences with respect to standards, are excluded, the remaining ice point data plus the calibration thermometer comparisons of 86/10/20 suggest that the thermometers were accurate within their limits of precision.

5.4.7 Meteorological Data: u,v,w Gill anemometers.

The complete and proper calibration of the Gill propeller-generator combination requires separate wind tunnel characterization for each unit (Horst, 1973; Businger, 1986a), an expensive activity out of the scope of this program.

Performance tests on the nine anemometer generators, with their propellers removed, were carried out with a 300 revolution per minute synchronous motor. At this rate of revolution, the generators should provide an output voltage equivalent to a 1.5 m/s wind speed. Table 5-15 shows the results of performance tests at the beginning and the end of monitoring. A maximum

Table 5-15

Performance Checks of Gill Anemometer Generators with 300 RPM Synchronous Motor: Response in m/s

SENSOR: CLOCKWISE (CW) or COUNTER-CLOCKWISE (CCW)

		86/5/4	86/6/1
u_1	CW	-1.55	-1.55
	CCW	+1.51	+1.50
v_1	CW	ND	-1.56
	CCW	+1.49	+1.50
w_1	CW	+1.49	+1.50
	CCW	-1.53	-1.54
u_1	CW	ND	-1.55
	CCW	+1.48	+1.49
v_1	CW	ND	-1.56
	CCW	+1.50	+1.48
w_1	CW	+1.47	+1.49
	CCW	-1.52	-1.53
u_1	CW	-1.50	-1.51
	CCW	+1.50	+1.52
v_1	CW	-1.50	-1.51
	CCW	+1.49	+1.52
w_1	CW	+1.49	+1.52
	CCW	-1.50	-1.51

Notes: ND = No data
Sign convention reversed on w anemometers

difference of 6 cm/s (4% of 1.50 m/s) was found. The clockwise (negative directions for u and v, positive (upward) for w) values show larger differences than the counter-clockwise values. The average difference was 1.9 cm/s (1.3%) for the two performance checks. Taken individually, the average difference for the first test, when the generators were newly-delivered, was 1.3 cm/s (0.9%); the average for the second test was 2.3 cm/s (1.6%), suggesting that some wear-related drift might have occurred during the field sampling.

5.5 Summary

A large effort was expended in quantifying the precision associated with each measurement in this project. This effort was needed owing to the stringent requirements of measuring small differences between relatively large values measured at several levels. The results are summarized in Table 5-16.

Table 5-17 summarizes the precision information from a different perspective regarding the gas data. That is, there are at least four measures of precision: (1) the standard deviation of repeated five to thirty minute averages of one-minute gas analyzer responses to calibration gases; (2) this standard deviation divided by the square root of the number of data points (standard deviation of the average); (3) and (4), these same two parameters derived for nearly-stationary ambient gas sampling conditions, when deposition velocities were being derived.

Table 5-17 again shows a difference in both measures of precision, from laboratory to field measurements. It is encouraging that field-measured standard deviations of averages are of similar magnitudes whether calibration or nearly-stationary ambient gas is being measured. (The third column of Table 5-17 is the data selection criterion used in Section 6.)

Table 5-16

Precision and Accuracy Methods and Estimates for Measurements in Dry Deposition Field Programs, 5/86 - 6/86

MEASUREMENT	CALIBRATION METHOD	RESULT
SO_2	Gas Calibrator based on mass flow meters and traceable SO_2	1) Precision measured as standard deviation of laboratory performance tests ≃ 0.2 ppb 2) Precision measured as standard deviation of field performance tests ≃ 1.0 ppb 3) Precision measured as standard deviation of average in field performance tests ≃ 0.06 ppb 4) Average difference between two sampling levels, in field performance tests ≃ 0.7 ppb 5) Average bias with respect to calibrator ≃ +11.7%
NO, NO_x	Gas calibrator based on mass flowmeters and traceable NO; NO_x results assume 100% molybdenum converter efficiency	1) Precisions measured as standard deviations of laboratory performance tests ≃ 1.3 ppb for NO, 0.7 ppb for NO_x 2) Precisions measured as standard deviations of field performance tests ≃ 3.5 ppb for NO, 3.2 ppb for 3) Precision measured as standard deviation of average in field performance tests ≃ 0.21 ppb for NO, 0.19 ppb for NO_x

Table 5-16 (continued)

Precision and Accuracy Methods and Estimates for Measurements in Dry Deposition Field Programs, 5/86 - 6/86

MEASUREMENT	CALIBRATION METHOD	RESULT
		4) Average difference between two sampling levels, in field performance tests ≃ 0.9 ppb for NO 5) Average bias with respect to calibrator ≃ +21.3% for NO, +15.9% for NO_x
HNO_3	No calibrations performed but balance of two channels is acceptable for static situations	
$SO_4^=$ (aerosol)	Gaseous sulfur from same calibration setup as used for SO_2	1) Standard deviation of field performance tests ≃ 1.5 ppb
Temperature	Distilled water ice slurry; isothermal comparisons with and without mercury calibration thermometer	1) Precision 0.1°C to 0.2°C 2) Accuracy within 0.2°C
Dewpoint Temperature	No calibrations	
Windspeed	300 RPM calibrator on generators; manufacturer's calibration	1) Generator precision 1.3% at 1.5 m/s

Table 5-17

Four Estimates of SO_2, NO, and NO_x Measurement Precisions (Data usually based on 30-minute averages; in some cases, however, shorter averaging times are involved)

	CALIBRATION GAS		AMBIENT SAMPLING	
Gas Species	Standard Deviation Repeated 5 to 30 Minute Averages, σ	Standard Deviation of Mean (Standard Error) $\sigma/\sqrt{N}$	Standard Deviation Repeated 30 Minute Averages σ	Standard Deviation of Mean (Standard Error) $\sigma/\sqrt{N}$
			(Data Selection criteria)	
SO_2	0.2 ppb (lab) 1.0 ppb (field)	0.005 ppb (lab) 0.06 ppb (field)	< 5 ppb	0.10 to 0.20 ppb
NO	1.3 ppb (lab) 3.5 ppb (field)	0.03 ppb (lab) 0.21 ppb (field)	< 5 ppb	0.20 to 0.30 ppb
NO_x	0.7 ppb (lab) 3.2 ppb (field)	0.02 ppb (lab) 0.19 ppb (field)	< 3 ppb	0.20 to 0.30 ppb

The calculation of deposition velocities involves the average concentration over a selected averaging time, in this case 30 minutes. Therefore, the standard error is proposed here as the best estimate of precision. The standard error for each instrument is well below the 1 ppb precision which is required to determine the concentration gradients.

The standard error as a measurement of precision has another advantage for the gradient method: when concentrations over the averaging period are <u>not</u> stationary (an assumption of the method), the standard error increases. As will be shown in Section 6, the variability of atmospheric concentration levels over the averaging period limits the applicability of the gradient method more than the repeatability of the measurement instrument.

6.0 RESULTS

6.1 Measurement Uncertainties and Interferences

Section 5 concluded with a summary of precision and accuracy estimates for measurements in this project.

The precision selected for each atmospheric constituent average (i.e., the concentration of each gas at each level averaged over 30 minutes) is the standard error ($\sigma/\sqrt{N}$). These standard errors are then combined with other measurement precisions, using the error propagation formulae of Bevington (1969) as explained in Appendix A. These propagated uncertainties are frequently of the same order of magnitude as the V_d estimates themselves (by contrast, note that the gas species standard deviations of the means are usually no greater than about 6% of the ambient gas concentrations.)

For comparison, estimated V_d uncertainties cited in a brief selection of published literature are as follows:

Species	Estimated V_d Uncertainty	Author(s)
Submicron particles	40%	Wesley et al. (1977)
NO_x	50%	Delaney & Davies (1983)
"Acid Precursor Gases"	25%	Durham & Ellestad (1984)

No documentation is given for the estimates of these uncertainties, however, and no clear basis exists for comparison of the confidence intervals derived in this project with those stated in these studies. It is the authors' belief that the propagated uncertainties reported here are the first to be analytically derived and that these are minimum uncertainties which are functions only of the measurement precisons.

Other uncertainties, which are not quantified by the error propagation scheme used here, are those associated with measurement method interferences and with deviations from the gradient model assumptions. These other, unaccounted uncertainties include:

- The NO_x measurement may include mixtures of species, including HNO_3 and PAN, because the hot molybdenum converter in the CSI 1600 analyzer converts these species to NO with high efficiency (Heubert, 1983b; Winer, 1974).

- The best measurements were often taken in a sea-breeze environment, with westerly winds carrying a continuously - modifying marine layer (e.g., Edinger, 1963) over the sampling site. At least two types of measurement interferences can result from this dynamic situation, and might apply to any site in the South Coast Air Basin. First, upwind sources were not very distant; a busy avenue was located on the upwind side of the region of acceptable fetch. The observed gradients may be due to causes other than orderly transport to a sink at the earth's surface. Fitzjarrald and Lenschow (1983) discuss the significant error in NO_x flux estimates that can result when another reactive species, O_3 is present.

  Second, entrainment or detrainment of gas species through the top of the marine layer can occur if this layer is changing its elevation, for example as a convective boundary layer is growing on the morning of a sunny day (Businger, 1986). The gradient method requires that the inversion heights do not change significantly during the course of most of the measurement sequences reported here.

- The observed temperature profiles generally did not fit a logarithmic distribution with height; instead, the level 1 temperature value was usually closer to the level 2 value than would be the case for a logarithmic distribution. This suggests the possibility of a flow distortion in the vertical plane, such that the lowest ~ 2.5 m have not equilibrated to the surface.

- The average vertical velocities ($\overline{w}$) (estimated on the basis of the heat and moisture fluxes, not taken from the Gill anemometers - see Appendix A) were almost always upwardly directed, and are of order 0.1 to 0.5 cm/s. This estimate is subtracted from the first calculation of V_d to give the final V_d estimate, i.e., all V_d initial estimates have been revised downward by 0.1 to 0.5 cm/s. If the magnitudes of the w's have been overestimated, then the V_d values have been underestimated; the converse is also true.

6.2 Data Selection Criteria

The data base was screened and corrected according to the validation criteria shown in Table 5-17. Data were sorted to select those 30-minute averages for which the following criteria were met:

- Wind direction from the 260° - 360° sector, corresponding to the most level, uniformly mown area of the fetch, with the fetch distance ranging from 350 m to 490 m.
- The minimum ambient concentration of each gas was required to equal or exceed 5 ppb, equal to a factor of 2 to 5 times the lower quantifiable limit (LQL) of the gas analyzers (see for example the LQL estimates for the Meloy 285 SO_2 analyzer in Mueller et al., 1983). The HNO_3 threshhold was lowered to 3 ppb when only seven data records survived the 5 ppb screen.
- The standard deviation of each 30 minute gas data set was required to be less than 5 ppb. This standard deviation then becomes part of the definition of "stationary". The time variation of the gas concentrations is expected to meet the gradient method stationarity requirements when the standard deviation was less than 5 ppb.
- The minimum horizontal wind speed (vector sum of the u and v components) was required to be 0.5 m/s or greater, in order to avoid the "dead zone" of the Gill propellor anemometers.
- Outlier values, defined as those separated from the average by more than 3σ, have been eliminated following the above selection steps.

6.3 Time Series

Figures 6-1(a) through 6-4(a) present the time series of the screened values of V_d for SO_2, NO, NO_x, and HNO_3. Owing to the suspected losses in the sampling lines, the sulfate aerosol data are not presented. These estimates are relevant to the 2.5 meter level. For reference, the corresponding Level 2 average gas concentrations are shown in Figures 6-1(b) through 6-4(b).

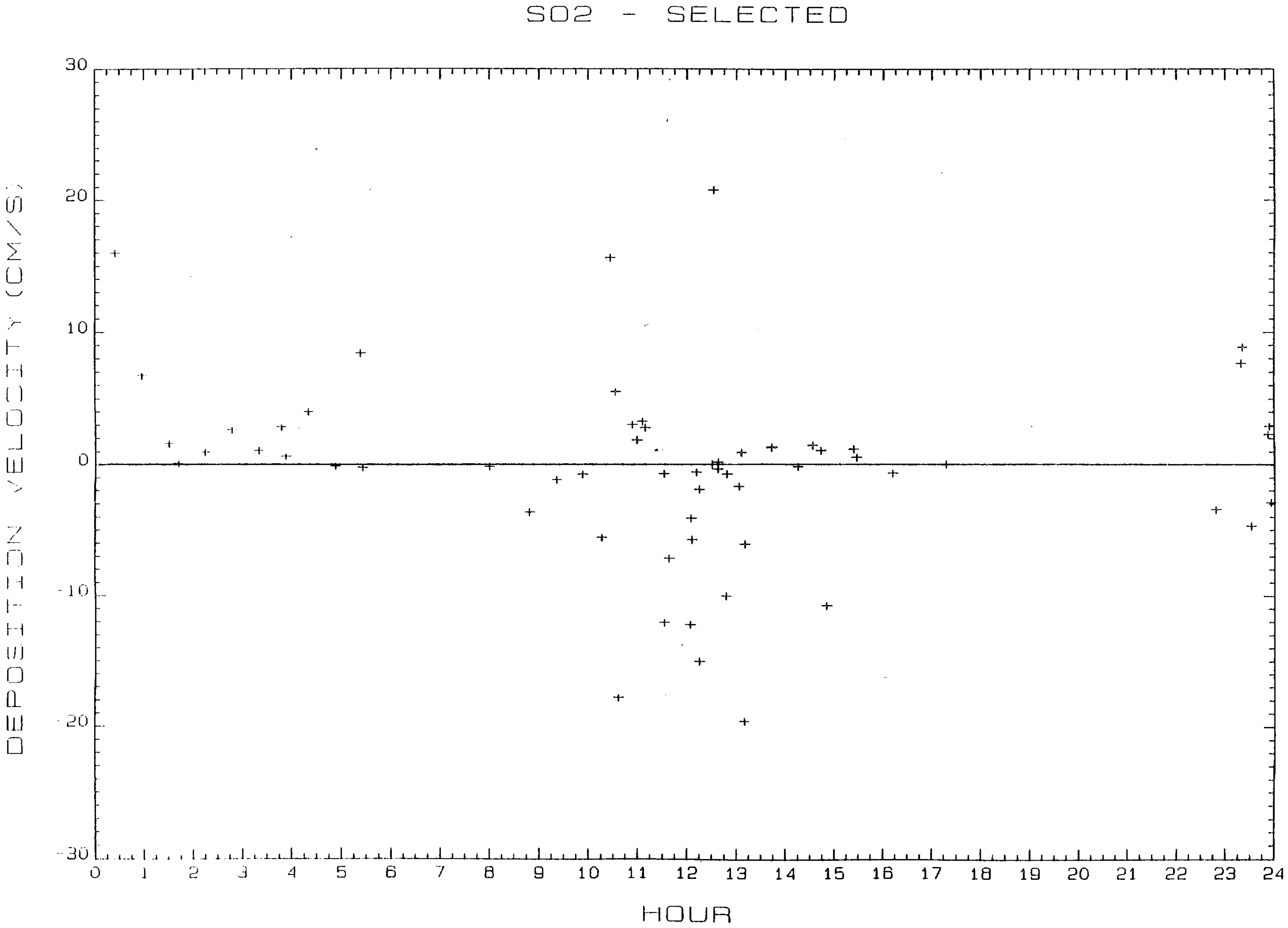


Figure 6-1(a) COMPOSITE DIURNAL TIME SERIES, SO_2 DEPOSITION VELOCITIES

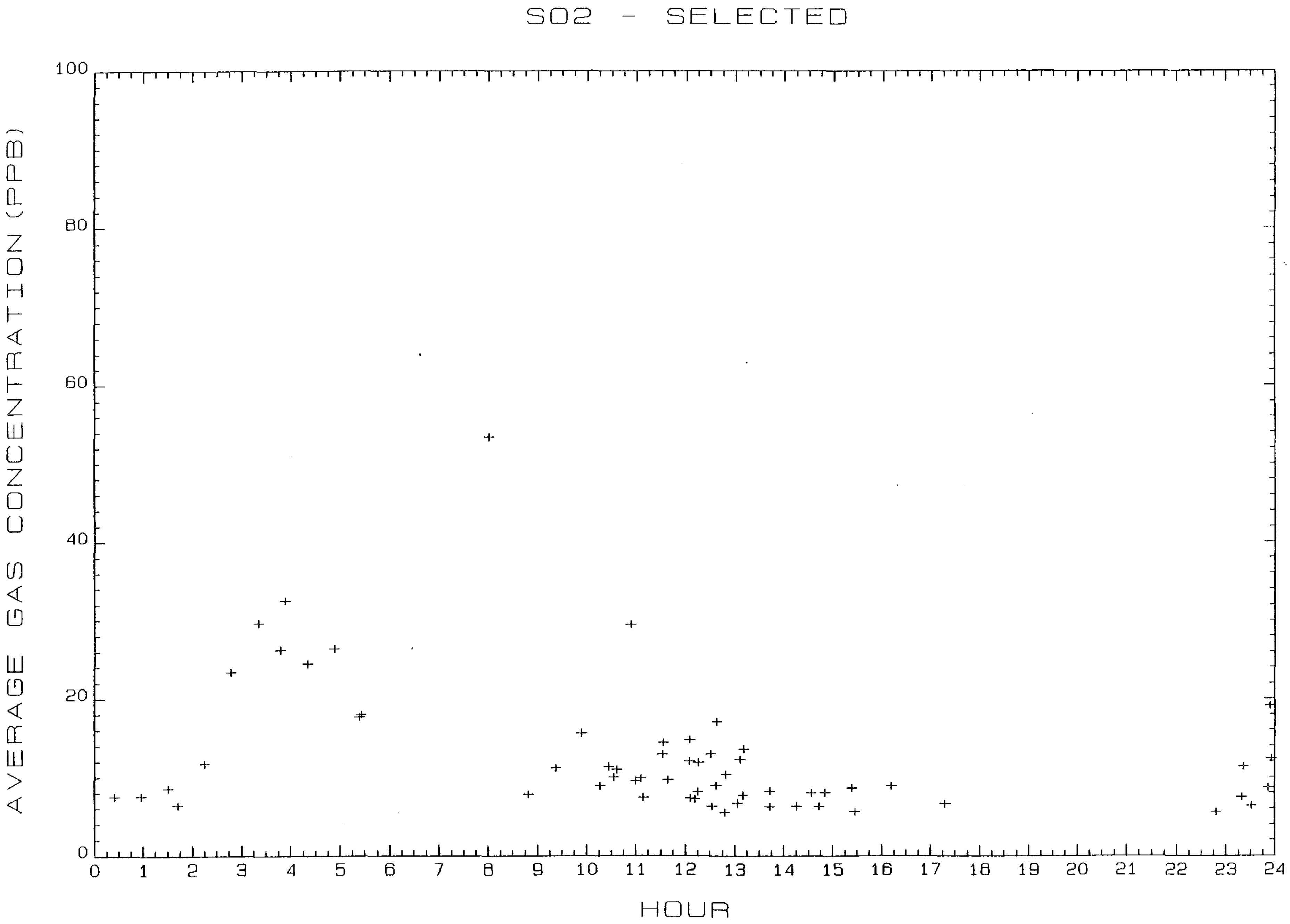


Figure 6-1(b) AVERAGE LEVEL 2 SO_2 CONCENTRATION FOR SELECTED DATA

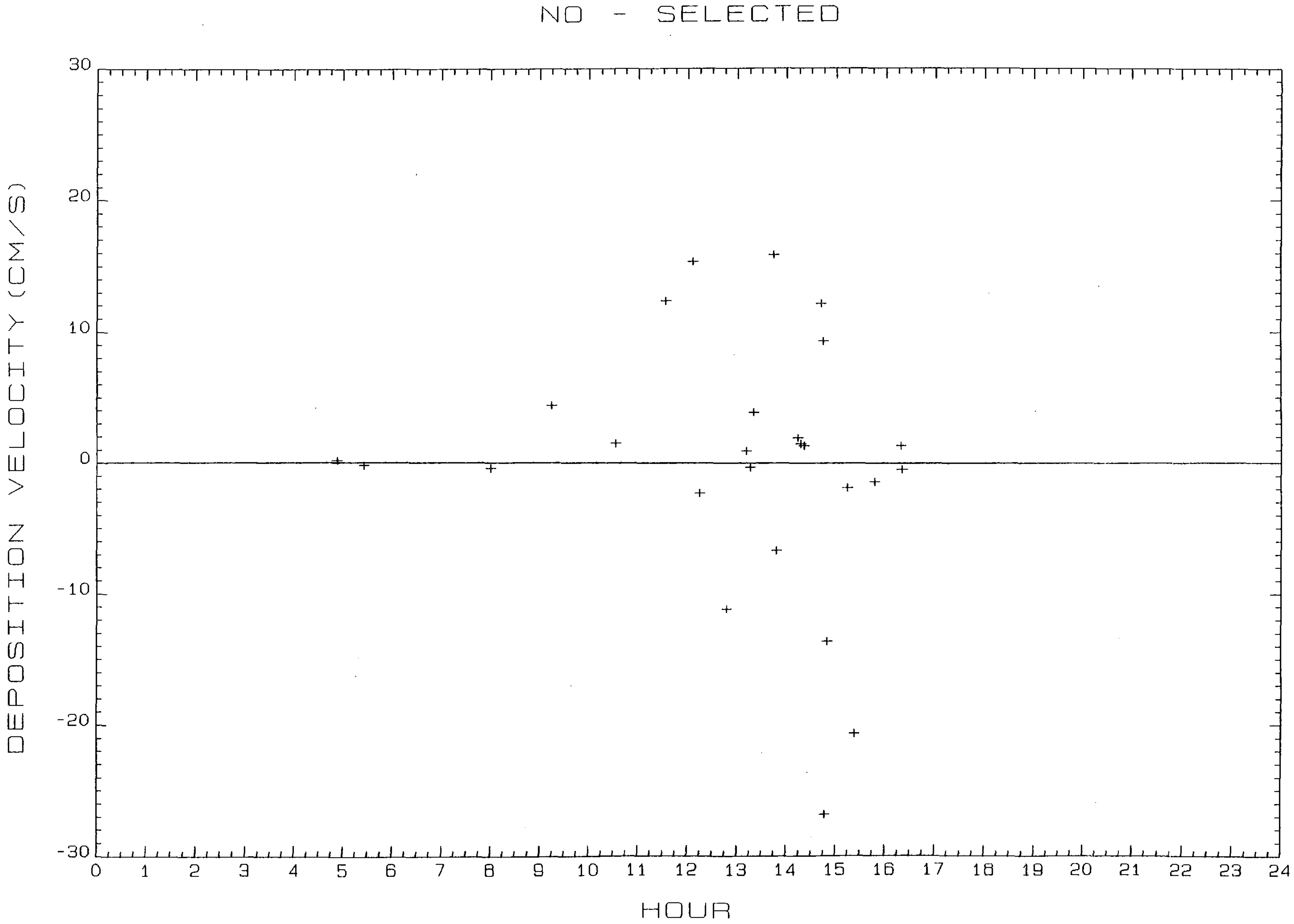


Figure 6-2(a) COMPOSITE DIURNAL TIME SERIES, NO DEPOSITION VELOCITIES

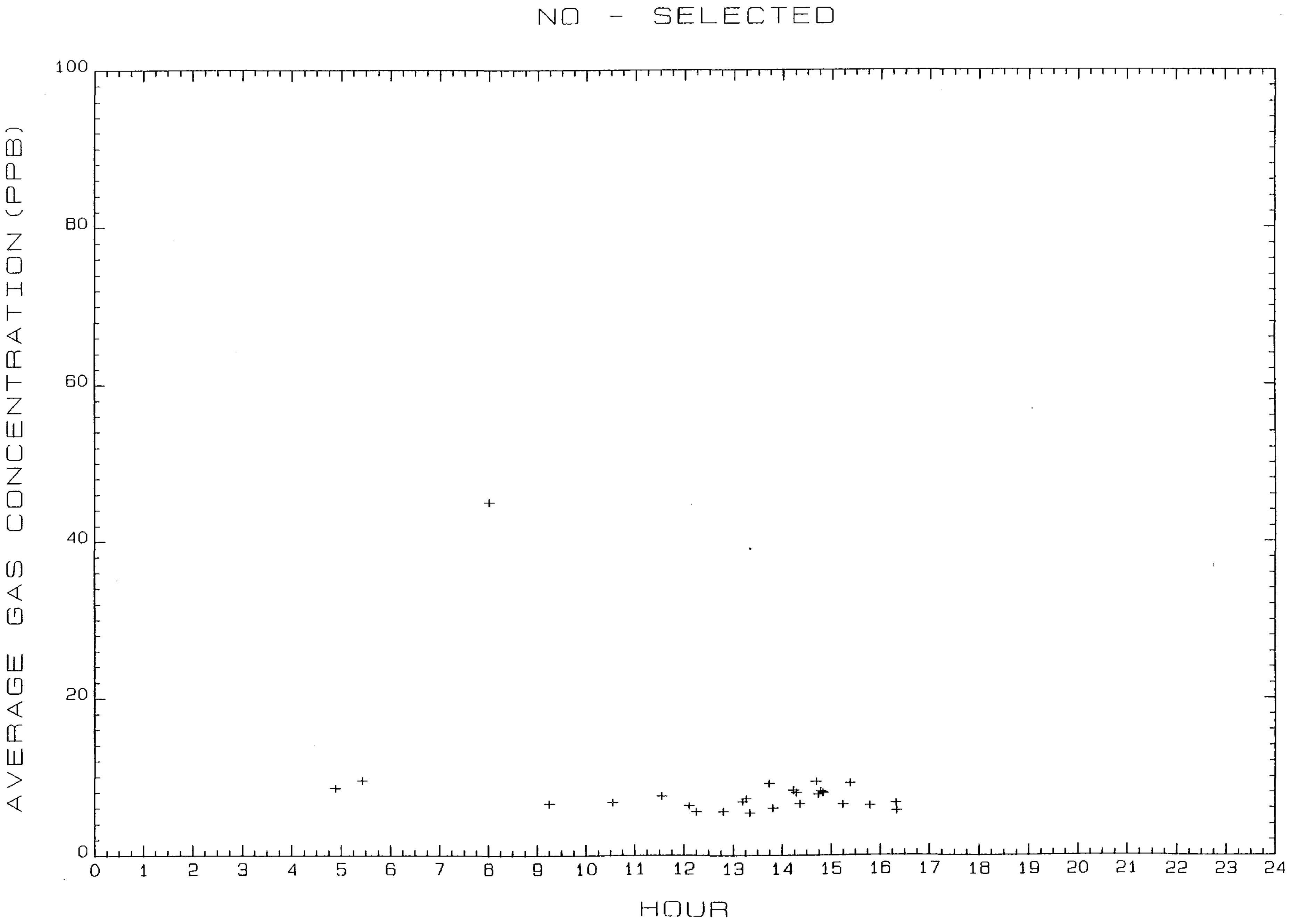


Figure 6-2(b) AVERAGE LEVEL 2 NO CONCENTRATIONS FOR SELECTED DATA

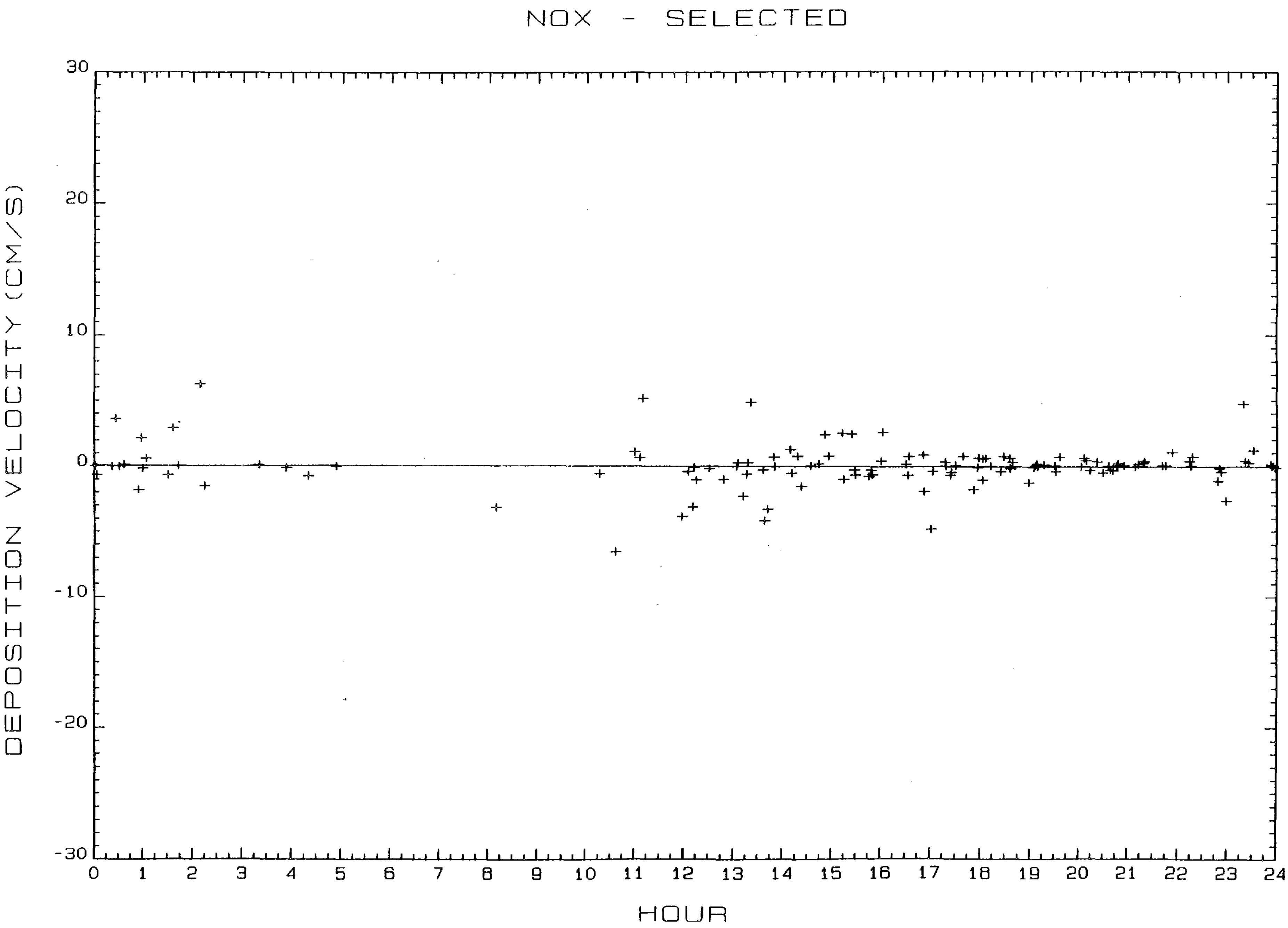


Figure 6-3(a) COMPOSITE DIURNAL TIME SERIES, NO_x DEPOSITION VELOCITIES

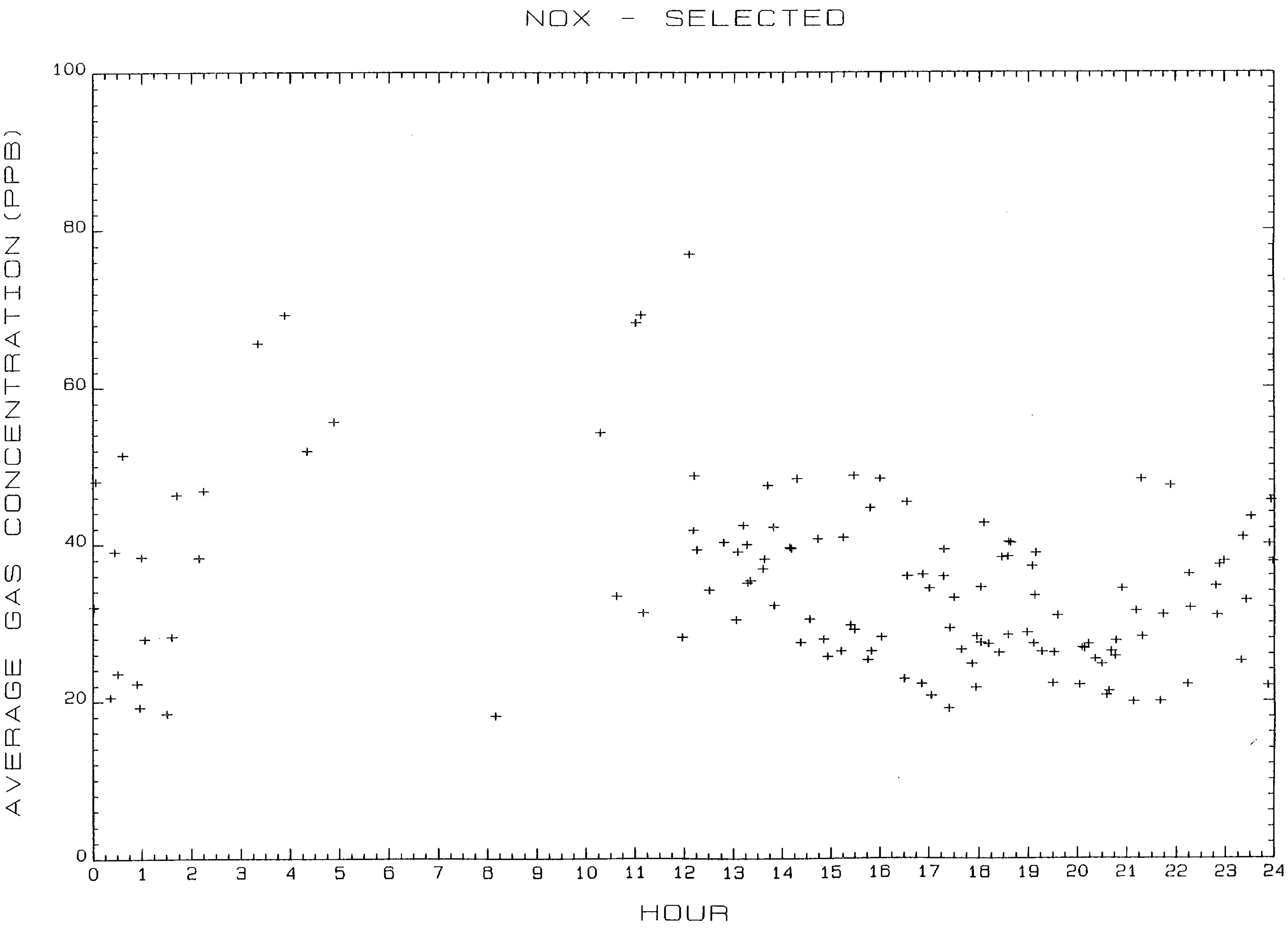


Figure 6-3(b) AVERAGE LEVEL 2 NO_x CONCENTRATIONS FOR SELECTED DATA

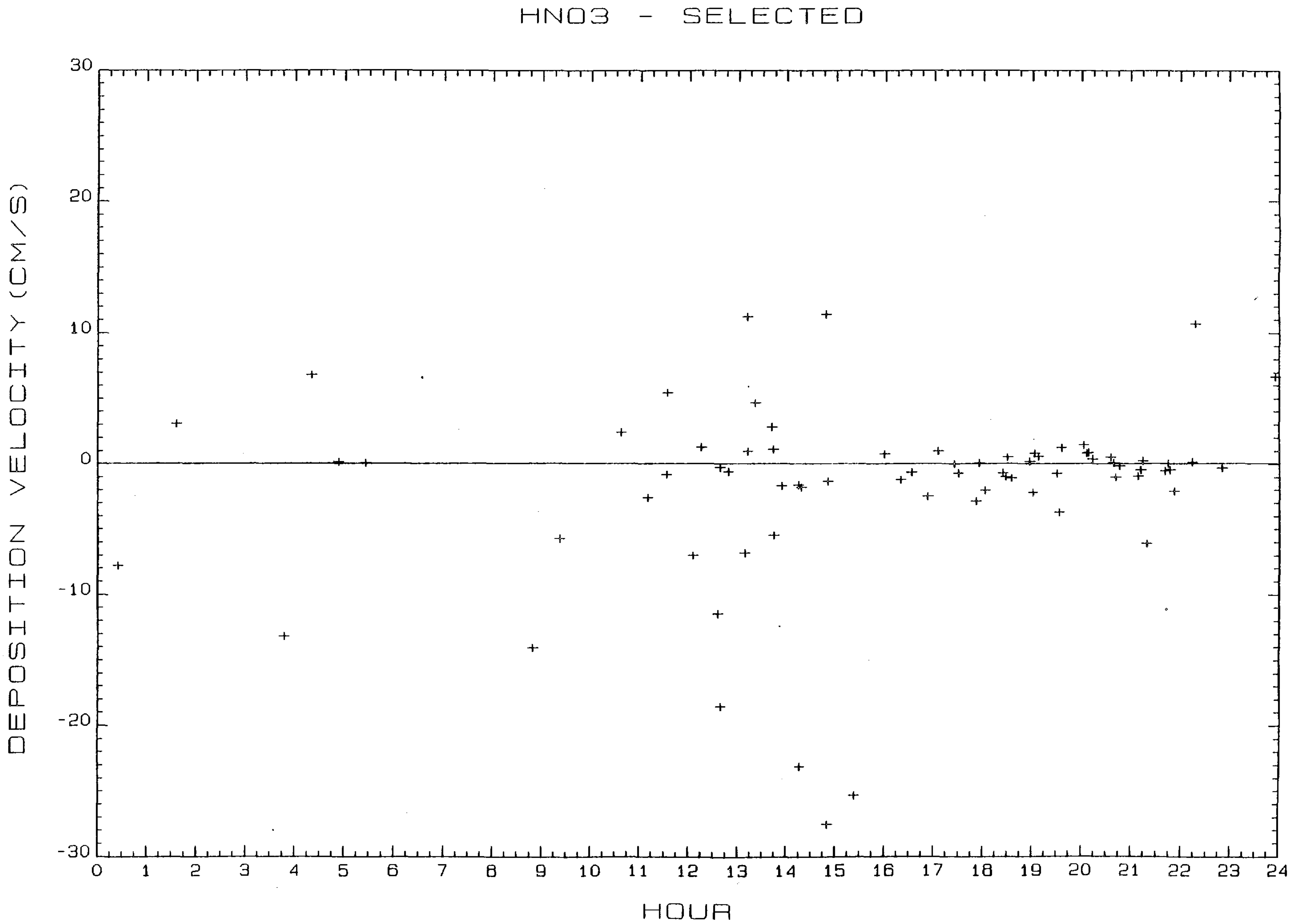


Figure 6-4(a) COMPOSITE DIURNAL TIME SERIES, HNO_3 DEPOSITION VELOCITIES

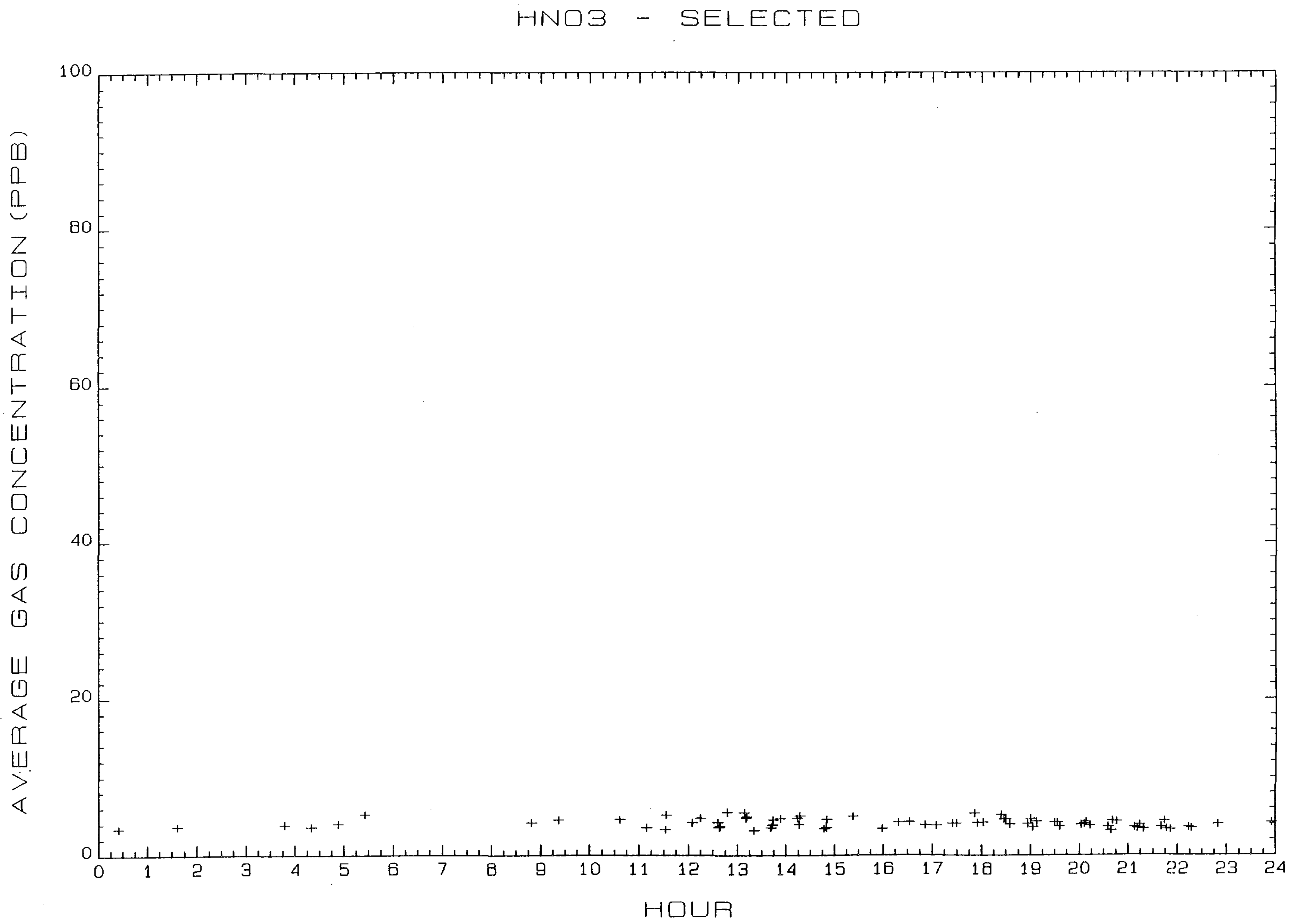


Figure 6-4(b) AVERAGE LEVEL 2 HNO_3 CONCENTRATIONS FOR SELECTED DATA

These data are also shown in Tables 6-1 through 6-4, which correspond to the figures of the same number. Table (a), for each number, is the selected daytime data, and (b) is the nighttime data, where the day and night periods are delineated by the clock times 0500 and 1900, PDT.

6.4 Discussion

6.4.1 Diurnal Variations

Figures and Tables 6-1 through 6-4 show that, for NO, NO_x, and HNO_3 there is no evident diurnal dependence of V_d, in the case of the NO data, this occurs because the nighttime data set is too small to show any significant difference. The gas concentrations usually show more scatter and higher values in the late morning - early afternoon hours, and then settle down to more consistent readings as the afternoon sea breeze (westerly winds) develops.

The SO_2 V_d data show more scatter than the NO or NO_x V_d. SO_2 also exhibits a distinction between the day and nighttime values; the average nighttime SO_2 V_d is +2.6 cm/s (downward direction), while the average daytime value is -2.1 cm/s (upward direction). The average propagated uncertainty (unvd) is 1 to 2 cm/s. The standard deviation of the valid V_d is 4.9 cm/s for nighttime values, and 6.7 cm/s for daytime values. This indicates that the measurement uncertainty is less than the environmentally caused variability of V_d. Brimblecombe (1978) and Hicks (1985) discuss the role of surface moisture in reducing the surface resistance to SO_2. In the present data, we speculate that the observed presence of dew at night may mean that the nighttime surface was a more effective sink for SO_2 than the daytime surface. The varying quantities of surface moisture throughout the sampling period may be a cause of the variability in V_d. Sources

Table 6-1(a)

SELECTED SO_2 DAYTIME DATA: 30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas, nimsl = so2 42

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
17	12.50	-0.02	3.34	0.08	13.00	3.68	11.17	0.05	0.57
18	13.05	0.00	3.35	0.06	6.71	4.86	36.31	-1.65	1.55
41	10.53	-4.15	2.49	0.46	10.03	1.58	2.93	5.52	1.38
42	11.08	-3.53	2.98	0.56	9.89	1.14	0.40	3.29	0.82
43	11.63	-3.28	3.22	0.67	9.67	1.72	1.62	-7.14	1.55
44	12.18	-0.10	3.33	0.10	7.25	1.43	10.32	-0.57	0.68
65	10.88	-5.85	1.97	0.42	29.56	2.38	0.07	3.06	1.60
72	14.72	-0.03	3.09	0.05	6.27	1.50	0.64	1.12	0.19
93	8.00	-17.98	0.63	0.14	53.37	4.08	2.11	-0.18	0.51
95	13.10	-0.05	3.69	0.10	12.31	2.14	0.06	0.95	0.15
154	15.45	0.00	3.35	0.05	5.63	2.00	1.92	0.59	0.22
170	14.55	-0.07	3.92	0.07	8.03	2.54	10.97	1.49	1.01
173	16.18	0.00	2.08	0.02	8.94	2.90	7.58	-0.58	0.24
175	17.28	0.00	2.39	0.01	6.66	2.82	4.46	0.08	0.18
188	10.27	-8.64	1.17	0.23	8.81	1.82	10.93	-5.58	3.85
207	12.25	-3.14	2.73	0.36	11.79	2.94	7.13	-15.00	3.16
208	12.80	-0.03	3.00	0.05	10.37	2.51	18.98	-0.70	0.88
217	14.83	-2.68	3.22	0.67	8.03	2.39	21.84	-10.72	10.71
218	15.38	-3.71	2.50	0.55	8.66	2.54	1.62	1.21	1.54
241	9.88	-7.07	1.52	0.46	15.56	2.97	5.12	-0.76	1.91
242	10.43	-3.95	2.62	0.70	11.41	2.84	0.58	15.61	1.60
243	10.98	-4.81	2.30	0.64	9.53	1.53	6.13	1.86	2.76
244	11.53	0.00	2.00	0.03	12.94	2.39	7.12	-0.69	0.18
245	12.07	-5.18	1.87	0.56	14.81	2.63	6.90	-4.07	2.98
246	12.62	0.00	2.32	0.04	17.08	1.94	1.08	0.22	0.04
247	13.17	-3.36	2.73	0.70	13.55	2.03	8.85	-6.03	4.24
248	13.72	-0.01	3.50	0.08	8.22	1.33	1.39	1.37	0.10
274	12.07	-3.60	2.72	0.69	12.00	2.00	6.39	-12.21	3.11
275	12.62	-2.96	3.17	0.77	9.01	1.08	1.82	-0.30	0.94
276	13.17	-2.59	3.26	0.77	7.66	2.72	0.61	-19.56	2.43
277	13.70	-0.03	3.16	0.08	6.26	0.74	5.54	1.33	0.27
278	14.25	-0.02	3.06	0.07	6.29	1.90	1.09	-0.10	0.13
325	5.38	-9.98	0.66	0.30	17.83	2.64	2.09	8.37	0.83
329	8.82	-11.75	0.80	0.26	7.77	1.99	2.72	-3.67	1.05
330	9.35	-8.32	1.52	0.34	11.14	2.12	1.92	-1.18	0.90
331	11.55	-3.55	2.63	0.63	14.37	2.96	6.38	-12.03	3.15
332	12.08	-14.42	3.46	2.54	7.36	1.27	2.00	-5.71	4.65
363	5.42	0.00	1.01	0.01	17.96	4.27	0.02	-0.24	0.04
364	10.60	-6.78	2.51	0.49	10.81	2.64	4.65	-17.81	2.99
365	11.15	-7.79	1.38	0.41	7.46	2.34	17.15	2.79	5.90
366	12.23	-0.10	3.24	0.11	8.15	1.69	2.29	-1.87	0.21
367	12.78	-2.15	3.64	0.83	5.50	1.54	8.43	-10.00	4.33
av		-3.61	2.56	0.39	11.61	2.30	5.93	-2.13	1.80
sd		4.28	0.88	0.43	7.97	0.86	7.06	6.66	2.05
mn		-17.98	0.63	0.01	5.50	0.74	0.02	-19.56	0.04
mx		0.00	3.92	2.54	53.37	4.86	36.31	15.61	10.71

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	0.57	1.00							
hws2m	0.68	0.61	1.00						
wbar+2	-0.07	-0.48	0.16	1.00					
gas2g	-0.49	-0.52	-0.52	-0.10	1.00				
mxsdgs	-0.23	-0.06	-0.33	-0.27	0.43	1.00			
vgas+2	0.19	0.16	0.15	-0.12	-0.20	0.38	1.00		
vd+2	-0.14	0.05	-0.18	-0.28	0.11	-0.06	-0.15	1.00	
unvd+2	0.04	-0.28	0.03	0.53	-0.13	-0.03	0.43	-0.46	1.00

Table 6-1(b)

SELECTED SO_2 NIGHTTIME DATA: 30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas,nimsl = so2 18

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
232	23.32	-17.74	0.57	0.10	7.56	2.85	1.98	7.65	1.48
233	23.87	-0.09	1.34	0.02	8.74	3.19	1.97	2.29	0.18
234	0.40	-12.19	0.87	0.20	7.69	1.45	12.18	16.00	4.17
235	0.95	-12.08	0.81	0.20	7.66	1.50	3.94	6.73	1.25
236	1.50	-13.87	0.65	0.19	8.58	0.63	5.97	1.58	1.66
263	22.80	-5.14	1.32	0.20	5.59	1.09	2.29	-3.40	0.78
264	23.33	-6.78	1.05	0.25	11.44	1.89	1.50	8.87	0.78
265	23.88	-10.09	1.00	0.26	19.18	4.27	9.31	2.96	2.97
290	23.50	-11.93	0.97	0.25	6.34	2.00	1.78	-4.68	1.32
294	1.70	0.00	0.85	0.01	6.42	0.75	0.29	0.11	0.02
295	2.23	-7.53	0.83	0.27	11.72	3.24	0.47	0.96	1.16
296	2.78	-7.71	1.17	0.28	23.41	2.68	2.39	2.62	0.82
297	3.33	-8.48	1.12	0.28	29.70	2.07	3.35	1.06	1.11
298	3.88	-13.49	0.66	0.16	32.53	1.15	0.44	0.61	0.16
321	23.92	-13.85	0.71	0.21	12.31	3.41	7.17	-2.89	1.93
360	3.78	-9.85	1.06	0.10	26.31	1.73	3.14	2.82	1.00
361	4.33	-6.44	1.14	0.11	24.49	1.13	2.27	3.98	0.71
362	4.87	0.00	0.87	0.01	26.37	3.57	4.30	-0.14	0.06
av		-8.74	0.94	0.17	15.34	2.15	3.60	2.62	1.20
sd		5.11	0.23	0.09	9.29	1.08	3.20	4.89	1.04
mn		-17.74	0.57	0.01	5.59	0.63	0.29	-4.68	0.02
mx		0.00	1.34	0.28	32.53	4.27	12.18	16.00	4.17

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	-0.07	1.00							
hws2m	0.21	0.61	1.00						
wbar+2	0.09	-0.48	0.04	1.00					
gas2g	-0.37	0.06	0.10	0.00	1.00				
mxsdgs	0.44	0.07	0.04	0.09	0.13	1.00			
vgas+2	0.00	-0.31	-0.14	0.20	-0.10	0.21	1.00		
vd+2	-0.23	-0.23	-0.13	0.02	-0.12	-0.10	0.42	1.00	
unvd+2	0.06	-0.55	-0.21	0.45	-0.26	0.15	0.87	0.51	1.00

Table 6-2(a)

SELECTED NO DAYTIME DATA:
30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas,nimsl = no 25

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
21	14.68	-2.70	3.34	0.69	9.38	4.18	0.44	12.14	3.24
22	15.23	0.00	3.22	0.05	6.44	3.84	10.48	-1.95	0.47
23	15.78	0.00	3.30	0.05	6.32	3.60	1.55	-1.50	0.40
24	16.33	0.00	2.75	0.04	5.69	4.21	9.30	-0.57	0.38
41	10.53	-4.15	2.49	0.46	6.72	3.31	5.58	1.50	3.21
93	8.00	-17.98	0.63	0.14	45.00	4.83	1.30	-0.39	0.39
98	14.73	-4.43	2.40	0.63	7.77	4.94	13.28	9.26	6.37
114	13.25	-3.15	3.17	0.79	7.18	3.60	7.58	-0.39	3.97
115	13.80	-4.14	2.44	0.63	5.92	3.10	7.06	-6.75	3.90
116	14.35	-2.45	3.51	0.66	6.50	3.65	1.76	1.25	3.91
271	9.23	-12.94	0.76	0.25	6.56	3.66	7.81	4.40	2.26
305	14.23	-0.03	3.06	0.07	8.23	4.30	3.06	1.85	0.33
306	14.78	-3.07	3.15	0.56	8.03	4.56	4.34	-26.85	3.90
331	11.55	-3.55	2.63	0.63	7.63	3.27	7.30	12.36	3.74
332	12.08	-14.42	3.46	2.54	6.32	3.22	6.09	15.33	13.96
334	13.18	-2.64	3.46	0.82	6.82	3.32	5.28	0.86	3.52
335	13.73	-2.72	3.23	0.80	9.20	3.49	20.60	15.82	10.93
336	14.28	-0.05	2.96	0.07	7.95	3.44	4.32	1.39	0.36
337	14.83	-2.36	3.27	0.61	7.86	3.68	5.47	-13.66	3.20
338	15.37	-2.18	3.54	0.67	9.04	3.50	1.87	-20.66	2.78
339	16.30	-0.08	3.18	0.08	6.69	3.39	26.54	1.26	1.91
363	5.42	0.00	1.01	0.01	9.53	4.56	2.95	-0.14	0.10
366	12.23	-0.10	3.24	0.11	5.55	3.09	11.69	-2.32	0.85
367	12.78	-2.15	3.64	0.83	5.51	3.31	0.40	-11.18	4.17
368	13.33	-1.96	3.74	0.85	5.40	3.21	7.10	3.83	4.60
av		-3.49	2.86	0.52	8.69	3.73	6.93	-0.20	3.31
sd		4.68	0.86	0.52	7.67	0.55	6.14	10.07	3.26
mn		-17.98	0.63	0.01	5.40	3.09	0.40	-26.85	0.10
mx		0.00	3.74	2.54	45.00	4.94	26.54	15.82	13.96

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	0.50	1.00							
hws2m	0.75	0.54	1.00						
wbar+2	0.01	-0.42	0.37	1.00					
gas2g	-0.43	-0.62	-0.56	-0.16	1.00				
mxsdgs	-0.16	-0.16	-0.48	-0.32	0.48	1.00			
vgas+2	0.25	0.15	0.07	-0.08	-0.20	-0.17	1.00		
vd+2	-0.19	-0.23	-0.12	0.25	0.00	-0.08	0.31	1.00	
unvd+2	0.05	-0.36	0.30	0.89	-0.18	-0.25	0.24	0.39	1.00

Table 6-2(b)

SELECTED NO NIGHTTIME DATA
(ONE RECORD ONLY)

```
         SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS
 gas.nimsl =          no          1
rec      hour      stab     hws2m     wbar+2     gas2g     mxsdgs     vgas+2     vd+2     unvd+2
362      4.87      0.00      0.87      0.01       8.54      3.19       0.38      0.26      0.06
 nimsl =            1
```

Table 6-3(a)

SELECTED NO$_x$ DAYTIME DATA:
30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas.nimsl = nox 65

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
7	18.08	0.00	1.73	0.02	42.68	4.22	6.81	0.54	0.28
8	18.63	0.00	1.12	0.02	40.11	4.31	8.03	0.21	0.24
16	11.95	-3.17	3.39	0.70	28.12	4.19	4.79	-3.82	2.63
17	12.50	-0.02	3.34	0.08	34.21	4.26	3.21	-0.18	0.17
18	13.05	0.00	3.35	0.06	30.43	4.12	9.41	-0.04	0.39
19	13.58	-0.03	3.63	0.09	36.84	4.13	5.47	-0.30	0.33
20	14.13	-0.04	3.21	0.08	39.61	4.59	5.32	1.22	0.40
22	15.23	0.00	3.22	0.05	40.82	4.95	6.37	-1.03	0.27
23	15.78	0.00	3.30	0.05	44.59	4.94	4.20	-0.34	0.19
42	11.08	-3.53	2.98	0.56	69.30	4.63	0.45	0.68	0.46
44	12.18	-0.10	3.33	0.10	48.73	4.73	1.94	-0.10	0.19
46	13.27	-0.06	3.44	0.08	35.10	4.12	1.55	0.26	0.11
47	13.82	-0.03	3.55	0.07	32.20	3.46	0.80	-0.07	0.09
48	14.37	-0.07	3.93	0.11	27.44	4.11	0.06	-1.57	18.87
49	14.92	-0.04	3.57	0.08	25.69	4.15	2.30	0.75	0.30
50	15.47	-0.06	3.56	0.08	29.10	4.24	5.87	-0.72	0.41
51	16.02	-3.07	2.92	0.48	28.26	4.09	1.38	2.55	0.97
69	13.07	-0.06	2.85	0.05	39.05	3.42	1.36	0.25	0.07
70	13.62	-8.30	3.45	1.37	38.07	3.80	0.28	-4.20	1.93
71	14.17	-0.03	3.00	0.04	39.39	4.42	1.13	-0.60	0.06
72	14.72	-0.03	3.09	0.05	40.64	3.40	0.04	0.14	0.07
74	15.80	-0.01	3.39	0.06	26.39	4.11	0.51	-0.69	0.13
104	18.03	-0.01	2.72	0.04	27.43	4.24	5.32	-1.11	0.27
105	18.58	0.00	2.72	0.03	28.44	4.28	21.17	-0.22	1.01
112	12.17	-7.88	1.53	0.34	41.69	4.23	3.46	-3.09	1.20
114	13.25	-3.15	3.17	0.79	39.93	4.34	0.64	-0.63	0.68
115	13.80	-4.14	2.44	0.63	42.19	3.55	0.51	0.68	0.57
141	17.27	0.00	3.06	0.03	35.85	4.19	0.09	0.26	0.08
154	15.45	0.00	3.35	0.05	48.74	3.77	0.88	-0.36	0.05
156	16.53	-0.04	3.37	0.06	35.94	4.91	4.32	0.72	0.31
158	17.63	0.00	2.74	0.03	26.56	3.32	1.49	0.70	0.09
159	18.18	0.00	2.46	0.02	27.28	3.06	10.14	-0.07	0.48
170	14.55	-0.07	3.92	0.07	30.46	4.72	8.23	0.02	0.75
175	17.28	0.00	2.39	0.01	39.31	4.51	0.89	-0.06	0.06
188	10.27	-8.64	1.17	0.23	54.23	4.12	1.54	-0.57	0.54
197	15.18	-1.41	4.15	0.41	26.42	4.81	4.98	2.48	8.70
198	15.73	-0.02	3.94	0.06	25.27	4.12	11.74	-0.81	0.72
200	16.83	-0.01	3.78	0.03	22.20	4.27	1.22	0.80	0.18
201	17.38	-0.06	3.51	0.04	19.06	3.81	6.59	-0.72	0.53
202	17.93	0.00	2.87	0.02	21.68	3.90	2.21	-0.15	0.13
217	14.83	-2.68	3.22	0.67	27.97	3.92	2.81	2.37	1.36
218	15.38	-3.71	2.50	0.55	29.79	3.50	5.50	2.40	2.51
220	16.48	0.00	2.39	0.03	22.83	3.59	3.34	0.12	0.10
221	17.02	-2.50	2.58	0.43	20.68	3.78	1.95	-0.43	1.18
222	17.85	-0.18	2.40	0.07	24.64	4.33	4.81	-1.86	0.43
223	18.40	0.00	1.91	0.02	26.19	3.69	13.17	-0.47	0.50
243	10.98	-4.81	2.30	0.64	68.34	4.70	1.70	1.12	0.78
245	12.07	-5.18	1.87	0.56	76.92	4.22	0.12	-0.40	0.31
251	15.98	-0.01	3.35	0.08	48.35	3.94	0.94	0.34	0.06
252	16.52	-0.01	3.46	0.06	45.37	4.98	4.70	-0.73	0.26
256	18.97	-0.50	2.26	0.06	28.69	4.80	5.70	-1.31	0.87
281	18.58	-0.03	2.87	0.05	40.23	4.06	4.13	-0.28	0.25
304	13.68	-2.90	3.20	0.82	47.40	4.69	2.60	-3.30	1.32
312	18.45	-0.01	2.47	0.04	38.25	4.72	1.20	0.66	0.08
334	13.18	-2.64	3.46	0.82	42.34	4.27	4.25	-2.28	2.18
336	14.28	-0.05	2.96	0.07	48.39	4.43	3.65	0.75	0.20
340	16.85	-0.20	3.46	0.11	35.99	4.99	1.25	-1.99	0.22
341	17.40	0.00	2.84	0.05	29.31	4.33	0.06	-0.52	0.09
342	17.95	0.00	2.62	0.04	28.21	3.85	0.39	0.57	0.08
366	12.23	-0.10	3.24	0.11	39.25	3.90	7.91	-1.04	0.56
367	12.78	-2.15	3.64	0.83	40.21	4.35	5.34	-1.02	2.71
375	17.48	0.00	2.36	0.04	33.17	3.48	2.80	0.00	0.10
376	18.03	-0.04	2.29	0.05	34.47	3.84	1.70	0.49	0.09
377	18.57	0.00	2.23	0.03	38.35	4.76	0.05	0.53	0.07
385	8.15	-10.56	1.02	0.28	18.02	2.86	1.44	-3.09	0.71
av		-1.27	2.92	0.21	36.04	4.16	3.66	-0.29	0.95
sd		2.41	0.70	0.29	11.43	0.48	3.74	1.34	2.55
mn		-10.56	1.02	0.01	18.02	2.86	0.04	-4.20	0.05
mx		0.00	4.15	1.37	76.92	4.99	21.17	2.55	18.87

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	0.63	1.00							
hws2m	-0.06	0.42	1.00						
wbar+2	-0.49	-0.68	0.07	1.00					
gas2g	-0.42	-0.26	-0.17	0.28	1.00				
mxsdgs	0.06	0.20	0.27	0.00	0.35	1.00			
vgas+2	0.24	0.23	0.00	-0.20	-0.26	0.04	1.00		
vd+2	0.25	0.35	0.04	-0.28	0.03	0.00	-0.03	1.00	
unvd+2	-0.12	-0.07	0.27	0.19	-0.14	0.05	-0.04	-0.09	1.00

Table 6-3(b)

SELECTED NO_x NIGHTTIME DATA: 30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas.nimsl = nox 53

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
29	19.07	0.00	1.80	0.01	37.15	5.00	5.42	-0.18	0.15
86	0.35	2.94	0.97	0.00	20.70	3.69	5.67	0.00	0.00
108	20.48	0.00	1.24	0.01	24.68	4.90	10.71	-0.56	0.30
126	20.08	0.00	1.21	0.00	26.81	4.75	10.46	0.54	0.34
127	20.63	0.00	1.81	0.01	21.25	3.06	3.96	-0.34	0.12
161	19.27	0.31	2.18	0.00	26.21	3.41	8.75	0.03	0.05
162	20.35	0.04	1.66	0.00	25.27	3.49	3.09	0.29	0.07
163	20.90	0.71	0.86	0.00	34.04	4.17	2.27	0.02	0.00
178	19.10	0.34	1.96	0.00	27.40	4.38	4.35	-0.05	0.02
182	21.28	0.09	0.97	-0.01	48.10	4.13	3.13	0.14	0.05
185	0.02	275.16	0.69	0.00	31.82	4.38	1.61	0.00	0.00
225	19.48	0.00	1.52	0.01	22.19	3.48	1.74	-0.03	0.07
226	20.03	0.00	1.77	0.02	22.03	4.16	5.94	-0.09	0.20
227	20.58	0.00	1.73	0.02	20.69	3.45	1.17	-0.04	0.07
228	21.13	0.00	1.41	0.02	19.88	3.70	6.84	-0.08	0.16
229	21.67	0.00	1.35	0.01	19.93	3.41	0.00	-0.04	0.05
230	22.22	0.00	0.85	0.01	22.05	3.61	0.94	0.31	0.03
233	23.87	-0.09	1.34	0.02	21.97	3.70	2.34	0.10	0.08
236	1.50	-13.87	0.65	0.19	18.41	3.52	3.02	-0.65	0.84
257	19.52	0.00	2.36	0.02	26.16	4.92	4.33	-0.48	0.18
262	22.25	-3.17	1.29	0.16	36.14	4.32	2.38	-0.04	0.60
263	22.80	-5.14	1.32	0.20	34.58	4.14	4.87	-1.19	1.41
264	23.33	-6.78	1.05	0.25	40.91	4.09	4.71	0.37	1.50
265	23.88	-10.09	1.00	0.26	40.04	3.60	1.13	-0.03	0.40
267	0.98	-13.45	0.78	0.15	38.40	4.00	1.99	-0.16	0.56
282	19.13	-0.02	2.75	0.04	38.85	4.62	3.81	-0.09	0.21
285	20.78	0.00	1.74	0.02	27.69	3.91	2.78	0.14	0.08
287	21.87	-4.30	1.16	0.18	47.44	4.51	2.85	1.00	0.80
290	23.50	-11.93	0.97	0.25	43.48	3.73	2.69	1.18	0.82
291	0.05	-14.70	0.81	0.21	48.00	4.12	2.43	-0.67	0.62
292	0.60	-17.16	0.78	0.12	51.44	3.51	0.03	0.15	0.20
294	1.70	0.00	0.85	0.01	46.27	3.69	0.27	0.02	0.01
297	3.33	-8.48	1.12	0.28	65.64	4.05	0.77	0.11	0.28
298	3.88	-13.49	0.66	0.16	69.20	3.58	1.45	-0.12	0.42
317	21.18	0.00	1.88	0.02	31.45	4.06	4.65	0.07	0.17
318	21.73	0.00	1.35	0.01	31.00	4.13	1.34	-0.04	0.04
319	22.28	-4.17	1.35	0.26	31.87	4.62	2.52	0.67	0.85
320	22.82	0.00	0.79	0.01	30.91	4.62	1.30	-0.20	0.03
321	23.92	-13.85	0.71	0.21	45.56	3.68	0.72	0.00	0.33
345	19.58	0.00	2.01	0.01	30.85	4.96	5.50	0.63	0.21
346	20.13	0.00	1.86	0.01	26.69	4.27	9.21	0.34	0.29
347	20.68	0.00	1.51	0.01	26.33	4.96	2.98	-0.37	0.07
351	22.87	0.00	1.49	0.01	37.31	3.60	10.11	-0.47	0.27
352	23.42	0.00	1.54	0.01	32.85	3.50	9.75	0.20	0.23
353	23.95	0.00	1.07	0.01	37.75	4.33	2.97	-0.13	0.06
354	0.50	0.00	1.58	0.01	23.56	3.09	1.74	0.02	0.05
355	1.05	-3.81	1.40	0.12	27.96	3.34	0.80	0.60	0.48
361	4.33	-6.44	1.14	0.11	51.86	4.45	0.88	-0.73	0.34
362	4.87	0.00	0.87	0.01	55.59	3.78	0.50	0.01	0.01
378	19.12	0.00	2.05	0.02	33.41	3.40	4.99	0.13	0.18
380	20.22	0.00	1.85	0.02	27.27	3.91	1.91	-0.36	0.07
381	20.77	0.00	1.62	0.02	25.71	4.38	4.06	0.01	0.12
382	21.30	-6.00	1.07	0.18	28.20	3.96	4.13	0.28	1.27
av		2.31	1.35	0.07	33.60	4.00	3.55	0.00	0.30
sd		38.54	0.48	0.09	11.63	0.51	2.81	0.41	0.36
mn		-17.16	0.65	-0.01	18.41	3.06	0.00	-1.19	0.00
mx		275.16	2.75	0.28	69.20	5.00	10.71	1.18	1.50

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	-0.21	1.00							
hws2m	0.39	-0.12	1.00						
wbar+2	-0.14	-0.21	-0.42	1.00					
gas2g	-0.34	-0.09	-0.41	0.49	1.00				
mxsdgs	0.22	0.12	0.15	-0.04	0.08	1.00			
vgas+2	0.34	-0.05	0.39	-0.30	-0.32	0.23	1.00		
vd+2	0.17	0.00	-0.01	0.12	0.06	-0.05	-0.03	1.00	
unvd+2	0.06	-0.19	-0.24	0.78	0.19	0.08	0.07	0.06	1.00

Table 6-4(a)

SELECTED HNO_3 DAYTIME DATA: 30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas.nimsl = hno3 39

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
222	17.85	-0.18	2.40	0.07	5.33	1.01	3.71	-2.85	0.34
223	18.40	0.00	1.91	0.02	5.23	1.39	11.17	-0.68	0.43
224	18.93	0.00	1.87	0.01	4.04	1.15	9.91	0.18	0.36
244	11.53	0.00	2.00	0.03	3.28	1.01	10.04	-0.76	0.25
245	12.07	-5.18	1.87	0.56	4.13	2.28	0.98	-6.97	3.08
246	12.62	0.00	2.32	0.04	3.60	0.93	10.95	-0.25	0.31
247	13.17	-3.36	2.73	0.70	4.80	1.58	0.40	11.26	2.16
248	13.72	-0.01	3.50	0.08	3.85	0.87	5.04	1.11	0.25
251	15.98	-0.01	3.35	0.08	3.43	1.31	3.57	0.77	0.20
252	16.52	-0.01	3.46	0.06	4.27	1.18	4.21	-0.61	0.23
253	17.07	0.00	3.30	0.04	3.80	1.26	2.39	1.00	0.22
302	12.58	-6.75	1.74	0.49	4.18	1.14	5.17	-11.45	2.41
303	13.13	-2.64	3.29	0.68	5.43	1.65	7.05	-6.78	3.49
304	13.68	-2.90	3.20	0.82	3.55	0.99	17.10	2.83	8.64
305	14.23	-0.03	3.06	0.07	4.75	1.49	4.56	-1.60	0.22
306	14.78	-3.07	3.15	0.56	3.42	1.07	0.90	11.44	1.77
311	17.90	-0.02	2.65	0.05	4.18	1.00	3.24	0.08	0.15
312	18.45	-0.01	2.47	0.04	4.61	1.28	1.05	-0.96	0.14
329	8.82	-11.75	0.80	0.26	4.12	1.26	0.33	-14.06	2.15
330	9.35	-8.32	1.52	0.34	4.49	1.00	7.45	-5.71	2.68
331	11.55	-3.55	2.63	0.63	5.18	1.07	9.67	5.49	4.65
334	13.18	-2.64	3.46	0.82	4.94	1.48	11.32	0.99	5.81
335	13.73	-2.72	3.23	0.80	4.47	0.99	12.38	-5.49	6.36
336	14.28	-0.05	2.96	0.07	5.02	1.34	2.98	-1.78	0.21
337	14.83	-2.36	3.27	0.61	3.51	1.03	8.69	-1.31	4.17
339	16.30	-0.08	3.18	0.08	4.23	0.93	12.67	-1.18	0.91
340	16.85	-0.20	3.46	0.11	3.84	1.14	2.08	-2.49	0.44
341	17.40	0.00	2.84	0.05	4.11	1.03	9.12	0.01	0.44
343	18.48	-0.02	2.41	0.05	4.65	1.11	13.55	0.51	0.73
363	5.42	0.00	1.01	0.01	5.21	0.91	8.08	0.06	0.13
364	10.60	-6.78	2.51	0.49	4.56	1.91	8.49	2.45	3.27
365	11.15	-7.79	1.38	0.41	3.55	0.94	7.48	-2.55	2.58
366	12.23	-0.10	3.24	0.11	4.74	0.99	2.40	1.31	0.22
367	12.78	-2.15	3.64	0.83	5.51	1.39	4.76	-0.55	2.41
368	13.33	-1.96	3.74	0.85	3.19	0.99	5.91	4.68	3.02
369	13.88	-0.09	3.74	0.14	4.69	1.70	4.68	-1.67	0.39
375	17.48	0.00	2.36	0.04	4.08	1.10	8.80	-0.68	0.31
376	18.03	-0.04	2.29	0.05	4.19	0.96	0.39	-2.01	0.15
377	18.57	0.00	2.23	0.03	3.98	0.97	2.86	-1.07	0.13
av		-1.92	2.67	0.29	4.31	1.20	6.30	-0.75	1.69
sd		2.90	0.77	0.30	0.64	0.30	4.25	4.69	2.05
mn		-11.75	0.80	0.01	3.19	0.87	0.33	-14.06	0.13
mx		0.00	3.74	0.85	5.51	2.28	17 10	11.44	8.64

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	0.60	1.00							
hws2m	0.32	0.46	1.00						
wbar+2	-0.40	-0.51	0.27	1.00					
gas2g	-0.10	0.05	-0.04	0.05	1.00				
mxsdgs	-0.12	-0.23	0.08	0.26	0.33	1.00			
vgas+2	-0.05	0.07	0.00	0.18	-0.01	-0.25	1.00		
vd+2	0.16	0.39	0.42	0.13	-0.11	-0.10	0.05	1.00	
unvd+2	-0.35	-0.50	0.15	0.87	0.00	0.13	0.46	0.00	1.00

Table 6-4(b)

SELECTED HNO_3 NIGHTTIME DATA: 30 MINUTE RECORDS, AND CORRELATION MATRIX

SECOND PASS - SELECTED DATA EXCLUDING OUTLIERS

gas.nimsl = hno3 29

rec	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
225	19.48	0.00	1.52	0.01	4.22	1.07	4.39	-0.72	0.14
226	20.03	0.00	1.77	0.02	3.91	0.88	21.50	1.43	0.76
227	20.58	0.00	1.73	0.02	3.61	1.51	5.64	0.50	0.18
228	21.13	0.00	1.41	0.02	3.58	1.08	3.12	-0.93	0.10
229	21.67	0.00	1.35	0.01	3.56	0.85	1.68	-0.54	0.07
230	22.22	0.00	0.85	0.01	3.59	1.14	4.37	0.14	0.06
234	0.40	-12.19	0.87	0.20	3.40	0.75	11.35	-7.78	3.46
313	19.00	-0.02	2.31	0.03	4.67	1.18	7.76	-2.18	0.34
314	19.55	-0.76	2.14	0.12	4.20	1.32	12.11	-3.74	2.43
315	20.10	0.00	1.59	0.02	4.06	0.88	12.14	0.81	0.42
316	20.63	0.00	1.84	0.02	3.17	0.99	6.04	0.08	0.22
317	21.18	0.00	1.88	0.02	3.49	1.21	10.71	-0.49	0.40
318	21.73	0.00	1.35	0.01	4.33	0.83	3.69	0.01	0.07
320	22.82	0.00	0.79	0.01	3.93	1.08	4.80	-0.30	0.07
321	23.92	-13.85	0.71	0.21	4.21	1.12	6.72	6.67	1.93
344	19.03	0.00	2.22	0.02	3.64	1.64	21.38	0.80	0.91
345	19.58	0.00	2.01	0.01	3.72	1.01	6.55	1.23	0.26
346	20.13	0.00	1.86	0.01	4.28	0.99	7.24	0.86	0.24
347	20.68	0.00	1.51	0.01	4.40	1.03	8.84	-1.00	0.23
348	21.22	0.00	1.30	0.01	3.89	1.41	1.41	0.21	0.06
349	21.77	0.00	1.47	0.01	3.36	0.96	7.64	-0.45	0.22
356	1.60	-4.32	1.72	0.13	3.69	1.14	0.11	3.08	1.11
361	4.33	-6.44	1.14	0.11	3.61	1.19	4.58	6.82	1.43
362	4.87	0.00	0.87	0.01	4.02	1.04	8.36	0.15	0.11
378	19.12	0.00	2.05	0.02	4.35	0.93	2.41	0.57	0.09
380	20.22	0.00	1.85	0.02	3.78	1.06	5.10	0.35	0.17
381	20.77	0.00	1.62	0.02	4.33	0.91	1.63	-0.18	0.08
382	21.30	-6.00	1.07	0.18	3.34	0.99	11.27	-6.11	3.51
383	21.85	-12.08	0.64	0.17	3.23	0.99	4.87	-2.09	1.43
av		-1.92	1.50	0.05	3.85	1.07	7.15	-0.10	0.71
sd		4.12	0.48	0.07	0.40	0.20	5.16	2.87	0.98
mn		-13.85	0.64	0.01	3.17	0.75	0.11	-7.78	0.06
mx		0.00	2.31	0.21	4.67	1.64	21.50	6.82	3.51

	hour	stab	hws2m	wbar+2	gas2g	mxsdgs	vgas+2	vd+2	unvd+2
hour	1.00								
stab	0.32	1.00							
hws2m	0.14	0.59	1.00						
wbar+2	-0.36	-0.92	-0.44	1.00					
gas2g	0.14	0.28	0.30	-0.26	1.00				
mxsdgs	0.08	0.16	0.29	-0.08	-0.04	1.00			
vgas+2	0.02	0.00	0.26	0.06	-0.06	0.16	1.00		
vd+2	-0.01	0.01	0.02	-0.13	0.17	0.22	-0.19	1.00	
unvd+2	-0.36	-0.74	-0.27	0.89	-0.28	-0.05	0.35	-0.39	1.00

of uncertainty other than the measurement uncertainty, or other environmental causes may also influence the variability of V_d.

Though the average daytime and nighttime V_d are different, they vary substantially and it cannot be said that there is a significant (i.e., greater than one sigma) difference between the day and nighttime V_d estimates. Factors other than time of day apparently influence the deposition velocity. The best summary of the situation seems to be as follows:

- The gas measurement propagated precision is sufficiently low to determine non-measurement causes of variability in V_d.
- The nighttime SO_2 V_d's tend toward larger positive values than the daytime data, but the difference is only marginally significant, i.e., the difference between the two averages is nearly equal to the estimated precision of the measurement. There is very much less evidence for significant day/night V_d differences for the other species (NO, NO_x, HNO_3), although in every case the nighttime V_d exceeds the daytime value by a small amount.

The HNO_3 data, based on very low ambient HNO_3 concentrations, showed an average V_d of -0.8 cm/s for daytime, and -0.1 cm/s for nighttime cases. The average "unvd" were 1.7 cm/s for daytime and 0.7 cm/s for nighttime cases, while the standard deviation of the V_d estimates ranged from about 3 to about 5 cm/s. These V_d values are at odds with the common belief that HNO_3 is effectively absorbed at almost any surface (Businger, 1986a). Results could be due to the difficulty in measuring HNO_3. However, Myers (1987), reporting recent work performed at Oak Ridge National Laboratory, also found near-zero values in measurements of the HNO_3 deposition velocity. So little is known about the origins, properties and measurement of HNO_3 at this time that a zero deposition velocity, under certain circumstances, is plausible.

Table 6-5 summarizes all the V_d estimates, by species and time, and the associated unvd estimates. Downward-directed V_d's carry a positive (+) sign.

6.4.2 Comparison to Results of Other Measurement Programs

For comparison, Table 6-6 shows V_d estimates obtained in this work and by selected other studies, for grass surfaces. The current results are comparable, except for daytime SO_2, and daytime and nighttime HNO_3 results. The SO_2, NO, and NO_x V_d estimates have not been corrected for the 10% to 20% positive biases reported in Table 5-4, as that correction is second-order with respect to other measurement uncertainties.

6.4.3 Correlations

Tables 6-1 through 6-4 also show correlations among parameter pairs. Correlation coefficients greater than 0.7 are summarized in Table 6-7. Of these seven pairs, four concern $\overline{w}$ vs. unvd. The $\overline{w}$ vs. unvd correlation seems plausible on the grounds that the final estimate of V_d is obtained by subtraction from an initial estimate; therefore uncertainty in $\overline{w}$ enters directly into V_d uncertainty, and the w uncertainty is proportional to the magnitude of $\overline{w}$. The remaining three cases involve several types of situations. As would be expected, stability is negatively correlated with $\overline{w}$ for nighttime HNO_3. The same relationship is found for other gases, though the correlation coefficient is less then 0.7. The unvd estimate is correlated to the gas profile goodness-of-fit parameter, vgas, for nighttime SO_2, and is negatively correlated with stability for nighttime HNO_3. The significance of these isolated correlations is not clear.

Table 6-5

Estimates of Deposition Velocities and Propagated Measurement Uncertainties, Based on Data from CSUDH Field Site, 5/86 - 6/86

Gas	Estimated V_d (cm/s) 1) Day 2) Night		Average Propagated Uncertainty, unvd (cm/s)
SO_2	1) -2.1	+-	1.8
	2) 2.6	+-	1.2
$SO_4^=$	Data Considered Invalid		
NO	1) -0.2	+-	3.3
	2) 0.3	+-	0.15*
NO_x	1) -0.3	+-	1.0
	2) 0.0	+-	0.3
HNO_3	1) -0.8	+-	1.7
	2) -0.1	+-	0.7

*one 30-minute record only

Table 6-6

Estimates of V_d for SO_2, NO, NO_x, and HNO_3, in this and Other Studies

SO_2	NO	NO_x	HNO_3	Author(s)
+2.6 cm/s (night)	+0.3 cm/s (night)	0.0 cm/s (night)	-0.1 cm/s (night)	This study
-2.1 cm/s (day)	-0.2 cm/s (day)	-0.3 cm/s (day)	-0.8 cm/s (day)	This study
0.2 - 3.0 cm/s				Sehmel (1980) (review of 12 studies)
2.1 cm/s				Dolske and Gatz (1985)
			2.5 cm/s	Huebert and Robert (1985)
		0.1 - 0.6 cm/s		Delaney and Davies (1983)
	+0.03 cm/s (night)			Sisterson, et al. (1987)
	-0.17 cm/s (day)			Sisterson et al. (1987)

Table 6-7

Variable Pairs with Correlation Coefficients Greater than 0.7

DAYTIME CASES

Gas	Variable 1	with	Variable 2	Correlation
NO	$\bar{w}$		unvd	0.89
HNO_3	$\bar{w}$		unvd	0.87

NIGHTTIME CASES

Gas	Variable 1	with	Variable 2	Correlation
SO_2	vgas		unvd	0.87
NO_x	$\bar{w}$		unvd	0.78
HNO_3	$\bar{w}$		unvd	0.89
HNO_3	Stability		$\bar{w}$	-0.92
HNO_3	Stability		unvd	-0.74

6.4.4 Effect of Exclusion of Outliers

Following the four data selection criteria discussed in Section 6.2, the V_d average and standard deviations, based on the surviving records, were calculated. Outlier records, defined as those for which V_d exceeded ± 3 standard deviations, were then excluded by a looping computation that stopped when no more outliers remained. Records were not excluded based on unvd. Exclusion of cases where unvd exceeded $\pm$ 3 standard deviations would be unlikely to have an effect on the V_d estimates; however, it would act to reduce their overall uncertainty. In a few cases, exclusion of outliers had a significant effect on the V_d estimates. In the following cases, the V_d estimates before and after exclusion of outliers differed by more than the uncertainty (unvd) of the final V_d estimate.

Gas	V_d before outlier exclusion	V_d after outlier exclusion
SO_2 (night)	6.2 cm/s	2.6 cm/s
NO_x (night)	0.4 cm/s	0.0 cm/s
HNO_3 (night)	-1.5 cm/s	-0.1 cm/s
HNO_3 (day)	-4.0 cm/s	-0.8 cm/s

The conclusions of this report are based on the estimates after exclusion of outliers; it may be that an even more stringent outlier exclusion rule could, with justification, be followed because the ± 3 σ limits exclude only a few percent of a normal distribution.

7.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

In the South Coast Air Basin (SoCAB) of California, the transport of acidic and acid precursor species to the surface by dry deposition processes may dominate over transport by wet processes. A three week measurement program designed to quantify the dry deposition of SO_2, NO, NO_x, and HNO_3 gases, and sulfate aerosol, was conducted at a field site on the campus of California State University, Dominguez Hills, near Carson, CA. The program design included detailed attention to data validation and the estimation of measurement precision.

The field site was selected after examination of twelve options in the highly urbanized SoCAB. A flat field offering 350 m of fetch on the E-W axis, covered with closely mown grass, was selected. The measurement approach was adjusted to be appropriate to the available fetch distance.

After consideration of three options, the gradient, or profile, method was chosen as offering the best approach to estimation of the rate of transport to the surface of the five species studied. The gradient method allows estimation of the species deposition velocities, based on careful measurement of their gradients on a 5 m tower. The acidic species were measured at three levels on the tower, together with three-axis wind measurements, temperature and dewpoint. The measurement precision of species concentrations was required to be 1 ppb or less, and this precision was shown to be achieved in the field program, as measured by the standard errors of 30-minute averages of the SO_2, NO, and NO_x concentrations. The precision is more difficult to quantify in the case of the HNO_3 measurement, where the response times of the two-channel measurement method may have differed. The sulfate aerosol data always indicated very low concentrations, and was attributed to aerosol particle losses in the sampling tubing. Therefore, while the field program experience indicated that confidence in the SO_2, NO, and NO_x measurements was generally justified, it also indicated the need for specific improvements in the HNO_3 and sulfate aerosol measurement methods.

The SO_2, NO, NO_x, and HNO_3 data were screened according to selection criteria including elimination of sampling periods when interfering activities took place, elimination of wind directions outside the acceptable fetch sector, selection of species concentrations above minimum thresholds, selection of "stationary" conditions as defined by species standard deviations less than maximum thresholds, and elimination of cases where wind speeds were below the proper operating thresholds of the anemometers. Outliers exceeding $\pm 3\ \sigma$ were also eliminated.

The data were stratified according to day/night sampling periods, but only the SO_2 deposition velocities showed a difference approaching a significant value. The average nighttime SO_2 deposition velocity exceeded the daytime value, and it is speculated that this effect may be due to reduction of surface resistance by surface moisture (dew). Table 7-1 summarizes the estimated deposition velocities and their uncertainties.

These deposition velocity estimates are similar to published values for the same species with the exception of the low HNO_3 values and the negative daytime SO_2 value. Published data rarely indicate that the HNO_3 deposition velocity is as low as zero and usually this species is thought to deposit very effectively, "sticking" to almost any surface. Inadequacies of the HNO_3 measurement method may explain this anomalous result although Myers (1987) has also reported a near zero value for the HNO_3 V_d.

Table 7-1

Summary of Estimated Deposition Velocities and their Uncertainties

Specie	Estimated Deposition Velocity (cm/s)		Propagated Uncertainty (cm/s)
SO_2 (day)	-2.1	+-	1.8
SO_2 (night)	2.6	+-	1.2
NO (day)	-0.2	+-	3.3
NO (night)	0.3	+-	0.1
NO_x (day)	-0.3	+-	1.0
NO_x (night)	0.0	+-	0.3
HNO_3 (day)	-0.8	+-	1.7
HNO_3 (night)	-0.1	+-	0.7

Recommendations for future work include:

- The present approach included only short periods of continuous monitoring of any species at one level. In a future program, provision for more continuous monitoring would allow discovery of whether or not fluctuations were occuring on a shorter time scale than the sampling and averaging time for each level.

- Although the horizontal wind speeds usually conformed to the expected logarithmic profiles, the 1.25 meter (lowest) sampling level may have been too close to the surface; it should be raised in future experiments. Fetch requirements may always be a limiting factor, however.

- The anemometer data acquisition rate was hardware-limited to 1 Hz; in future efforts, 2 to 5 Hz is desirable.

- The proximity of the instrument trailer to the instrumented tower resulted in part from the requirement of minimizing the gas specie travel times. This distance should be increased in future studies if at all possible.

- Separate, electrically-conducting tubing with enhanced flows should be employed for sulfate aerosol measurements in the future; this would most likely reduce aerosol particle losses to acceptable levels.

- The two-channel HNO_3 detection system (modified Monitor Labs 8440 analyzer) needs to be improved, to attain both static and dynamic balance of the two channels. A field HNO_3 calibration standard also needs to be developed for field performance checks.

- The current data base should be re-analyzed to determine the optimal averaging time for which the uncertainty due to non-stationary conditions equals the uncertainty due to instrument repeatability. Non-stationarity is the major contributor to the standard error of the 30 minute averages, <u>not</u> the instrument repeatability.

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APPENDIX A

APPENDIX A:

This appendix discusses measurement averages and quantities derived from measurement averages at each of three sampling levels. It also addresses the uncertainties associated with these averages and derived quantities. For notational convenience the uncertainty associated with a quantity X will be denoted as δX, and the subscript i, $i=1,2,3$ will refer to level i. These levels are located at 1.25, 2.50, and 5.00 meters above ground level, respectively, for temperature, dew point temperature and gas concentrations averages. The corresponding elevations are 0.89, 2.13, and 4.60 meters above ground level respectively, for the horizontal wind speed averages. (The geometry of the Gill anemometers located the horizontal wind velocity sensors approximately 0.40 m below the vertical velocity sensors).

The h_u and h_v, the horizontal wind speed averages in the u and v directions, are adjusted for the non-cosine response of the Gill anemometers, using the average and standard deviation of the wind direction over the sampling period (Horst, 1973). This adjustment assumes a normal distribution of measurements over the averaging period. The averages are then reduced by a factor of 10% to correct for overspeeding (Businger et al., 1971).

An uncertainty is associated with each average measurement. This uncertainty is taken to be the standard deviation of the values included in the average divided by the square root of the number of values in the average. This statistic is an estimate of the standard error of the average or the standard deviation of a sequence of averages. Since this uncertainty reflects random errors involved in the measurement process as well as changes in ambient conditions over the averaging period, it is conservative in that it should be greater than or equal to the uncertainty observed under stationary or laboratory conditions.

Average horizontal wind speed and the uncertainties associated with them

Average horizontal wind speed and the uncertainties associated with them are given by

$$h_s = \left\{ h_u^2 + h_v^2 \right\}^{1/2}, \tag{A-1}$$

and

$$\delta h_s = \left[(h_u \; \delta h_u)^2 + (h_v \; \delta h_v)^2 \right]^{1/2} / h_s \, . \tag{A-2}$$

These horizontal wind speed averages are fitted to the profiles given in Businger et al., (1971) in the following manner. Under neutral conditions the horizontal wind speed profile is given by

$$\text{grad } (h_s) = u^*/(kz), \tag{A-3}$$

where u* is the friction velocity and k is von Karman's constant. This is the well known logarithmic profile; for this profile a quantity measured at level 2 will be the arithmetic mean of the quantities measured at levels 1 and 3. Furthermore, the slope of the profile at level 2 is given by the slope of the line connecting the points on the profile at levels 1 and 3.

For non-neutral conditions Equation A-3 is modified to

$$\text{grad } (h_s) = \phi_m \, u^*/(hz), \tag{A-4}$$

where ϕ_m is an empirically derived function of the stability, ζ, which is defined as

$$\zeta = z/L, \tag{A-5}$$

where L is the Obukov-Monin length. Integration of (A-4) gives

$$h_s = h_{s1} + \frac{u^*}{k} \int_{z_1}^{z_2} (\phi_m/z)\,dz, \tag{A-6}$$

where h_{s1} is the horizontal wind speed at level 1. Equation (A-6) is fitted to the horizontal wind speed averages by adjusting h_{s1}, u*, and L by a non-linear least squares fitting algorithm. This fit gives fitted horizontal wind speeds h'_{s1}, h'_{s2}, and h'_{s3}. The associated uncertainties are

$$\delta h'_s = \max(\delta h_s, | h_s - h'_s |). \tag{A-7}$$

For the gradient of the horizontal wind speed Equation (A-4) is evaluated at $z = 2.5$ meters with its associated uncertainty.

$$\delta h'_s = \left[(h'_{s1} \ \ \delta h'_{s1})^2 + (h'_{s3} \ \ \delta h'_{s3})^2 \right]^{1/2} / h'_s. \tag{A-8}$$

Equation (A-8), which is exact for neutral stability, avoids the need to differentiate the empirical function ϕ_m. Extrapolation of the fitted curve to $h_s = 0$ gives the roughness length z_0. The goodness of fit is described by

$$V_m = \Sigma_{i=1,3} \left[(h_{si} - h'_{si})^2 \right]^{1/2} / h'_{s2}. \tag{A-9}$$

The Obukov-Monin length, L, obtained above gives the Richardson's number, R_i, via an empirical function given in Businger et al., (1971). The eddy diffusivities for momentum and heat, K_m and K_h, with associated uncertainties are

$$K_m = k^2 z^2 \text{grad } (h'_s)/\phi_m{}^2, \tag{A-10}$$

$$K_h = \phi_m K_m / \phi_h, \tag{A-11}$$

$$\delta K_m = k^2 z^2 \delta \text{ grad } (h'_s)/\phi_m^2 , \tag{A-12}$$

and

$$\delta K_h = \phi_m \ \ \delta K_m / \phi_h. \tag{A-13}$$

A similar fitting procedure can be applied to the temperature data to obtain fitted temperatures, T_1', T_2', and T_3', and uncertainties along with gradients given by

$$\text{grad}\ (T) = \phi_h T^*/(kz)$$

where ϕ_h is another empirical function given in Businger et al, (1971) and T^* is the scaling temperature. A goodness of fit measure is given by

$$V_t = \Sigma_{i=1,3} \left[(t_i - t_i')^2 \right]^{1/2} / t_2' \qquad \text{(A-15)}$$

This procedure differs from that used with the horizontal wind speeds only in that the Obukov-Monin length is set at that obtained from the horizontal wind speed fit. Since the horizontal wind speed data has the best fit to the theory, this was felt to be appropriate.

Dew point temperatures are converted to humidity mixing ratios, q, using

$$q = (M_w/M_a)\ (p_v/p), \qquad \text{(A-16)}$$

where M_w and M_a are the molecular weights of water vapor and air molecules, respectively, p_v is the ambient water vapor pressure, and p is the total ambient pressure. P_v is determined from the dew point temperature using an empirical formula from Pruppacher and Klett, (1978) p. 625. In this experiment equation (A-16) was applied to levels 1 and 3 only since the level 2 dew point meter malfunctioned over the course of the experiment. An uncertainty is associated with q for each level through use of

$$\delta q = (q/p_v)\ (dp_v/dT_d)\ \delta T_d. \qquad \text{(A-17)}$$

Since level 2 dew point temperatures were missing in this experiment, the data are not fitted to the theory. The gradient of q, grad (q) is defined as

$$\mathrm{grad}(q) = (q_3 - q_1)/(z_3 - z_1), \tag{A-18}$$

where z_1 and z_3 denote the height above ground for levels 1 and 3 respectively. The uncertainty associated with the gradient of q is given by

$$\delta\ \mathrm{grad}(q) = \left[\delta q_1^2 + \delta q_3^2 \right]^{1/2} / (z_3 - z_1), \tag{A-19}$$

As mentioned above, for the logarithmic profile Equation (A-18) gives grad (q) at level 2. Heat and moisture fluxes Q_h and Q_e with associated uncertainties are

$$Q_h = -\rho C_p K_h\ \mathrm{grad}\ (T), \tag{A-20}$$

and

$$Q_e = -\rho\ F_l\ K_h\ \mathrm{grad}\ (q), \tag{A-21}$$

where ρ is the density of air, $C\rho$ is the heat capacity of air at constant pressure, and F_l is the latent heat of vaporization of water. These fluxes are then used to calculate $\overline{w}$, the average vertical velocity due to the heat and moisture fluxes (Businger, 1986) as well as its associated uncertainty,

$$\begin{aligned} \overline{w} = {} & (M_a Q_e)/(M_w\ \rho F_l) \\ & + (1 + M_a q_m/M_w)\ Q_h/(\rho C_p T_2') \end{aligned} \tag{A-22}$$

and

$$\begin{aligned} \delta\overline{w} = {} & \left\{ \left[\delta Q_e/(\epsilon\ \rho F_l)\right]^2 + \left[\delta q Q_h/(\epsilon\ \rho C_p T_m')\right]^2 \right. \\ & + \left[\delta Q_h q_m/(\epsilon \rho C_p T_m') \right]^2 \\ & \left. + \left[(1 + q_m/\epsilon)\ \delta T Q_h / (\rho C_p T_m'^2) \right]^2 \right\}^{1/2}, \end{aligned} \tag{A-23}$$

where q_m denotes the humidity mixing ratio at level 2 and T_m denotes the fitted temperature at level 2 in degrees Kelvin. Since measurements of q at level 2 were available in this experiment, the arithmetic mean of q at levels 1 and 3 was calculated; as discussed previously, this is appropriate for a logarithmic profile.

The fitting procedure described for the temperature is applied to the average concentrations for each gas to obtain fitted concentrations g_1', and g_2' and g_3' uncertainties along with gradients given by

$$\mathrm{grad}(g) = \phi_h\, g^*/(hz), \tag{A-24}$$

where g* is a scaling concentration, and goodness of fit measure given by

$$v_g = \left[\Sigma_{i=1,3}\, (g_i - g_i')^2\right]^{1/2} / g_2'. \tag{A-25}$$

This analysis assumes that ϕh is appropriate in fitting the gas concentrations since they are scalar quantities, as is temperature. Gas fluxes and deposition velocities (Businger, 1986) with associated uncertainties are

$$Q_g = -K_h\, \mathrm{grad}\, (g), \tag{A-26}$$

$$\delta Q_g = -K_h\, \delta\, \mathrm{grad}\, (g), \tag{A-27}$$

$$V_d = -Q_g/g_2' - \bar{w}, \tag{A-28}$$

and

$$\delta v_d = \left[(\delta Q_g/g_2')^2 + (Q_g\, \delta q_2'/(g_2')^2)^2 + \delta\bar{w}^2\right]^{1/2}. \tag{A-29}$$

APPENDIX B

State of California **The Resources Agency**

Memorandum

To : John Kowalski, Manager
Environmental Laboratory Section

Date : July 24, 1986

Subject: Parallel HNO_3
Sampling with DRI
at Dominguez Hills

From : Jack Horrocks
Air Resources Engineering Associate
Air Resources Board

Introduction

As part of a Research Division-sponsored study, the Desert Research Institute (DRI) installed a temporary sampling site at Cal State University, Dominguez Hills, to assess the dry deposition of nitric acid (HNO_3) and sulfur dioxide (SO_2) at a site in the South Coast Air Basin. The site was chosen primarily for its availability and the nearly flat, smooth, open terrain in the immediate vicinity. The terrain allowed measurement of meteorological parameters and roughness factors needed in evaluating dry deposition by the gradient method. The Dominguez Hills area is characterized by high hydrocarbon concentrations caused by nearby oil-refining operations. Ambient measurements consisted of north-south, east-west and vertical wind speed/wind direction at three elevations, and continuous measurement of HNO_3 and SO_2 at the three elevations using a modified Monitor Labs NO/NOx analyzer, a Meloy SO_2 analyzer, and a switching system. The NO/NOx analyzer was modified to provide measurements of NOx and (NOx-HNO_3) by installing a second converter in what is normally the NO channel, and a 0.65u Nylasorb (nylon) filter in one channel (the NOx-HNO_3 channel) to remove nitric acid. A Teflon particulate prefilter was also installed at the sample inlet to the analyzer.

At the request of the Research Division, ELS staff installed a diffusion denuder at the site so that parallel measurements using independent sampling methods could be made. The diffusion denuder provided measurements of HNO_3 and fine particulate nitrate (NO_3^-). Samples were collected during five four-hour intervals between May 28 and May 30, 1986, at the mid-elevation level at a height 2.5 meters above the ground. For the data comparison, DRI provided integrated HNO_3 measurements for the five sampling periods.

No parallel SO_2 measurements were made.

Results and Discussion

A summary of the results appears in Table 1. Although the correlation between the data sets was good ($r = 0.85$), the DRI nitric acid measurements were all at least 100% higher than the corresponding ARB measurements. However, concentrations were low (13 to 56 n moles/m^3 based on ARB data) and the data set was quite limited ($n = 5$). The DRI and ARB measurements did tend to rise and fall together, as indicated by the positive regression slope ($m = 0.58$ when ARB measurements are plotted along the y-axis and DRI measurements are plotted along the x-axis).

Loss of particulate nitrate from inert Teflon prefilters producing positive errors in HNO_3 measurement has been documented.(1) Such loss of particulate nitrate can result from volatization of nitrate salts or by reaction of such salts with gaseous or particulate strong acids. Losses between 40% and 90% have been observed, depending on experimental conditions.

Loss of particulate nitrate to HNO_3 is to be expected with any continuous monitoring system using a Teflon prefilter such as the DRI system, and would result in a positive bias. The bias is, however, limited by the amount of particulate nitrate present. The DRI HNO_3 measurements can be modeled as:

$$HNO_3(DRI) = C\ (HNO_3 + V \times NO_3-) \qquad \text{(Eq. 1)}$$

Where:
C = calibration factor (assume $C=1$)
V = volatization factor ($0 \le V \le 1$)
HNO_3 = ambient nitric acid concentration, $nmoles/m^3$
NO_3- = ambient particulate nitrate concentration, $nmoles/m^3$

The ARB diffusion denuder measurements can be modeled as:

$$HNO_3\ (ARB) = HNO_3 \qquad \text{(Eq. 2)}$$

The ratio of HNO_3 measurements by the two systems is therefore equal to:

$$\frac{HNO_3(DRI)}{HNO_3(ARB)} = 1 + V \times \frac{NO_3-}{HNO_3} \qquad \text{(Eq. 3)}$$

If ambient concentrations of NO_3- and HNO_3 are known, the volatization factor can be determined from Eq. 3. In the following discussion it is assumed that the diffusion denuder measurements accurately represent NO_3- and HNO_3. Eq. 3 also indicates that the DRI HNO_3 measurements would be highest (relative to the ARB HNO_3 measurements) when the ratio NO_3-/HNO_3 is highest, and this was observed (see Table 1), indicating that factors associated with particulate nitrate levels are related to the observed differences between the two methods. Volatization factors V ranging between 400% and 1400% were observed for the five sample comparisons.

Volatization factors greater than 100% imply the presence of gaseous species which are removed by the Nylasorb filter in the DRI Monitor Labs ($NOx-HNO_3$) channel, and are reduced to nitric oxide (NO) in the NOx channel converter. The retention by the Nylasorb filter of gaseous species such as peroxyacetyl nitrate (PAN), ethyl nitrate, ethyl nitrite, and n-propyl nitrate, which are known to be reduced to NO in the converter(2), should be investigated if nitric acid measurements collected by the DRI method are used for research or other purposes.*

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* Nitroethane is not significantly reduced in molybdenum converters(2) and would not be an interferring compound with instruments using "moly" converters.

The negative intercept (b = -15.9 n moles/m^3) of the linear regression is comparable to concentration levels and could be the result of a systematic bias in either the ARB data (negative bias) or DRI data (positive bias). A negative ARB bias, for example, could be caused by HNO_3 losses in the Teflon cyclones. A positive DRI bias could be caused by a zero offset in one of the two Monitor Labs channels. In Figures 2 and 3 the regression curve is forced through the origin assuming a positive DRI bias (Figure 2) or, alternatively, a negative ARB bias (Figure 3). Table 2 indicates that even when the data are corrected for possible systematic bias, volatization factors greater then 200% still occurred in all cases.

Summary and Conclusions

The DRI method to measure HNO_3 at Dominguez Hills using a modified, continuous NO/NOx monitor consistently yielded results at least 100% higher than ARB measurements using the diffusion denuder method. The high results are likely due to loss of particulate nitrate to nitric acid on the Teflon prefilter of the DRI system and the presence of interfering gaseous species which are both removed by the Nylasorb filter in the (NOx-HNO_3) channel, and reduced to NO in the NOx channel converter. Such gaseous species could be PAN, ethyl nitrate, ethyl nitrite, n-propyl nitrate or other nitrogenous species. Significant quantities of interfering nitrogenous species may have been present during sampling at this site, which is characterized by high hydrocarbon levels. HNO_3 data collected using the continuous monitor method at Dominguez Hills should be used with care. Interferences are likely to be less a problem at other sites which experience more reasonable hydrocarbon levels.

Attachment

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Sample Number	Sample Period	ARB Diffusion Denuder			DRI		
		Particulate Nitrate (NO_3^-) n moles/m^3	Nitric Acid (HNO_3) n moles/m^3	$\frac{HNO_3+NO_3^-}{HNO_3}$	Nitric Acid (HNO_3) n moles/m^3	$\frac{HNO_3(DRI)}{HNO_3(ARB)}$	Volatization Factor
1	5/28/86 0631-1031 PST	5.21	56.2	1.09	114.5 (2.8 ppb v/v)	2.04	1100%
2	5/28/86 1203-1602 PST	2.98	35.3	1.08	69.5 (1.7 ppb)	1.97	1200%
3	5/29/86 0700-1100 PST	19.19	29.5	1.65	98.2 (2.4 ppb)	3.33	400%
4	5/29/86 1100-1510 PST	9.98	12.9	1.77	61.3 (1.5 ppb)	4.75	500%
5	5/30/86 0700-1100 PST	2.73	17.6	1.16	57.3 (1.4 ppb)	3.26	1400%

Table 1. ARB vs. DRI Nitric Acid Measurements at Dominguez Hills May 28-30, 1986.

Sample Number	Assumed DRI positive bias corrected			Assumed ARB negative bias corrected		
	$\frac{HNO_3+NO_3^-}{HNO_3}$	$\frac{HNO_3(DRI)}{HNO_3(ARB)}$	Volatization Factor	$\frac{HNO_3+NO_3^-}{HNO_3}$	$\frac{HNO_3(DRI)}{HNO_3(ARB)}$	Volatization Factor
1	1.09	1.55	600%	1.07	1.59	800%
2	1.08	1.19	200%	1.06	1.36	600%
3	1.65	2.39	200%	1.42	2.16	300%
4	1.78	2.61	200%	1.35	2.13	300%
5	1.15	1.69	500%	1.08	1.71	900%

Table 2. Volatization Factors After Correcting Data for Possible Systematic Bias.

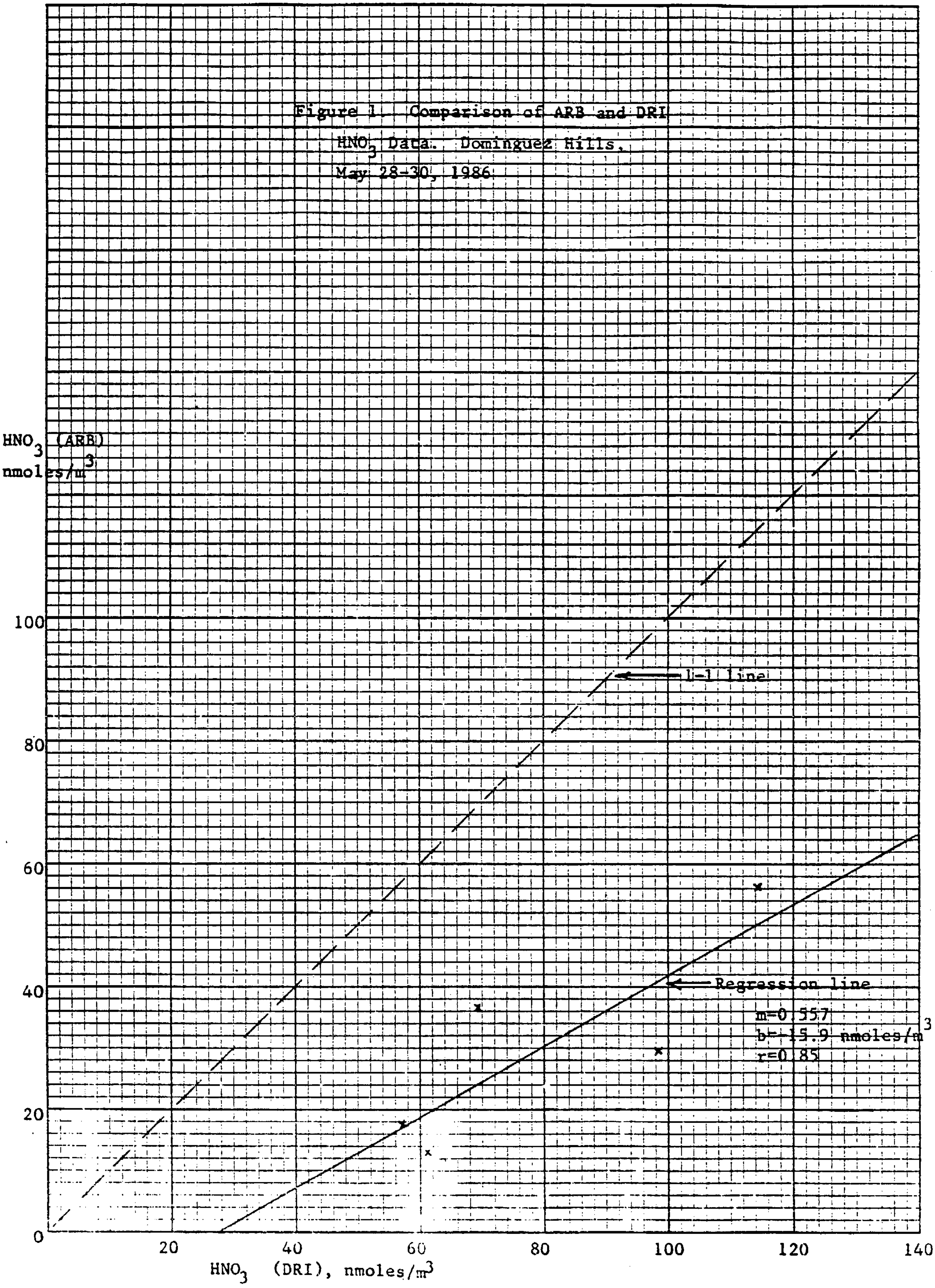

Figure 1. Comparison of ARB and DRI HNO_3 Data. Dominguez Hills, May 28-30, 1986

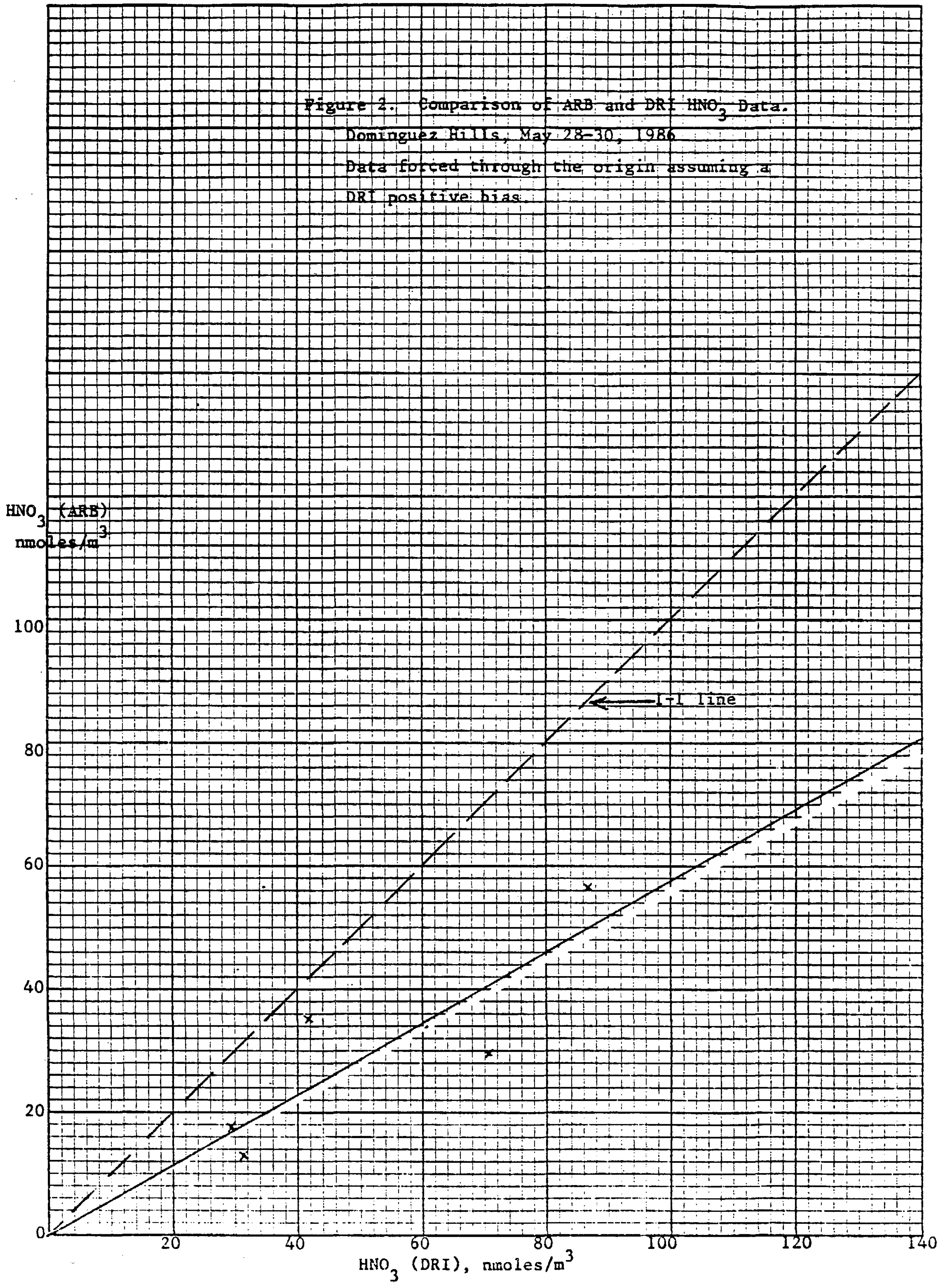

Figure 2. Comparison of ARB and DRI HNO$_3$ Data.
Dominguez Hills, May 28-30, 1986
Data forced through the origin assuming a DRI positive bias.

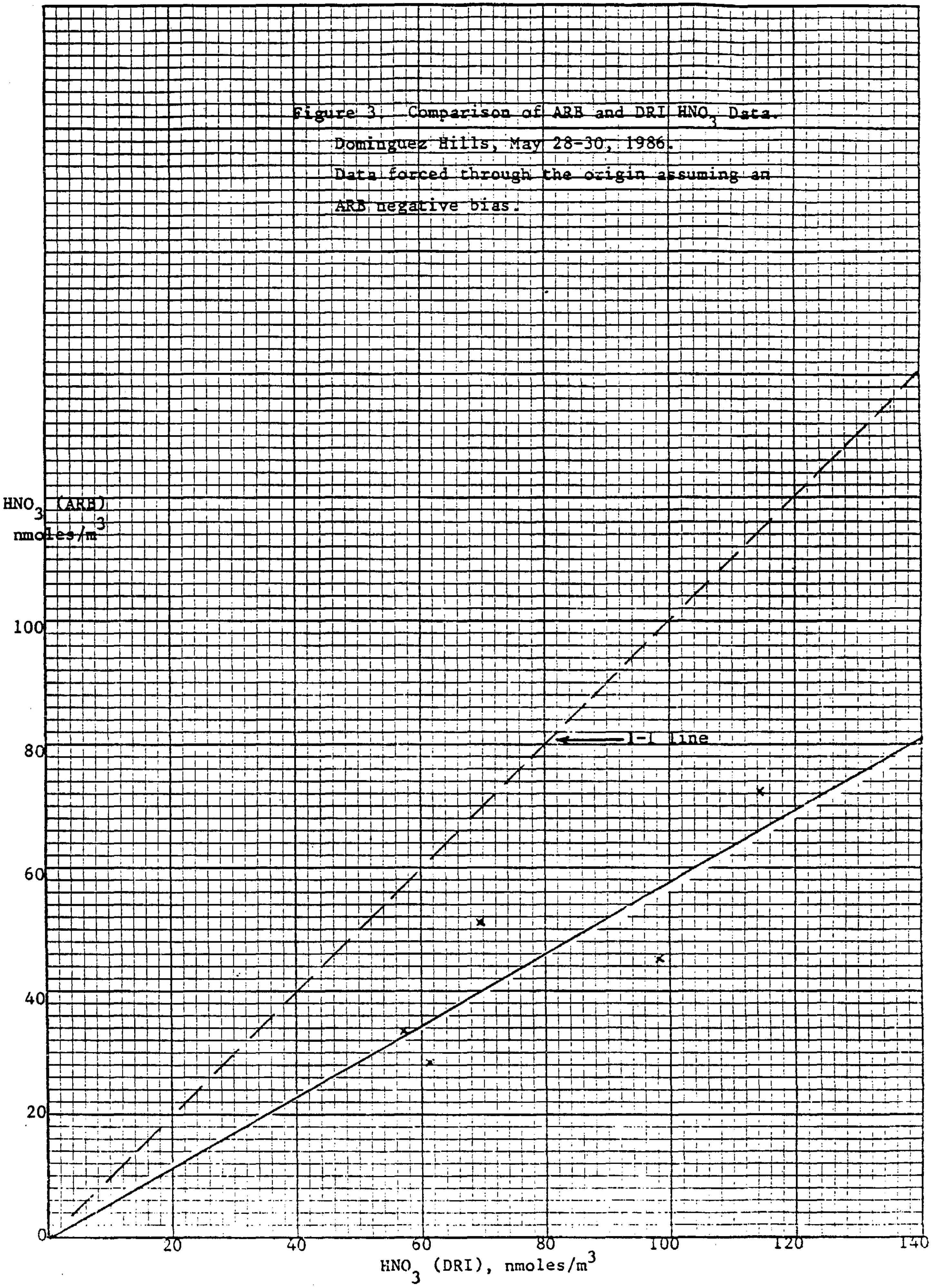

Figure 3. Comparison of ARB and DRI HNO_3 Data.
Dominguez Hills, May 28-30, 1986.
Data forced through the origin assuming an
ARB negative bias.

References

1. Appel, B.R. et al Evaluation and Development of Procedures for Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air - Phase II, Final Report Contract No. ARB A8-111-31 (October, 1980).

2. Winer, Arthur M., J. W. Peters, J. P. Smith and J. N. Pitts, Jr. Response of Commercial Chemiluminescent NO-NO_2 Analyzers to Other Nitrogen Containing Compounds Environ. Sci. + Tech. 8, 13 (December 1974).