United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-79-034a
August 1979

Air

EPA

Analysis of High NO_2 Concentrations in California, 1975-1977

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Analysis of High NO_2 Concentrations in California, 1975-1977

by

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Contract No. 68-02-2835

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

August 1979

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Publication No. EPA-450/4-79-034a

ABSTRACT

During the period 1975-1977, 51 monitoring stations in California collectively recorded about 1,800 site-days in which hourly nitrogen dioxide (NO_2) concentrations exceeded 0.20 ppm. This work investigates potential causes of these high NO_2 events, the physical phenomena involved in their occurrence, and their spatial and temporal patterns. In addition, the potential association between emission sources and the frequency and magnitude of high NO_2 levels at the various locations is analyzed using detailed site-description data compiled in this study. The relationship between annual maximum hourly levels and annual mean concentration is explored, and the quality of the NO_2 data is evaluated.

This report was submitted in fulfillment of Contract 68-02-2835 under the sponsorship of the U.S. Environmental Protection Agency.

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ACKNOWLEDGMENTS

The authors thank Dr. Harold G. Richter, EPA Project Officer, for his assistance and encouragement in the preparation of this report.

We also thank Mr. Russell Trudeau and Ms. Joyce Kealoha of SRI for technical contributions.

EXECUTIVE SUMMARY

Objectives and Background

The objective of this study is to analyze the occurrence and potential causes of hourly concentrations of nitrogen dioxide (NO_2) greater than 0.20 parts per million (ppm) recorded in California during 1975-1977. The investigation was performed in support of the current efforts of the U.S. Environmental Protection Agency to determine whether a new national short-term ambient air quality standard for NO_2 should be established. (The current national NO_2 standard is 0.05 ppm annual arithmetic mean.)

Summary of Findings

Major topics investigated were:

- Monitoring site features.
- Data quality.
- Physical processes associated with high NO_2 levels.
- Spatial and temporal variations of high NO_2 concentrations.
- Relationship between annual maximum and mean NO_2 concentration.

The principal findings can be summarized as follows:

Monitoring Site Features

All the sites reporting $NO_2 > 0.20$ ppm (hereafter, NO_2 levels greater than 0.20 ppm will be referred to as "NO_2 exceedances") are located in urban and suburban areas, with half the sites in the South Coast Air Basin (Los Angeles, Orange, Riverside and San Bernardino counties).

Examination of the local neighborhood of the monitoring stations revealed that mobile-source emissions predominated at most sites. Local point sources such as power plants and heavy industries were few in number. Probable point-source impacts from a steel mill were detected at one site.

In the South Coast Air Basin, probable source/receptor relationships were identified between stationary NO_x sources and several monitoring stations. In particular, the sites at Long Beach and Whittier showed the most pronounced stationary-source impacts.

Data Quality

The investigation of data quality considered data anomalies, accuracy, and the comparability of colorimetric and chemiluminescent measurements. Few anomalies were found in the data. Only 62 of approximately 1800 site-days were judged to contain anomalous NO_2 measurements and were eliminated from the data base. This resulted in the deletion of two of the 51 stations originally reporting NO_2 exceedances. A third station was also eliminated because its NO_2 levels did not exceed 0.20 ppm.

Regarding data accuracy, a recent study by the California Air Resources Board found that because of calibration procedures used in the state, actual NO_2 levels in California are from 10 to 17 percent lower than measured.

Simultaneous colorimetric and chemiluminescent NO_2 measurements were compared at three sites. The two types of measurements were correlated at two sites, with correlation coefficients of 0.71 and 0.86, but no correlation was evident at the third station. In general, the chemiluminescent measurements tended to be higher than the colorimetric observations.

Physical Processes Associated with High NO_2 Levels

Physical phenomena associated with NO_2 exceedances were classified into three categories:

- Chemical synthesis--$NO \rightarrow NO_2$ conversion by peroxy radicals.
- Titration--$NO + O_3 \rightarrow NO_2 + O_2$.
- Other--Transport and point-source effects.

Chemical synthesis was found to be the most common mechanism leading to NO_2 exceedances. NO_2 exceedances resulting from titration were about two-thirds as frequent as those associated with synthesis and appear to be ozone-limited, rather than nitric oxide-limited. Titration effects are most common at downwind sites where transported ozone reacts with local nitric oxide. Pasadena and Pomona in the South Coast Air Basin are examples of this type of site. Transport and point-source effects linked to NO_2 exceedances were infrequent: Examples of these effects are found at sites such as Long Beach, Whittier, Barstow and Victorville.

Spatial and Temporal Variations of High NO_2 Concentrations

Over 5,400 site-hours with NO_2 > 0.20 ppm were recorded statewide during 1975-1977. The concentrations ranged from 0.21 to 0.62 ppm, with a median concentration of 0.24 ppm. About 92 percent of the NO_2 exceedances were recorded in the South Coast Air Basin, with Los Angeles County accounting for 80 percent of the statewide total. On a statewide basis, between 34 and 46 percent of the NO_2 exceedances would be eliminated if the NO_2 data were adjusted downward to compensate for the 10-17 percent bias.

NO_2 exceedances occur most frequently during the period November through February. The seasonal pattern is evident statewide. In the South Coast Air Basin, the seasonality of the NO_2 exceedances appears to coincide with increased contributions from stationary area sources of NO_x, contributions which are largely a result of emissions related to space heating using natural gas.

The diurnal variation of NO_2 exceedances appears to be associated with the traffic cycle in the more densely urbanized areas. The distribution of NO_2 concentrations exceeding 0.20 ppm that occurs during the time intervals 0-0500 and 2200-2300 differs quantitatively from the distributions that prevail during 0600-1300 and 1400-2100 at six of nine sites tested. In general, NO_2 levels during 0-0500 and 2200-2300 were lower than at the other times. By contrast, seven of nine stations tested showed no statistically significant differences between the distribution prevailing during 0600-1300 and that for 1400-2100.

A widespread pattern of interstation correlations was found among fifteen selected stations in the South Coast Air Basin. The incidence of high NO_2 levels recorded at two or more sites the same day surpassed that of single-site events by better than a 2:1 margin. The pattern of interstation correlations is consistent with the typical flows that prevail in the South Coast Air Basin.

Relationship Between Annual Maximum and Mean NO_2 Concentration

Peak/mean ratios ranged from 3.3 to 12.9, with a median ratio of 6.3. Peak and mean NO_2 were found to be linearly correlated. The correlation was highly statistically significant, the coefficient being 0.82 for the pooled 1975-1977 data. A linear regression equation relating peak and mean NO_2 was derived. The equation is: peak = 5.5 mean + 0.05, where the concentrations are in ppm and the standard error of estimate is 0.07 ppm.

Conclusions

In California, high NO_2 concentrations seem to be primarily an urban phenomenon. The pattern of NO_2 exceedances strongly suggests that a high density of emissions of NO_x and hydrocarbons are required for synthesis to lead to levels of $NO_2 > 0.20$ ppm. Titration-related NO_2

exceedances require high levels of both NO and O_3 and appear to be ozone-limited, rather than NO-limited.

The evidence suggests that NO_2 is not transported over long distances and that NO_2 exceedances are essentially confined to urban areas and their immediate surroundings. The finding that nighttime levels of NO_2 are significantly lower than daytime values indicates that NO_2 has a short lifetime, and supports the hypothesis that, unlike O_3, high levels of NO_2 do not undergo long distance transport.

NO_2 exceedances occurred most frequently during the period November-February. Although the more stagnant meteorological conditions that prevail in California during these months are certainly an important contributing factor, the possibility exists that the high NO_2 levels may be enhanced by increased NO_x emissions from space heating using natural gas. The seasonal pattern of NO_x emissions in the South Coast Air Basin supports this hypothesis.

The recent discovery by the California Air Resources Board that NO_2 concentrations in the state are between 10 and 17 percent lower than indicated by the measurements is particularly important for regulatory applications. Contemplated regulatory actions must specify the adjustment factor to be applied to the data.

The interstation correlation with respect to same-day NO_2 exceedances between various pairs of sites in the South Coast Air Basin suggests that area sources, rather than point sources, are the principal proximate causes of the elevated NO_2 levels in the area. This is supported by the association between the daily traffic cycle and the hourly fluctuations of the high NO_2 concentrations.

The derived linear-regression equation relating peak and mean NO_2 implies that the current California hourly standard of 0.25 ppm is more restrictive than the national annual standard of 0.05 ppm. Consequently, if a national hourly standard of 0.25 ppm were established, the hourly rather than the annual standard could become the controlling factor in abatement efforts. This is the situation that currently exists in California. Thus, in setting a national hourly standard for NO_2, the relationship between peak and mean NO_2 needs to be considered to ensure that the two standards reinforce each other.

I INTRODUCTION

A. Objectives and Background

This study investigates the occurrence and potential causes of hourly concentrations of nitrogen dioxide (NO_2) greater than 0.20 parts per million (ppm) that were recorded in California during 1975-1977. The analysis includes examining spatial and temporal patterns of high NO_2 levels, as well as various physical phenomena associated with their occurrence.

The investigation is motivated by the current efforts of the U.S. Environmental Protection Agency (EPA) to determine whether a new national short-term ambient air quality standard for NO_2 should be established (the current NO_2 standard is 0.05 ppm annual arithmetic mean): hence, the emphasis on high hourly NO_2 concentrations. Various concentration thresholds ranging from 0.10 to 0.50 ppm have been mentioned in connection with an hourly NO_2 standard (Thuillier and Viezee, 1978);* this study concerns NO_2 levels that exceed 0.20 ppm. For comparison, it should be noted that California currently has an hourly NO_2 air quality standard with a threshold level of 0.25 ppm.

B. Methodology

The study examined the following aspects of the problem:

- Characteristics of monitoring sites recording high NO_2 levels--the local environment of individual monitoring sites was scrutinized to identify factors that may influence the occurrence of high NO_2 levels.
- Quality of the NO_2 data--the study considered the accuracy of the measurements and the possible presence of anomalous values in the data base.
- Physical processes associated with high NO_2 concentrations--the primary processes that lead to the high levels of NO_2, a secondary pollutant, were identified.
- Spatial and temporal patterns of occurrences of high NO_2 levels--the spatial distribution of high-NO_2 events and their seasonal and diurnal variations were examined.
- Relationship between annual maximum hourly values and mean NO_2 concentrations--to estimate the potential effect of control strategies on peak NO_2 levels, the study derived an equation that relates the annual NO_2 peak to the mean concentration.

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*References are listed at the end of this report.

The text of this report describes in detail the analytical methods used in the research areas outlined above and presents the conclusions that were developed from the study.

C. Organization of the Report

Section II describes the geographical coverage of the monitoring sites that recorded NO_2 levels exceeding 0.20 ppm and contains the analysis of the site-description data. Data quality considerations are examined in Section III; Section IV presents the results of the analysis of physical processes. Spatial and temporal patterns of high NO_2 events are discussed in Section V. Section VI describes the investigation of peak/mean relationships. Conclusions and recommendations are presented in Section VII.

Two separately bound appendices are part of this report. Appendix A contains plots of NO_2 and other pollutants for all the days with $NO_2 > 0.20$ ppm. Appendix B contains detailed site-description data for all monitoring stations, including site maps.

II ANALYSIS OF MONITORING STATIONS

A. Geographic Setting

During 1975-1977, 51 monitoring stations distributed throughout California reported at least one hour when NO_2 exceeded 0.20 ppm.* Table 1 lists the stations, including SAROAD code number, site name, county, and street address. The sites have been numbered sequentially from 1 through 51 for ease of reference; site numbers are shown in the first column of Table 1.

Figures 1-4 show the geographical area covered by the 51 stations. The statewide distribution of the sites is displayed in Figure 1 (site numbers are keyed to Table 1). Only a few stations have been identified in Figure 1 because of space limitations; the other sites are identified in Figures 2-4. Figure 1 shows that the majority of the sites are clustered around three metropolitan areas:

(1) The San Francisco Bay area, in the north

(2) The Los Angeles area, in the south

(3) The San Diego area, near the southern border of the state.

(It is hardly surprising that most of the sites of interest are located around the three population centers in the state.) Seven sites are sprinkled throughout central California, ranging from Sacramento (Site 37) in the north to Barstow (Site 4) and Victorville (Site 50) in the south/central desert. Three other stations (Sites 7, 31, and 43) are located near the coast, northwest of Los Angeles.

Figures 2 through 4 provide enlarged views of the disposition of the monitoring sites near San Francisco (Figure 2), Los Angeles (Figure 3), and San Diego (Figure 4); nine sites are found in the San Francisco Bay area, 26 in the Los Angeles area (including Orange, Riverside and San Bernardino counties), and six in the San Diego area.

The maps (Figures 1-4) provide a broad picture of the placement of the monitoring stations reporting NO_2 exceedances. From these illustrations, it may appear that few, if any, parts of the state are immune from high NO_2 levels. However, our research shows that NO_2 exceedances are by no means uniformly distributed geographically. In fact, over 90 percent of all the NO_2 exceedances recorded during 1975-1977 occurred in the Los Angeles area. The data review (see Section III) revealed that three sites (Sites 3, 25, and 31) did not experience any NO_2 exceedances, which leaves some gaps in the NO_2 distribution shown in

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*Hereafter, the term "NO_2 exceedance" will be used exclusively to denote hours with $NO_2 > 0.20$ ppm.

Table 1

CALIFORNIA MONITORING STATIONS RECORDING HIGH NO_2

Site			County	Address
No.	SAROAD Code	Name		
1	050230001I01	Anaheim	Orange	1010 S. Harbor Blvd.
2	050500002I01	Azusa	Los Angeles	803 Loren Ave.
3	050520003F01	Bakersfield	Kern	225 Chester Ave.
4	050580001I01	Barstow	San Bernardino	200 E. Buena Vista
5	050900002I01	Burbank	Los Angeles	228 W. Palm
6	050920002I01	Burlingame	San Mateo	1229 Burlingame
7	051030003I01	Camarillo	Ventura	Elm Dr.
8	051300001I01	Chino	San Bernardino	Central & Riverside
9	051360001I01	Chula Vista	San Diego	80 E. "J" St.
10	051600001I01	Concord	Contra Costa	991 Treat Blvd.
11	051740001I01	Costa Mesa	Orange	2631 Harbor Blvd.
12	052220002I01	El Cajon	San Diego	110 E. Lexington
13	052390001I01	El Toro	Orange	23022 El Toro Rd.
14	052460002I01	Escondido	San Diego	600 E. Valley Pkwy.
15	052680001I01	Fontana	San Bernardino	14838 Foothill Blvd.
16	052780001I01	Fremont	Alameda	40733 Chapel Way
17	052800005F01	Fresno	Fresno	3250 E. Olive
18	053620001I01	La Habra	Orange	621 W. Lambert
19	053900001I01	Lennox	Los Angeles	11408 La Cienega
20	054100002I01	Long Beach	Los Angeles	3648 N. Long Beach
21	054180001I01	Los Angeles	Los Angeles	434 S. San Pedro
22	054180002I01	Los Angeles	Los Angeles	2351 Westwood Blvd.
23	054200001I01	Los Angeles	Los Angeles	18330 Gault St.
24	054260001I01	Lynwood	Los Angeles	11220 Long Beach
25	054580001F01	Merced	Merced	Eighteenth & "S" St.

Table 1 (Concluded)

Site			County	Address
No.	SAROAD Code	Name		
26	055120001I01	Newhall	Los Angeles	24811 San Fernando
27	055300004F01	Oakland	Alameda	Jackson St.
28	055320003I01	Oceanside	San Diego	100 S. Cleveland
29	055760004I01	Pasadena	Los Angeles	1196 E. Walnut St.
30	056040001I01	Pomona	Los Angeles	924 N. Garey Ave.
31	056080001I01	Port Hueneme	Ventura	Naval Civil Eng. Lab.
32	056200001I01	Redlands	San Bernardino	216 Brookside Ave.
33	056240001I01	Redwood City	San Mateo	897 Barron Ave.
34	056300003I01	Richmond	Contra Costa	1144 Thirteenth St.
35	056400003F01	Riverside	Riverside	7002 Magnolia Ave.
36	056535001I01	Rubidoux	Riverside	5888 Mission Blvd.
37	056580003F01	Sacramento	Sacramento	1025 "P" St.
38	056680001I01	San Bernardino	San Bernardino	172 W. Third St.
39	056800004I01	San Diego	San Diego	1111 Island Ave.
40	056800006I01	San Diego	San Diego	5555 Overland Ave. (Kearney/Mesa)
41	056860003I01	San Francisco	San Francisco	939 Ellis St.
42	056980004A05	San Jose	Santa Clara	1208 N. Fourth St.
43	057200004F01	Santa Barbara	Santa Barbara	831 State St.
44	057670001I01	Simi Valley	Ventura	5400 Cochran St.
45	058040002F01	Stockton	San Joaquin	1601 E. Hazelton
46	058080001I01	Sunnyvale	Santa Clara	251 S. Murphy Ave.
47	058220001F01	Temple City	Los Angeles	Las Tunas Dr.
48	058440003I01	Upland	San Bernardino	155 "D" St.
49	058440004F01	Upland	San Bernardino	1350 San Bernardino
50	058510001I01	Victorville	San Bernardino	1556a Eighth St. (County Bldg. 1557)
51	058720001I01	Whittier	Los Angeles	14427 Leffingwell

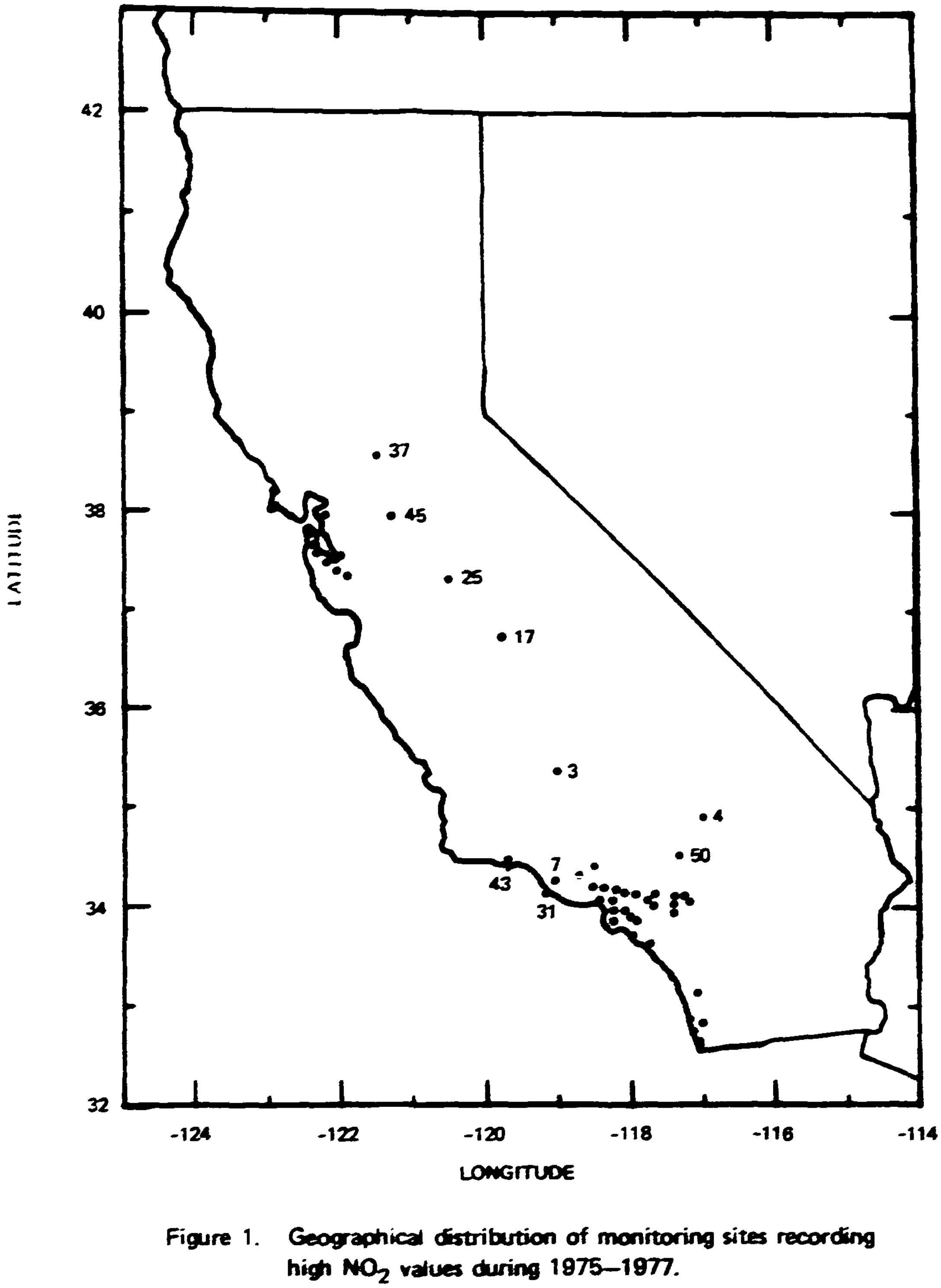

Figure 1. Geographical distribution of monitoring sites recording high NO_2 values during 1975–1977.
Site numbers are keyed to Table 1.

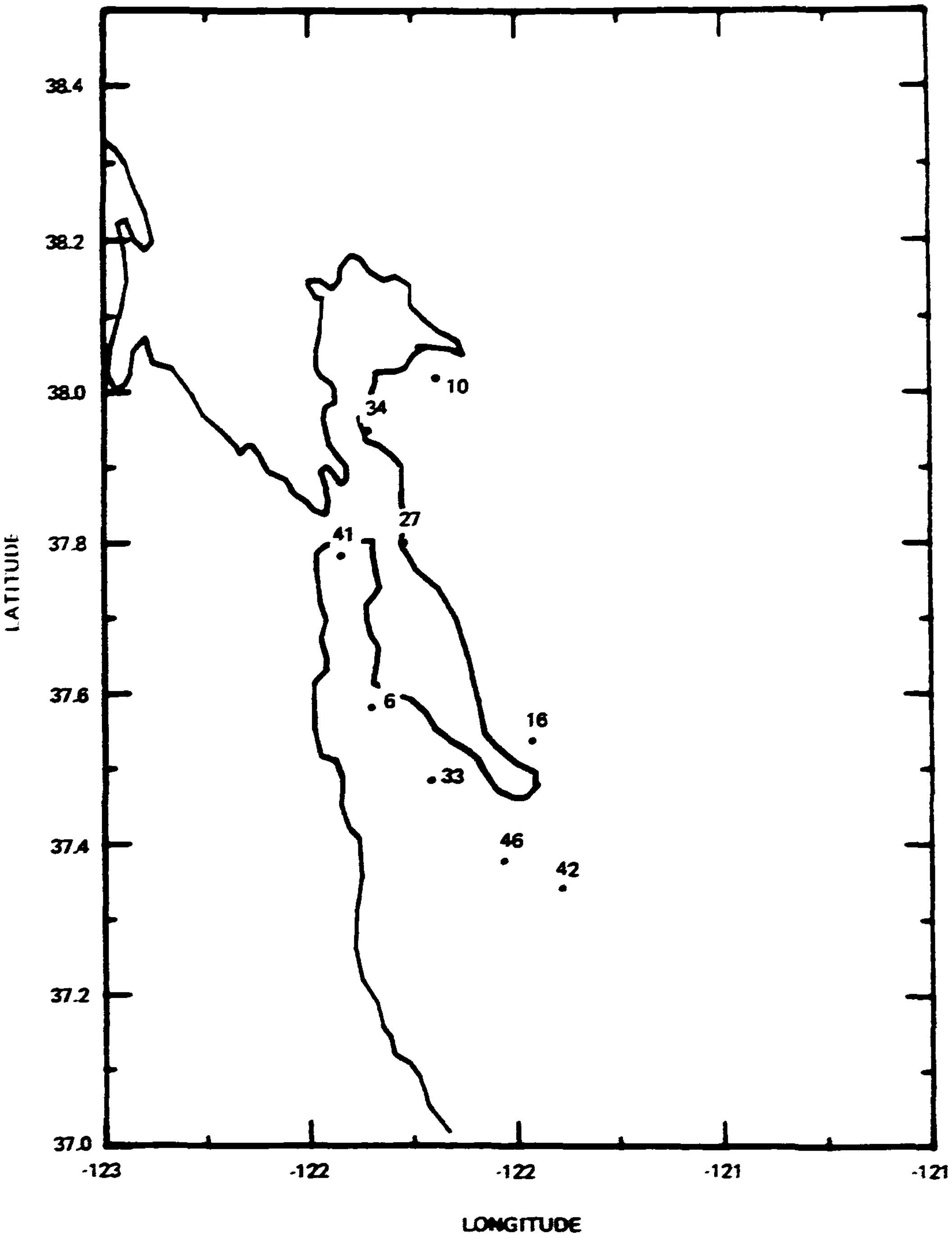

Figure 2. NO_2 monitoring sites located in the San Francisco Bay Area. Site numbers are keyed to Table 1.

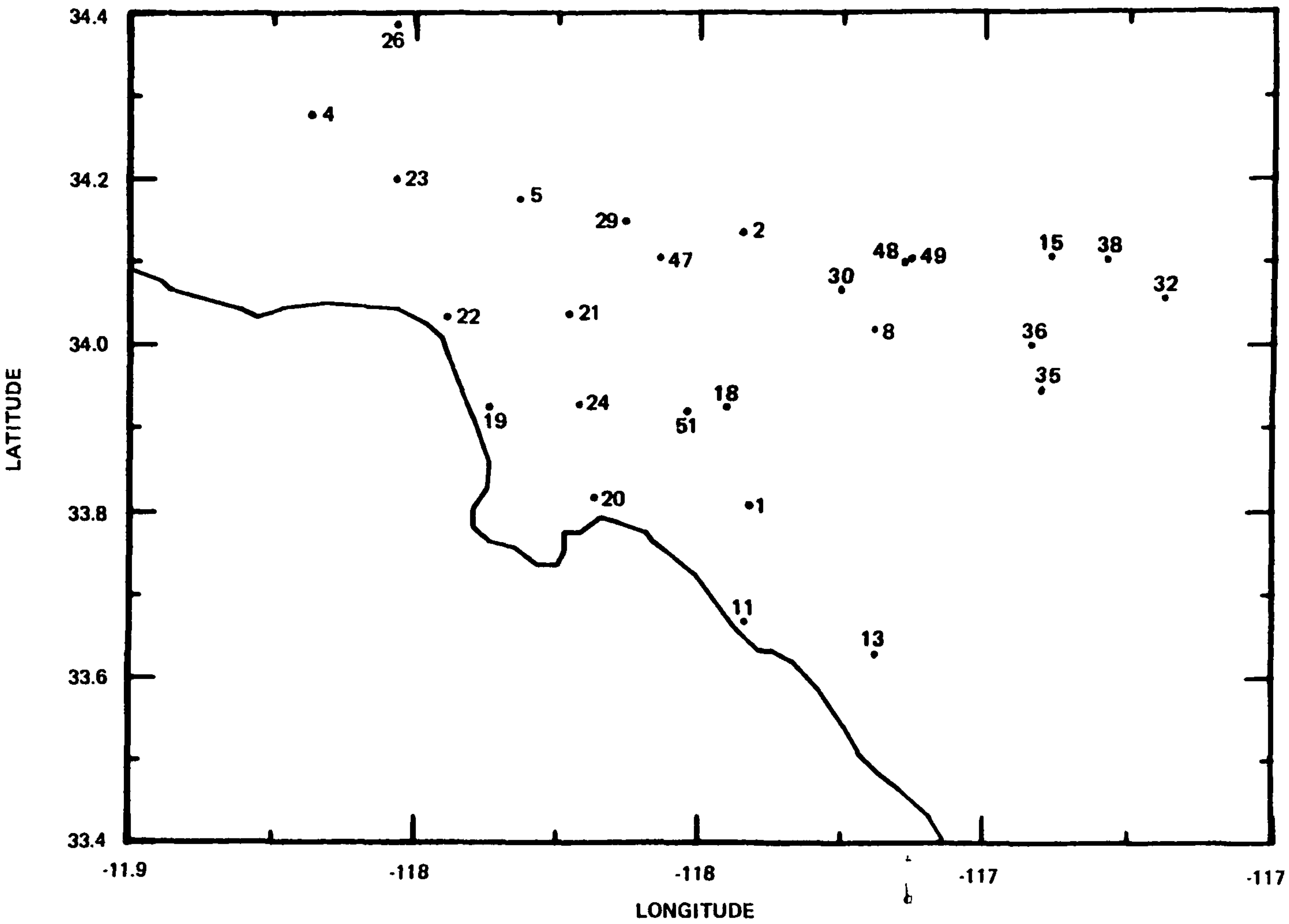

Figure 3. NO_2 monitoring sites located in the South Coast Air Basin. (Los Angeles, Orange, Riverside and San Bernardino Counties). Site numbers are keyed to Table 1.

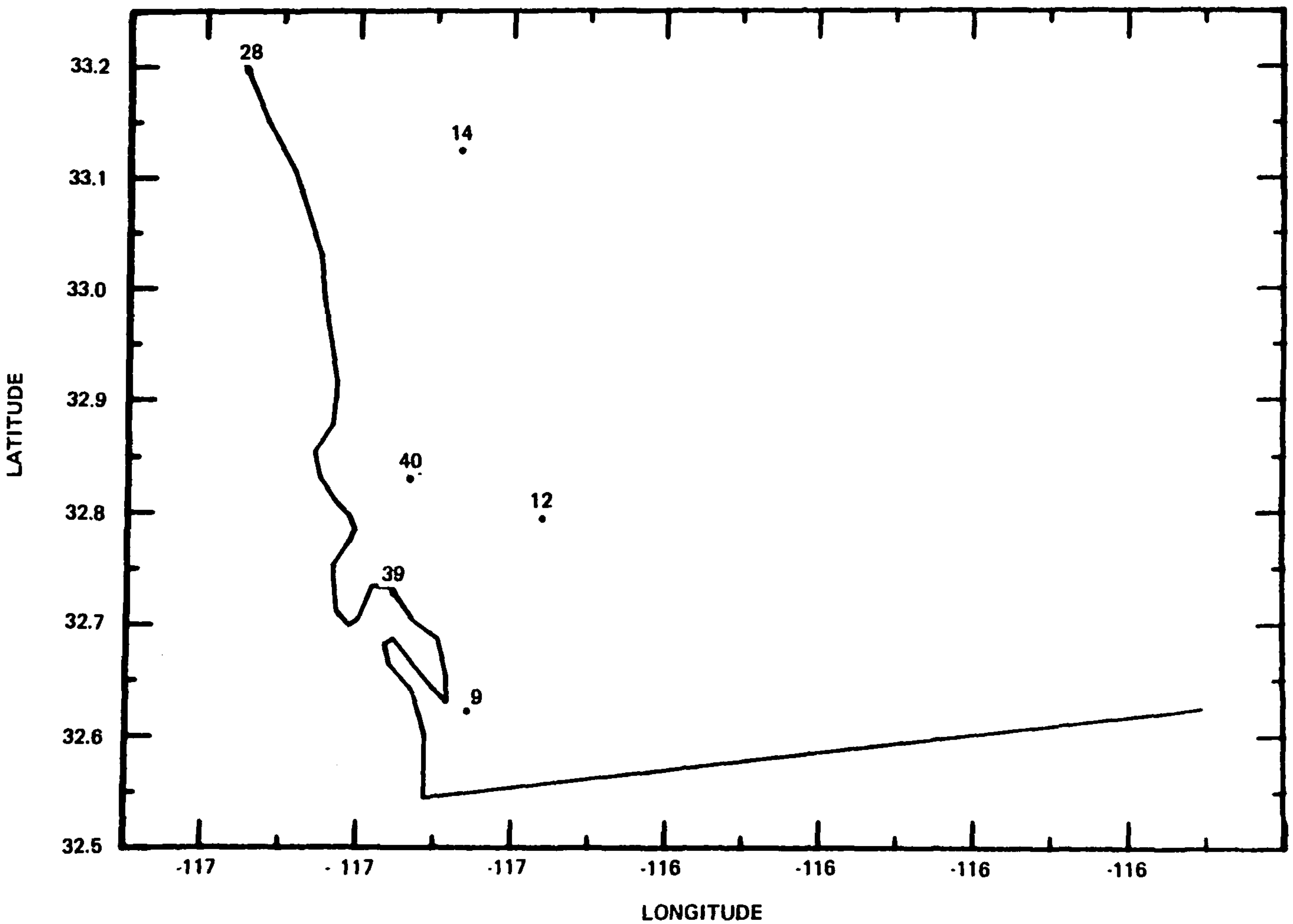

Figure 4. NO_2 monitoring sites located in the San Diego Area. Site numbers are keyed to Table 1.

Figure 1. As a result, NO_2 exceedances seem to be most closely associated with areas that have a high population density, and appear to be an essentially urban phenomenon.* More evidence supporting this hypothesis is presented later in this report.

What sources influence the occurrence of high NO_2 levels at these monitoring stations? The next sections describe the analysis of the immediate surroundings of individual stations in order to identify potentially significant local sources, and examine potential source/receptor relationships in the Los Angeles area on a regional scale.

B. Description and Classification of Monitoring Sites

Information describing each monitoring site and its surroundings was tabulated to detect local factors that might influence the occurrence of NO_2 exceedances at each site. For example, the presence of a power plant or a busy highway near the site would be of special interest.

The site-description data were obtained from the California Air Resources Board (CARB). For the most part, these data were provided to the CARB by the local air-pollution control agencies. The site data were compiled and supplemented by SRI using forms similar to those shown in Figure 5. In many cases, the available data were incomplete, and all the blanks in the form could not be filled. This was especially true of the traffic data for most sites except those located in the Los Angeles area.

In addition to the written data, a map showing the station location and its surroundings (within a five mile radius) was prepared for each site. An example is shown in Figure 6 for Anaheim; the dot at the center of the circle marks the station location. The maps provide a visual indication of the site's environment. It is apparent that the Anaheim station is surrounded by roads, with no significant point sources nearby: Disneyland is essentially a large parking lot, which contributes to the mobile-source emissions from the nearby roads. It is clear that traffic-related emissions should be the major influence at this site.

The site-description forms and associated maps for all 51 stations are included as Appendix B of this report.

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*Note that there may also be gaps in the monitoring network.

SUPPLEMENTARY SITE INFORMATION FOR NO2 SITES

A. SITE IDENTIFICATION

1. Date ______
2. City ______
3. State ______
4. Lat/Long. or UTM coordinates ______ , ______
5. SAROAD site code ______
6. State site number ______
7. Local site number ______
8. Names of nearest intersecting streets: ______
9. Outstanding landmarks ______
10. Sketch of site; detail:
    - (a) North direction N↑
    - (b) Inlet probe ⊗
    - (c) Obstructions
    - (d) Emission sources
    - (e) Roadways ═
    - (f) Parking areas [P]
    - (g) Vacant areas [V]
    - (h) Buildings (indicate no. of stories) ⊞

B. POLLUTANTS & METEOROLOGICAL PARAMETERS CURRENTLY MEASURED AT SITE

______

1. Check one or more under each column

	Industrial	Commercial	Near urban	Agricultural	Mobile	Residential	Old	New
Remote								
Rural								
Suburban								
Outer								
Inner								
Central Business								
Outer core								
Inner core								

2. Indicate representativeness:

Street canyon ______ Background ______
Neighborhood ______ Source oriented ______
Corridor ______

C. SITE ENVIRONMENT

1. Nearby sources: Power plants, roadways, industrial sources of NO_x, etc. Direction and distance to site-associated pollutants. Note and consider elevated sources within 5 miles of the site. Consider all elevated point sources emitting more that 1500 tons/yr. NO_x within 10 miles of monitor.

Source	Direction	Distance	Pollutants

2. Type of traffic near the site:

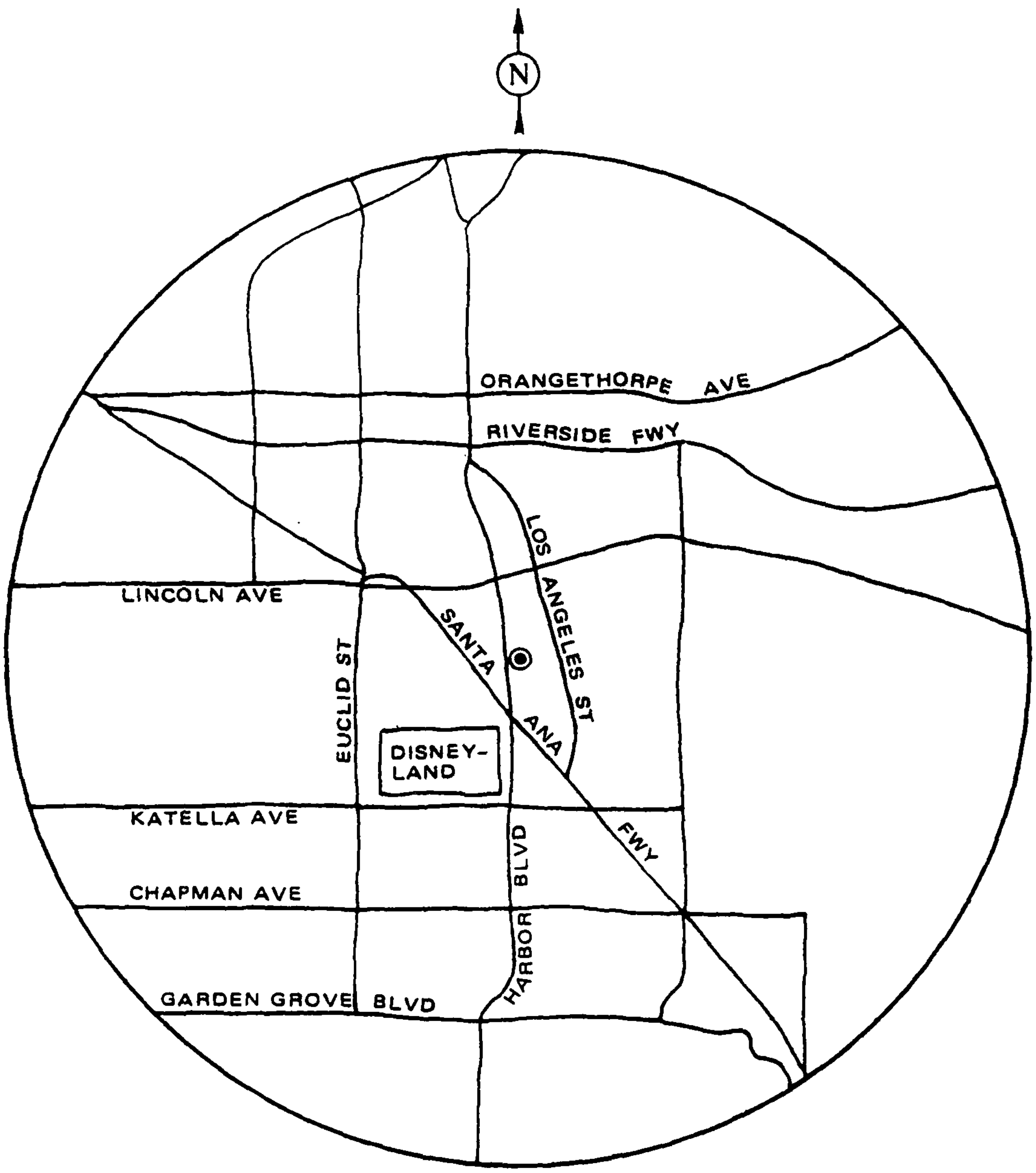
Arterial highway ______ Major street/highway ______
Expressway ______ Through street/highway ______
Freeway ______ Local street/road ______
Parkway ______ Intersection ______

If data already exists.

3. What is average daily traffic? ______
4. What is average vehicle speed? ______
5. What are number of traffic lanes of the roadway? ______
6. What are number of parking lanes of the roadway? ______
7. Terrain characteristics:

   Smooth ______
   Rolling ______
   Rough ______

Figure 5. Sample form for site description data.



SITE NO. 050230001: 1010 S. HARBOR BOULEVARD
ANAHEIM, CALIFORNIA

Figure 6. Sample map of monitoring site location and its surroundings. Dot marks station location.

Using the compiled site descriptions, the monitoring sites were classified under various categories:

- Site type--Urban, suburban, or rural
- Site representativeness--Street canyon, neighborhood
- Traffic type
  - Heavy (more than 24,000 vehicles/day)
  - Medium (6,000-24,000 vehicles/day)
  - Light (less than 6,000 vehicles/day)
  - Intersection
- Stationary sources--Power plant or miscellaneous.

The classification of all the sites is shown in Table 2.

Table 2 shows that all sites are located in urban or suburban environments. This could imply that rural areas are not impacted by high NO_2 levels, but this inference must be tempered by the knowledge that rural locations are seldom monitored. The data may merely reflect the fact that the monitors are found in urban and suburban areas rather than in rural regions. Consequently, judgments about the prevalence of high NO_2 in rural areas must be withheld pending further study. Nevertheless, Table 2 makes it clear that high NO_2 levels are definitely associated with the conditions that exist in urbanized areas.

The table also shows that a number of monitoring stations are located in street canyons; hence, NO_2 levels should be directly tied to traffic influences. The "neighborhood" classification denotes commercial or residential areas that may be near large point sources, so "neighborhood" sites should reflect the ebb and flow of traffic as well as any point-source impacts.

Five sites, all from the Los Angeles area, are located near heavily traveled roads. Twelve stations fall in the moderate-traffic category, while nine are classified as light-traffic sites. Twenty sites are located near intersections with varying degrees of vehicle activity. All of these sites should be locally affected by mobile-source emissions.

Power plants are located near five of the sites: Burbank, Chula Vista, San Diego, and the two Upland stations. At the first three sites, subsequent analysis revealed that pollutant histories on high NO_2 days do not indicate any impact from stationary sources as shown by SO_2 levels. This is not surprising, considering that the plant stacks are designed to prevent precisely such localized impacts (except perhaps under conditions of fumigation). Another possible explanation for the apparent lack of power plant impact is that the plants may have used natural gas on the days investigated. If this were the case, there would be no SO_2 effects and the power plant impact would go undetected.

Table 2

CLASSIFICATION OF NO_2 MONITORING SITES

Site Name	SAROAD ID Number	Site Type*			Representativeness†		Traffic Type‡				Stationary Sources		Remarks
		1	2	3	4	5	6	7	8	9	Power Plant	Misc.	
Anaheim	050230001		x				x					x	31,000 veh/day
Azusa	050500002		x						x				800 veh/day
Bakersfield	050520003	x				x				x			
Barstow	050580001	x						x					6,000 veh/day
Burbank	050900002	x							x	x	x		Power plant-1 block; 2,400 veh/day
Burlingame	050920002	x			x					x			
Camarillo	051030003	x						x		x			Freeway-600 ft
Chino	051300001	x							x				7,000 veh/day
Chula Vista	051360001		x			x					x		Power plant-2.5 mi
Concord	051600001		x			x							
Costa Mesa	051740001		x				x						48,000 veh/day
El Cajon	052220002	x				x							Freeway-0.5 mi
El Toro	052390001		x			x			x				Freeway-1 mi
Escondido	052460002	x			x								
Fontana	052680001		x						x			x	Kaiser steel plant
Fremont	052780001	x				x							
Fresno	052800005		x							x			
La Habra	053620001		x			x		x					14,000 veh/day
Lennox	053900001		x				x					x	Los Angeles Int'l Airport
Long Beach	054100002		x			x	x			x			25,000 veh/day
Los Angeles	054180001	x						x		x			14,000 veh/day
Los Angeles	054180002	x						x		x			21,000 veh/day
Los Angeles	054200001	x				x			x	x			2,000 veh/day; freeway-1.5 mi
Lynwood	054260001	x						x					16,000 veh/day
Merced	054580001		x			x				x			
Newhall	055120001		x					x					12,000 veh/day
Oakland	055300004	x				x							
Oceanside	055320003	x			x							x	RR switchyard-1/4 mi
Pasadena	055760004	x						x					18,000 veh/day
Pomona	056040001	x					x						24,000 veh/day
Port Hueneme	056080001		x									x	Dock machinery and vehicles; cargo vessels
Redlands	056200001	x			x				x				5,000 veh/day
Redwood City	056240001		x			x				x		x	Paint spray shop-1 block
Richmond	056300003		x			x						x	Refinery-2 mi
Riverside	056400003	x								x			
Rubidoux	056535001		x					x					
Sacramento	056580003	x			x								
San Bernardino	056680001	x			x			x		x		x	Norton AFB-2 mi; 9,000 veh/day
San Diego	056800004	x									x	x	Tire recapping; power plant-1 mi
San Diego	056800006		x			x						x	Naval Air Station-2 mi
San Francisco	056860003	x			x					x			
San Jose	056980004	x				x				x			
Santa Barbara	057200004	x			x			x					
Simi Valley	057670001		x			x			x				
Stockton	058040002		x							x			
Sunnyvale	058080001	x				x							
Temple City	058220001	x			x					x			
Upland	058440003	x									x		Power plant-7 mi
Upland	058440004	x				x				x	x	x	Steel mill-7.5 mi; airport-3 mi; power plant-7 mi
Victorville	058510001	x							x	x		x	Cement plant-2 mi; 2,000 veh/day
Whittier	058720001		x					x		x			20,000 veh/day

*Site Type: 1 = Urban, 2 = Suburban, 3 = Rural

†Representativeness: 4 = Street Canyon, 5 = Neighborhood

‡Traffic Type: 6 = Heavy, 7 = Moderate, 8 = Light, 9 = Intersection

These plants burn either oil or natural gas, depending on availability, and used oil most frequently during 1975-1977. Consequently, the natural gas hypothesis is unlikely, but cannot be ruled out. No power plant effects could be detected at Upland, because SO_2 was not monitored there.

The Fontana and Upland sites would be expected to show some impact from the Kaiser steel mill. Fontana showed enhanced SO_2 levels, which indicates that the steel plant's emissions probably impact the site. But no effects were evident at the Upland sites because, as noted above, SO_2 was not monitored.

Not shown in Table 2, but evident in the data sheets in Appendix B, is the fact that many of the stations are located near parking lots, gas stations, and other small sources. These miscellaneous local sources must affect the pollutant burden measured at the site, but their individual contributions are too small and diffuse to be detected in the air quality data; they become part of the background pollution.

In summary, the site classifications suggest that mobile sources are the predominant local emitters at nearly all the stations. Potentially significant local point sources such as power plants and heavy industries were found to be few in number: There are indications of impacts from a steel mill at one site (Fontana), but possible power-plant influences at three other sites could not be detected. Finally, a variety of small stationary sources (e.g., parking lots, gas stations) undoubtedly contribute to the general pollution level, but individual impacts are small and indistinguishable from the overall contamination.

C. Potential Source/Receptor Links in the Los Angeles Area

This section extends the spatial scale from the local level of the previous section to the regional level, seeking possible source/receptor links for stationary sources in the Los Angeles regional area. The monitoring sites have been plotted on maps of stationary-source emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x). Examining source locations, monitoring stations, and known meteorological patterns for the area may reveal likely source/receptor relationships.

Figures 7 and 8 are gridded emissions maps of NO_x and SO_x, respectively, from stationary sources; the NO_2-monitoring stations are plotted on each map. (Each grid cell is 10 km square.) The NO_x data were obtained from Bartz et al. (1974) and the SO_x data from Hunter and Helgeson (1976). The numbers shown on the perimeter of the grid are Universal Transverse Mercator (UTM) coordinates in km. The range of emissions associated with individual grid squares is indicated by different shadings. The dots mark the monitoring site locations, and the site numbers shown are keyed to Table 1. These figures also show average streamline patterns that typify those that occur in the interval

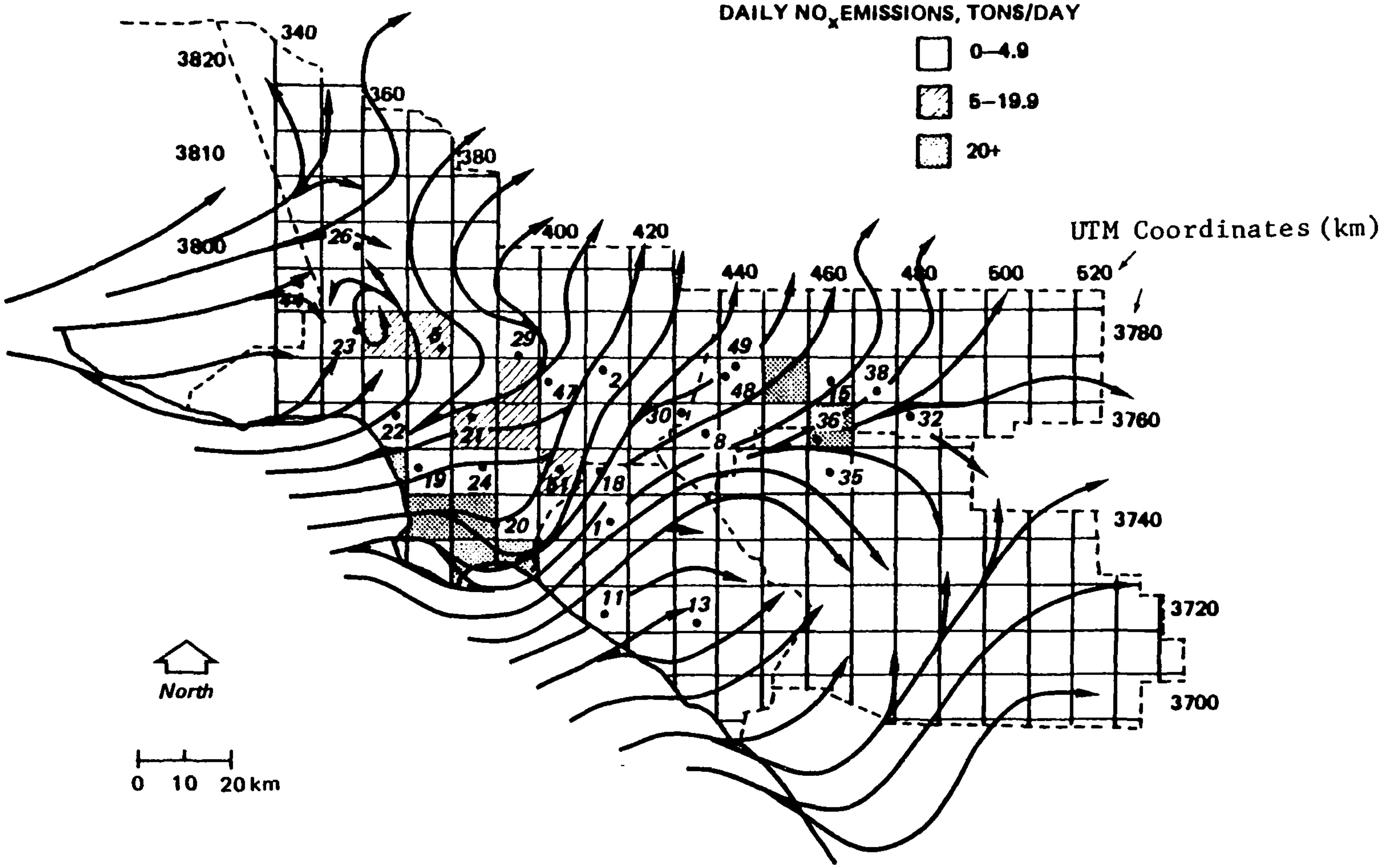


Figure 7. Map of stationary-source NO_x emissions in the South Coast Air Basin.

Dots mark location of NO_2 monitoring sites; the site numbers are keyed to Table 1. Streamline pattern shown is typical of winter afternoon conditions.

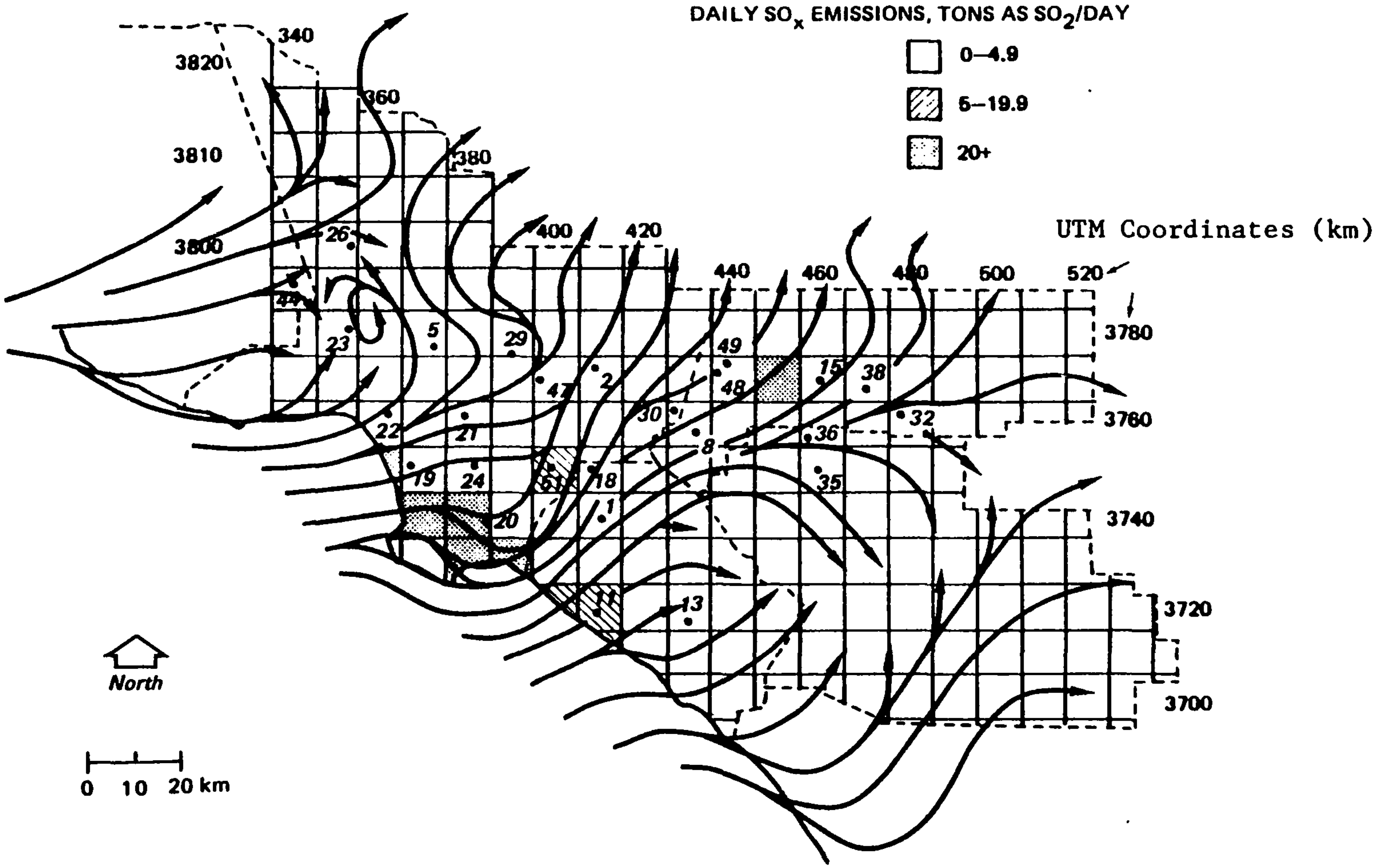


Figure 8. Map of stationary-source SO$_x$ emissions in the South Coast Air Basin. Dots mark location of NO$_2$ monitoring sites; the site numbers are keyed to Table 1. Streamline pattern shown is typical of winter afternoon conditions.

1200-1700 (PST) in January (De Marrais et al., 1965). There is very little difference between streamline patterns in winter and those for other times of year.

Figure 7 shows that sites at Long Beach (Site 20) and Rubidoux (Site 36) are located in grid squares that have a high density of NO_x emissions from stationary sources. In addition, the stations at Burbank (Site 5), Los Angeles/San Pedro (Site 21) and Whittier (Site 51) are in squares of moderate emissions density. These five sites should experience the strongest impact from stationary sources of NO_x. (In fact, Section IV will show that Long Beach and Whittier exhibit such impacts.) The streamlines show that many other monitoring stations are downwind of the major sources, and thus are likely candidates for stationary-source impacts: examples are Anaheim (Site 1), La Habra (Site 8), Lennox (Site 19), Los Angeles/Gault St. (Site 23), Lynwood (Site 24), and San Bernardino (Site 38). Note also that Whittier (Site 51), in addition to being in a square of medium emissions density, is downwind of the coastal NO_x sources, and is thereby exposed to a multiplicity of sources. It can also be seen in Figure 7 that the Fontana site (Site 15) is downwind of squares with high emissions density, consistent with the earlier observation regarding evidence of stationary-source impact at Fontana.

Since SO_x is primarily associated with stationary sources, its presence identifies areas that may be impacted by such sources. It is evident from Figures 7 and 8 that grid squares with high NO_x and SO_x emissions coincide in most cases, enhancing the use of SO_x as an indicator of stationary-source effects for NO_x. Figure 8 shows that Long Beach (Site 20) is located in an area of high SO_x emissions density and that Whittier is located in an area of moderate emissions density. Since Whittier is in a downwind location, as shown in Figure 7, it is thus likely to receive additional pollutants from the coastal SO_x sources. The impacts of SO_x emissions will be discussed in greater detail in Section IV.

The pattern of streamlines in Figure 8 suggests that other sites may also be influenced by SO_x sources: Anaheim (Site 1), Fontana (Site 15), La Habra (Site 18), Lennox (Site 19), Los Angeles/San Pedro (Site 21), and Lynwood (Site 24) are likely candidates. However, except for Fontana, the levels of SO_x observed at these sites were generally low, indicating that small effects from stationary sources may be the rule. Fontana did show appreciable levels of SO_2. (Plots of SO_2 concentrations for those sites where SO_2 was measured are shown in Appendix A of this report.)

Thus, Figures 7 and 8 provide graphic evidence linking stationary sources and emissions levels at certain monitoring stations. The flow field also suggests that levels at many of the stations may be correlated, since several sites lie on the path of the same air trajectories. This theme is again addressed in Section V, which examines the correlation between station pairs.

III EVALUATION OF DATA QUALITY

An important concern of the study was to assess the quality of the NO_2 data. The evaluation considered:

- Data anomalies
- Measurement accuracy
- Experimental methods.

The procedures used in the data-quality assessment and the results obtained are described below.

A. Data Anomalies

In this study, detecting anomalous data meant identifying NO_2 exceedances that could have been erroneous. Thus, no effort was made to detect errors for NO_2 concentrations in the range 0-0.20 ppm. It is emphasized that while a number of NO_2 exceedances were found to be questionable and were subsequently excluded from our analyses, the original data records (which were unavailable to us) must be examined to determine whether or not these data are in fact invalid.

The error-detection procedure consisted of four steps:

(1) For each site, plot concentration histories for NO_2 and other pollutants for all days that report at least one NO_2 exceedance.

(2) Define error-detection criteria.

(3) Visually scan each plot and identify questionable data by applying the error-detection criteria.

(4) Check the questionable data against the original data record and accept or reject the data.

The plots generated in Step 1 are found in Appendix A of this report. In addition to NO_2, the graphs include NO, O_3, CO, and SO_2 whenever these data were available. Because of the chemical links between NO, NO_2, and O_3, the adequacy of the NO_2 data could be evaluated in relation to NO and O_3. CO and SO_2 are relatively inert chemically compared to the others, and can be helpful in judging the effect of sources and meteorological conditions. Thus, a very high NO_2 level that occurs on a day when CO is low can be flagged as suspect, pending further checking of the data.

Pollutant data were also plotted for the days immediately preceding and following the date of the NO_2 exceedance. The extended data record enriched the context in which the NO_2 data were judged. For example, if the NO_2 instrument was operating during only part of the day when an exceedance occurred, the record of the instrument's behavior on the preceding and following day provides information about the likelihood of erratic behavior when the exceedance was recorded.

The following attributes served to detect questionable data:

(1) Sudden increases (spikes) or drops in the NO_2 data.

(2) High NO_2 concentrations occurring immediately before or after an instrument malfunction.

(3) Very high NO_2 concentrations (apparent outliers).

(4) NO_2 exceedances preceded and followed by gaps in the data record (isolated exceedances).

(5) Simultaneous existence of high NO and O_3.

After verification that the flagged data were real, and not the result of a plotting error, the data were usually rejected if they satisfied any of the above criteria. However, not all data that satisfied the first three criteria were rejected: Such cases were examined in relation to other pollutants, and a subjective judgment was made about whether the instrument was working properly. The "data gap" criterion led to immediate rejection if the length of the data record was short compared to the length of the gaps; that is, if the degree of isolation was large. Otherwise, a subjective judgment was made about the likelihood of erratic instrumental behavior, and the data accepted or rejected. The last criterion always resulted in rejection of the data, since the coexistence of NO and O_3 for any extended period is chemically untenable. It is possibile that the O_3 instrument, rather than the NO/NO_2 equipment, was malfunctioning, but in those few instances when this criterion was applied, it seemed more likely that the NO/NO_2 instrument was operating erratically.

In general, these decisions were conservative and data was rejected more often than not. Yet, even though the net was fine, the catch was small. Of approximately 1,800 site-days when NO_2 exceedances were recorded, only 62 were rejected. Table 3 lists the sites and dates when data were rejected, along with the applicable rejection criteria. The plots corresponding to these days are found in Appendix A of this report. The table shows that the "data gap" criterion was invoked most frequently, followed by the "spike" and "instrument malfunction" criteria. The third criterion, presence of apparent outliers, was used infrequently, and always in combination with some other criterion. As noted in Table 3, some of the outliers are decimal-point errors. The fifth criterion, the coexistence of high values of NO and O_3, was invoked only six times.

The five error-detection criteria were not strictly applicable to the rejected data for 9 September 1976 at Chino and for 15 July 1977 at Fontana. At Chino, the data were rejected because they appear to continue the pattern of erratic behavior observed on 8 and 10 September.

Table 3

ANOMALOUS NO_2 DATA

Site	Date	Data Rejection Criteria*					Remarks
		1	2	3	4	5	
Anaheim	16 Sep 75		x				
Bakersfield	23 Apr 77	x					
	10 Oct 77	x		x			Apparent decimal-point error
	26 Oct 77	x		x			Apparent decimal-point error
Barstow	3 Jul 76	x					
	19 Jul 76		x				
	3 Jun 77				x		
Burbank	22 Mar 76				x		
Camarillo	19 Jan 77				x		
Chino	15 Jan 75	x		x			
	3 Sep 76	x				x	
	8 Sep 76	x				x	
	9 Sep 76						Erratic behavior
	10 Sep 76	x					
	13 Sep 76					x	
	14 Sep 76					x	
	15 Sep 76				x		
Costa Mesa	23 Sep 75		x				
	3 Nov 76	x					
Fontana	27 Aug 76					x	
	28 Aug 76					x	
	15 Jul 77						Strange NO patterns
La Habra	13 Jan 76		x				
	24 Nov 76				x		
	8 Dec 76		x				
Lennox	2 Dec 75	x	x				
	19 Jan 76	x					
	21 Jan 76	x	x				
	19 Apr 76		x				
	28 Dec 76				x		
	30 Nov 77				x		
Long Beach	17 Oct 75		x				
	7 Mar 77		x				
	14 Nov 77				x		
Los Angeles/San Pedro	27 Feb 76				x		
	16 Aug 77				x		
	25 Oct 77			x	x		
	26 Oct 77				x		
	3 Nov 77				x		
	22 Nov 77				x		
Los Angeles/Westwood	22 Dec 75				x		
	27 Jan 76		x				
	2 Feb 76		x				
	25 Jun 76				x		
	19 Jan 77				x		
	5 Apr 77				x		
Los Angeles/Gault	8 Mar 77	x	x		x		
Lynwood	16 Oct 75	x					
Merced	26 Feb 77	x					Apparent decimal-point error
Oceanside	24 Nov 76		x				
Pasadena	8 Feb 77				x		
	6 Apr 77		x				
Riverside	30 Jan 76†				x		
Sacramento	15 Nov 77	x					Apparent decimal-point error
	31 Dec 77	x					
San Diego/Island	30 Aug 76				x		
San Jose	23 Jul 75‡	x					Apparent decimal-point error
	21 Dec 76†			x	x		
Temple City	30 Dec 77	x					
Whittier	24 Aug 76		x				
	16 Aug 77		x				
	16 Nov 77				x		

*1 = Data spike, 2 = Instrument malfunction, 3 = Outliers, 4 = Data gaps, 5 = Simultaneous NO and O_3

†Colorimetric method

‡Chemiluminescent method

At Fontana, the data for 15 July were rejected because they duplicate the pattern observed on 27 and 28 August, when the fifth criterion was invoked. However, the ozone data were missing on 15 July, and the fifth criterion was not strictly applicable. The Fontana data show strong indications of point-source impacts. Thus, what appears to be a strange, and possibly erroneous, pattern in the data could be an accurate reflection of actual conditions. In the absence of additional information, the data were rejected.

We consider a data-rejection rate of about 3 percent to be quite low, and indicative of the fact that the data underwent extensive editing and checking before being entered in the data bank. Therefore, we conclude that the presence of anomalously high NO_2 concentrations is not cause for concern in subsequent analyses.

The data check resulted in eliminating three stations from the list of those reporting NO_2 exceedances: Bakersfield, Merced, and Port Hueneme. The exceedances recorded at Bakersfield and Merced were few, and all but one appear to be decimal-point errors. The NO_2 data for Port Hueneme displayed no anomalies: NO_2 at Port Hueneme equalled but did not exceed 0.20 ppm.

B. Measurement Accuracy

The term "accuracy" refers to systematic errors or bias in the measurements. To determine the accuracy of experimental data, observations must be compared with some standard or reference level. Since only field data were available in this study, an independent estimate of the accuracy of the NO_2 data was not possible. However, a recent study by the CARB (CARB, 1979) provides the desired information about the accuracy of NO_2 data in California.

The principal finding of the CARB study is that the so-called "Saltzman factor", which characterizes the efficiency of the NO_2 conversion, is higher than has been assumed in California experimental protocols. The factor was assumed to be 0.72, but the CARB found it to be 10-17 percent higher. This implies that actual NO_2 levels in California are from 10-17 percent lower than indicated by the measurements. These results apply to both colorimetric and chemiluminescent instruments, because both use the same calibration procedure in California.

It is emphasized that these findings apply only to pre-1980 NO_2 data for California. Similar studies should be performed by other states that have used the Saltzman procedure for calibration to determine what, if any, error may be present under their particular experimental conditions. Accuracy problems caused by using the Saltzman procedure will be eliminated in 1980 and thereafter because EPA regulations require that other calibration methods be used beginning in January 1980 (Federal Register, 10 May 1979).

In this study, the NO_2 data have not been adjusted in any way. However, the implications of the 10-17 percent bias are discussed in the analyses that follow.

C. Experimental Methods

The NO_2 data used in this study were obtained using colorimetric and chemiluminescent instruments. Colorimetric instruments were used at 30 stations. Table 4 lists the 21 sites where chemiluminescent instruments were used, and the years when the instrument was in operation and recorded NO_2 exceedances. Since two different kinds of instrument were

Table 4

MONITORING STATIONS
USING CHEMILUMINESCENT INSTRUMENTS

Site		
No.	Name	Years*
3	Bakersfield	1977
8	Chino	1976-1977
9	Chula Vista	1975-1977
12	El Cajon	1976-1977
13	El Toro	1975
14	Escondido	1975-1977
15	Fontana	1975-1977
17	Fresno	1976-1977
25	Merced	1977
27	Oakland	1975-1976
28	Oceanside	1975-1976
31	Port Hueneme	1977
35	Riverside	1975-1977
36	Rubidoux	1976-1977
39	San Diego	1975-1977
40	San Diego	1975-1977
42	San Jose	1975-1977
44	Simi Valley	1977
47	Temple City	1976-1977
49	Upland	1975-1977

*Only those years reporting NO_2 exceedances are shown.

used, it is of interest to examine the comparability of the data obtained by the two methods. Such analysis is possible since both kinds of instrument were operated simultaneously at four stations. Table 5 lists the sites and shows the number of days when NO_2 exceedances were detected by each method. The table suggests some discrepancy between the two types of measurement.

Table 5

NUMBER OF HIGH NO_2 DAYS DETECTED
BY TWO DIFFERENT MEASUREMENT METHODS

No.	Name	SAROAD Code	Measurement Method	Number of Days with NO_2 > 0.20 ppm		
				1975	1976	1977
35	Riverside	056400003	Colorimetric	13	3	N.A.*
			Chemiluminescent	13	14	8
36	Rubidoux	056535001	Colorimetric	2	2	1
			Chemiluminescent	N.A.	0	4
42	San Jose	056980004	Colorimetric	4	6	2
			Chemiluminescent	5	5	7
49	Upland	058440004	Colorimetric	7	2	N.A.
			Chemiluminescent	9	5	5

*N.A. = Data not available for specified method.

A correlation analysis was performed to examine the relationship between the NO_2 concentrations measured by the two techniques. The data used in the analysis were the paired concentrations for the hour when <u>either</u> method measured NO_2 > 0.20 ppm. The three possible types of concentration-pairs are represented by AB, $A\bar{B}$, and $\bar{A}B$, where A = colorimetric > 0.20 ppm, B = chemiluminescent > 0.20 ppm, and $\bar{A}$ and $\bar{B}$ denote the complement. The results of the analysis are described below. No analysis was performed for Rubidoux because the number of concentration pairs was too small (one).

Figures 9 through 11 are scatterplots of colorimetric concentrations as a function of chemiluminescent concentrations for Riverside, San Jose, and Upland. The correlation statistics are shown in Table 6. As the table indicates, only Upland shows the expected high correlation. The correlation for Riverside is low but statistically significant, but San Jose shows no significant correlation.

Figure 9 shows that the Riverside data contain two clusters, labeled A and B, that dominate the correlation. Table 7 shows the

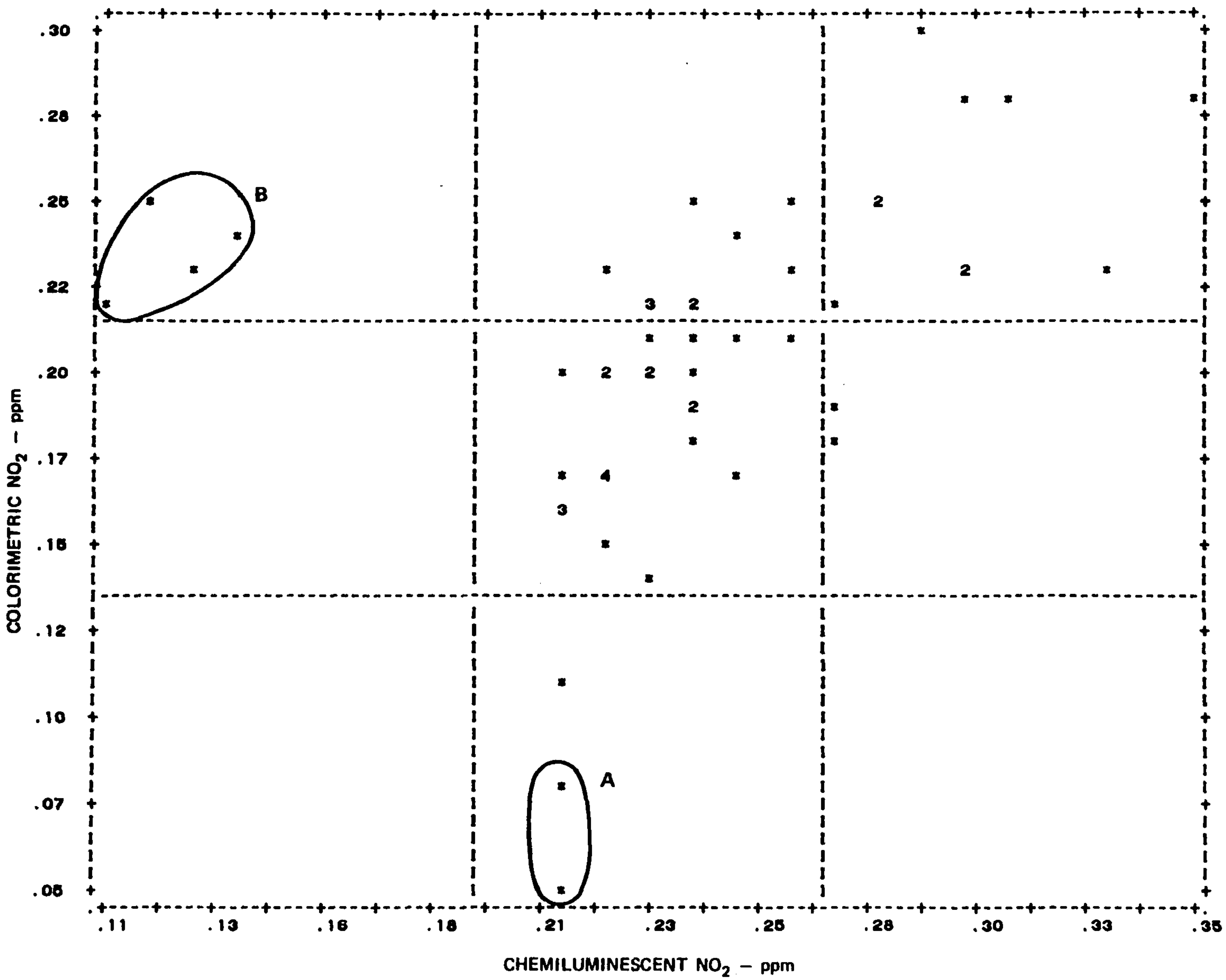


Figure 9. Scatter diagram of colorimetric as a function of chemiluminescent NO_2 at Riverside. Number of points plotted is 53. See text for explanation of the data labeled A and B.

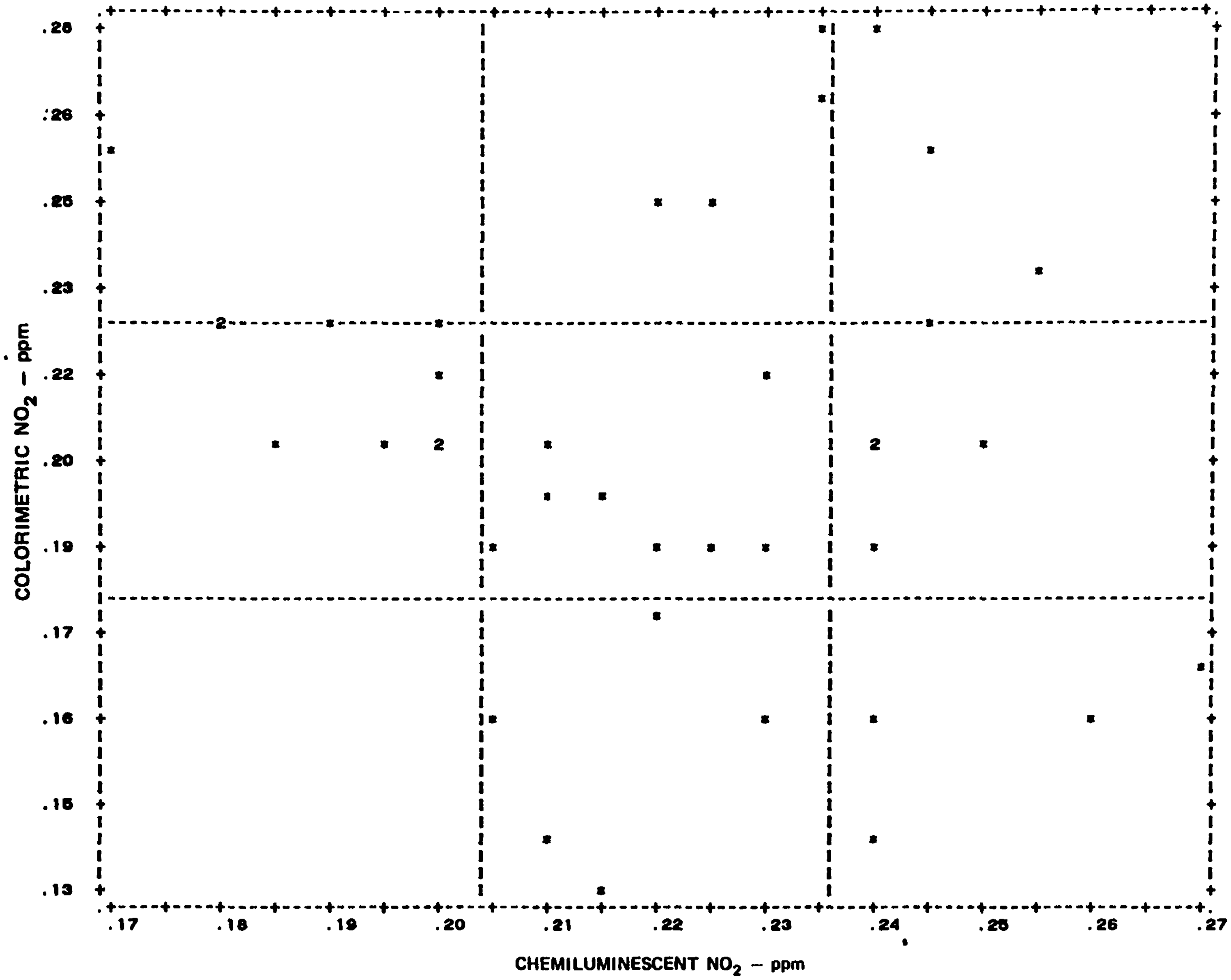


Figure 10. Scatter diagram of colorimetric as a function of chemiluminescent NO_2 at San Jose. Number of points plotted is 39.

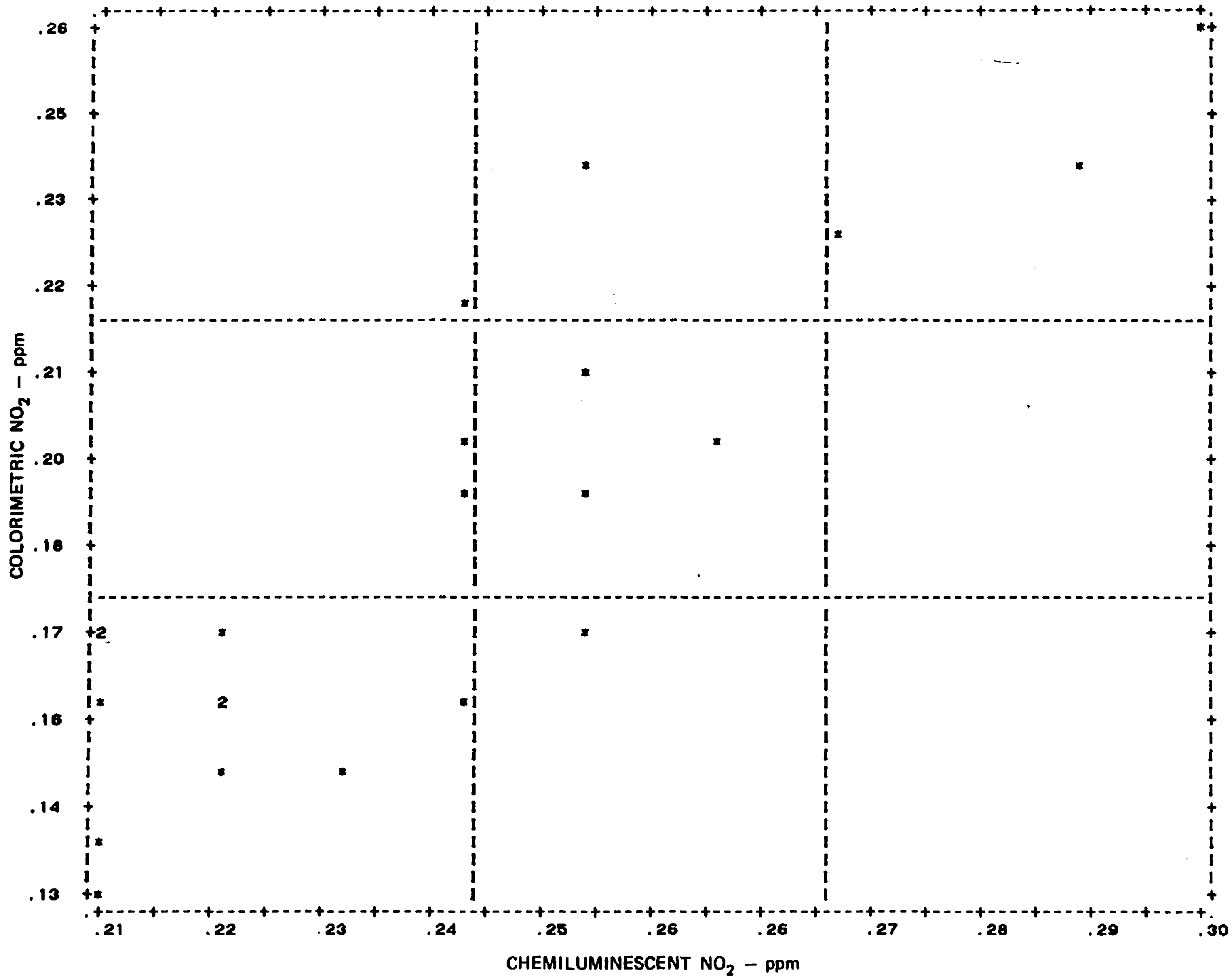


Figure 11. Scatter diagram of colorimetric as a function of chemiluminescent NO_2 at Upland. Number of points plotted is 22.

Table 6

CORRELATION BETWEEN MEASURED COLORIMETRIC AND CHEMILUMINESCENT NO_2 CONCENTRATIONS

Site Name	Number of Data Points	Correlation Coefficient	Significance Level
Riverside	53	0.53	<0.006
San Jose	39	-0.12	N.S.*
Upland	22	0.86	<0.0001

*Not statistically significant

Table 7

DATA CLUSTERS FOR RIVERSIDE

Cluster	Colorimetric NO_2 (ppm)	Chemiluminescent NO_2 (ppm)	Date	Hour (PST)
A	0.08	0.21	2 Feb 1976	0100
A	0.05	0.21	2 Feb 1976	0600
B	0.23	0.13	26 Feb 1976	1700
B	0.24	0.14	26 Feb 1976	1800
B	0.25	0.12	26 Feb 1976	1900
B	0.22	0.11	26 Feb 1976	2000

cluster contents and the dates and hours that correspond to the data in the clusters. The table shows that both points in Cluster A were observed on the same day: 2 February 1976. The situation is similar for Cluster B: these four points were measured on 26 February 1976. Perusal of the data record for 2 February reveals some gaps in the chemiluminescent data, which suggests that this instrument may have behaved erratically that day. On 26 February the colorimetric measurement increased abruptly from 0.12 ppm at 1600 to 0.23 ppm at 1700, the level remaining as shown in Table 7 until 2100 when it decreased to 0.19 ppm. By contrast, the chemiluminescent data remain steady throughout. The evidence suggests, therefore, that Clusters A and B represent anomalous cases that may be reasonably eliminated from the data comparison.

In view of the above, Clusters A and B were eliminated and the correlation was recomputed. The new correlation, 0.71, is statistically significant ($p < 0.0001$); it is also in line with the correlation seen at Upland. The regression line for the modified data set is $y = 0.83x + 0.001$, where y = colorimetric NO_2 and x = chemiluminescent NO_2. The standard error of estimate for this regression is 0.03 ppm. The slope of the line indicates that, on the average, colorimetric NO_2 is 17 percent lower than chemiluminescent NO_2, when the latter exceeds 0.20 ppm. The remarkable agreement between this 17 percent factor and that discovered by the CARB is purely coincidental.

The diagram for San Jose (Figure 10) shows the large amount of data scatter that led to the insignificant correlation between the two types of measurement. In contrast to Riverside, the San Jose data show no pattern or data clusters that exert undue influence on the correlation. The only plausible conclusions seem to be that the instruments were either measuring different things or were improperly operated, or both.

The behavior of the Upland data is displayed in Figure 11. It is apparent that a linear relationship exists between the two quantities. The regression line is $y = -0.10 + 1.19x$, where y and x are colorimetric and chemiluminescent NO_2, respectively, and the standard error of estimate is 0.02 ppm. The figure shows that colorimetric levels are always lower than chemiluminescent measurements, yet the slope of the line is greater than one. The relatively large negative intercept compensates for the slope and indicates that the two data types are offset by a significantly high constant difference in favor of chemiluminescent NO_2. Thus, the chemiluminescent instrument reports NO_2 exceedances more frequently than the colorimetric instrument. Differences in zero-setting procedures could account for the offset.

In summary, two of the three sites analyzed (Riverside and Upland) showed a reasonably linear relationship between colorimetric and chemiluminescent measurements. However, both sites exhibited systematic biases between the instruments. In general, it seems that the chemiluminescent instrument registers higher readings than the colorimetric equipment. This may be a result of differences in calibration or to positive interferences in the chemiluminescent instrument (no significant interferences are expected for the colorimetric instrument).

The remaining site (San Jose) showed no correlation between the two instrument types. In view of the results for the other stations, it appears that the instruments at this location were either poorly adjusted or were not colocated, or both.

IV ANALYSIS OF PHYSICAL PROCESSES

A. Definition of Physical Phenomena

The aim of this analysis is to identify chemical and other phenomena associated with NO_2 exceedances. The main physical processes are defined as follows:

- Synthesis--NO $\rightarrow NO_2$ conversion by peroxy radicals
- Titration--$NO + O_3 \rightarrow NO_2 + O_2$
- Other--Transport and point-source effects

The synthesis process is the backbone of the photochemical-smog cycle. The oxidation of NO to NO_2 by peroxy radicals such as RO_2 and HO_2 results in a rapid depletion of NO, and leads to a high NO_2/NO ratio, setting the stage for the formation of O_3 via NO_2 photolysis. Ozone accumulation usually follows; its level is controlled by meteorological conditions. In urban areas, this process takes place in a few hours between 0600 and 1300; most of the NO is gone by 0900 or 1000. The initial charge of NO is of course a result of the morning-traffic rush.

In the absence of NO, O_3 lingers in the atmosphere for several hours until more NO is injected to react with O_3 in the titration process, or meteorological factors cleanse the air, or a combination of the two. On weekdays in urban areas, the early-evening traffic emits fresh NO that yields NO_2 via titration. Thus, we expect that the titration process generally occurs in the evening.

Other factors may also account for the occurrence of NO_2 exceedances. Transport effects are indirect manifestations of synthesis and/or titration, since NO_2 is a secondary pollutant. Thus, NO_2 transported to a monitoring station was chemically produced along the way. Nevertheless, for our purposes we define transport as a separate effect to differentiate between nonlocal and local impacts. In the discussion that follows, transport will be associated with nonlocal impacts, while synthesis and titration will be linked to short-term effects. In terms of hours, an exceedance of NO_2 is defined as short-term if it is the result of synthesis occurring between 0600 and 1300, and titration between 1600 and 1900. NO_2 exceedances occurring at other times are more likely to be related to transport.

Point-source effects in this study are identified by relating NO_2 and SO_2 concentration histories. The tacit assumption is that SO_2 is an indicator of large point sources, such as power plants (unless they are gas-fired) and certain heavy industries, and that simultaneous SO_2 and NO_2 peaks signal the presence of a point-source impact. As has been noted, only a few sites showed unambiguous evidence of these effects (see Section II). In a point-source plume that is initially rich in NO,

NO_2 would be produced via thermal oxidation by the three-body reaction $2NO + O_2 \rightarrow 2NO_2$. This reaction is slow, however, and NO concentrations must be on the order of several hundred ppm to make it significant. As the plume mixes with the ambient air, it may entrain peroxy radicals that oxidize NO via the synthesis process described earlier. It is also possible that a plume rich in NO may undergo fumigation or otherwise impact the ground downwind of the source and lead to high NO_2 levels via the titration of NO and O_3. Whatever the cause of the NO_2 in the plume, or of NO_2 associated with a plume, point-source impacts will be identified separately.

The next section presents several examples of the physical processes defined above, and Section IV-C describes the physical phenomena associated with all the monitoring stations.

B. Examples of Physical Processes

1. Chemical Synthesis

Figures 12 through 14 contain typical examples of chemical-synthesis phenomena at two sites in Los Angeles County. The three days shown are weekdays and display the typical morning and evening peak in NO that is due to the traffic. Although it is evident that mobile sources influence these two sites, there are some differences in the time phasing of the NO peak. Figure 12 shows that the NO maxima occur before 0800 at the Los Angeles/San Pedro site, but after 0800 at Temple City (Figure 13). This is consistent with the location of these stations; Temple City is farther inland than Los Angeles/San Pedro. The delayed appearance of the NO maximum at Temple City also suggests that transport influences this site.

The shape of the NO and NO_2 curves in Figures 12 and 13 is typical of the NO_2 synthesis process. Thus, the fast decay of NO is accompanied by an equally rapid increase in NO_2. Note, however, that the NO_2 peak occurs at 1000 at Los Angeles/San Pedro and at 1300 at Temple City. This suggests that local effects are the primary influence in Los Angeles, but some minor transport influence is likely at Temple City.

Figure 14 exhibits NO_2 concentrations exceeding 0.20 ppm that are the result of several factors. The significant feature of this figure is the high level of NO_2 that is present during the period midnight-0900. This phenomenon is termed "carryover" because it is presumed to be caused by pollution from the previous day that remains in the area (a situation that would prevail under stagnant meteorological conditions). Note that the nighttime NO_2 level hovers about 0.20 ppm: thus, it is easy for the threshold to be exceeded when NO_2 synthesis comes into play. This "carryover" phenomenon was observed on a number of occasions at Los Angeles County sites, but not elsewhere. The phenomenon was seen most frequently at the Los Angeles/San Pedro, Los Angeles/Westwood, Lennox

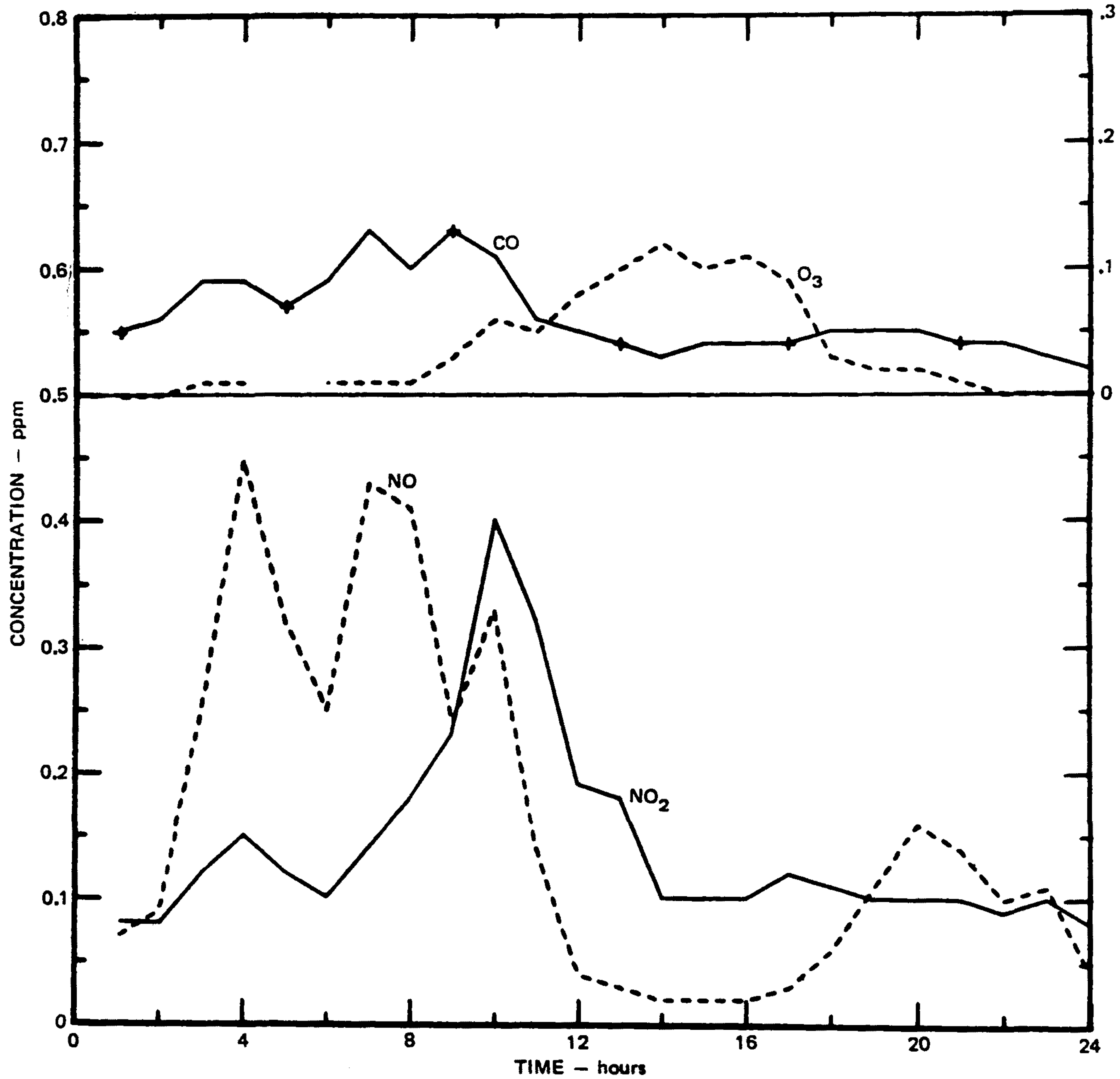


Figure 12. Example of NO_2 formation by chemical synthesis at the Los Angeles/San Pedro St. station on 6 April 1977.

CO levels are scaled by 0.01.

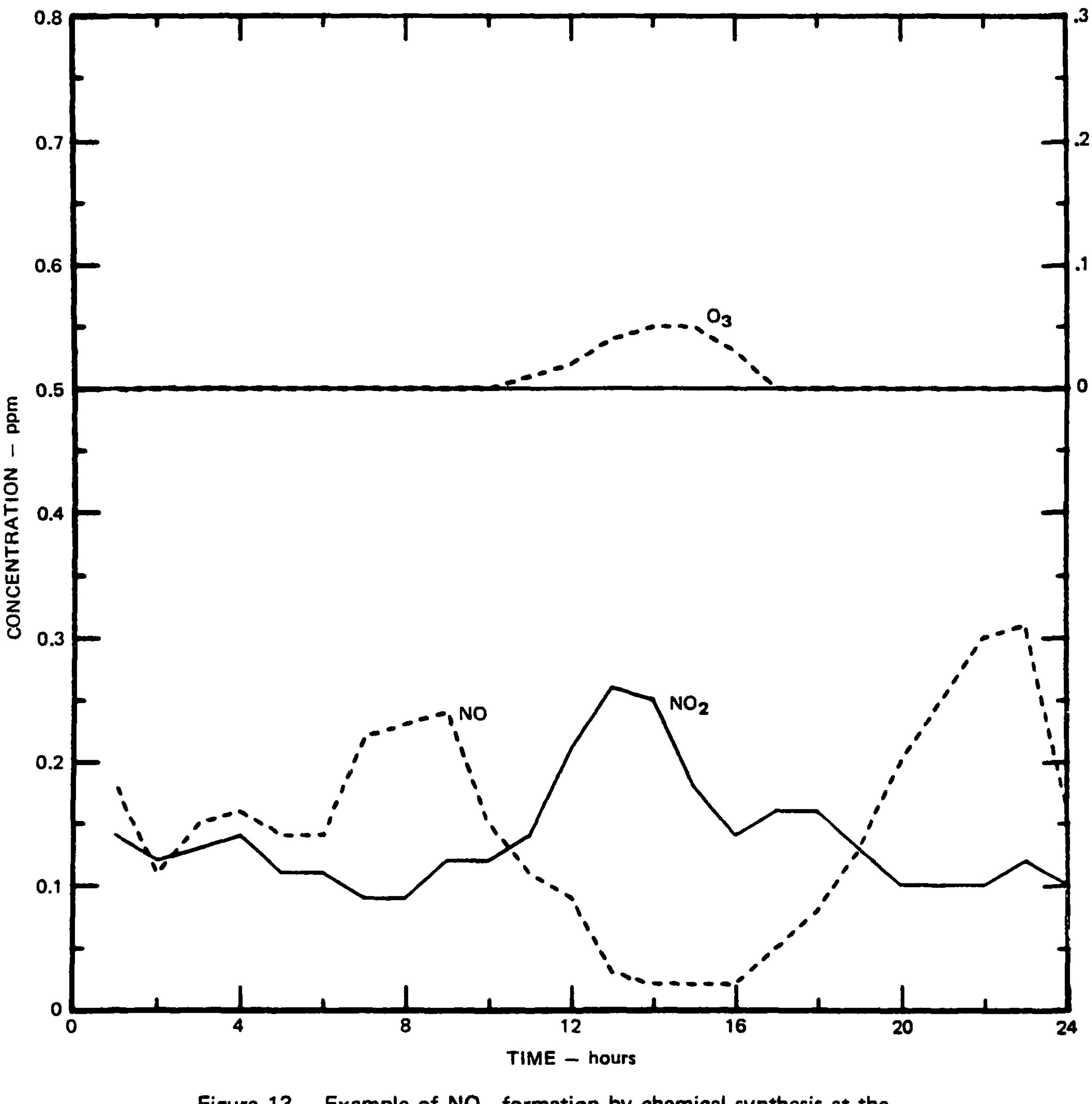


Figure 13. Example of NO_2 formation by chemical synthesis at the Temple City station on 8 February 1977.

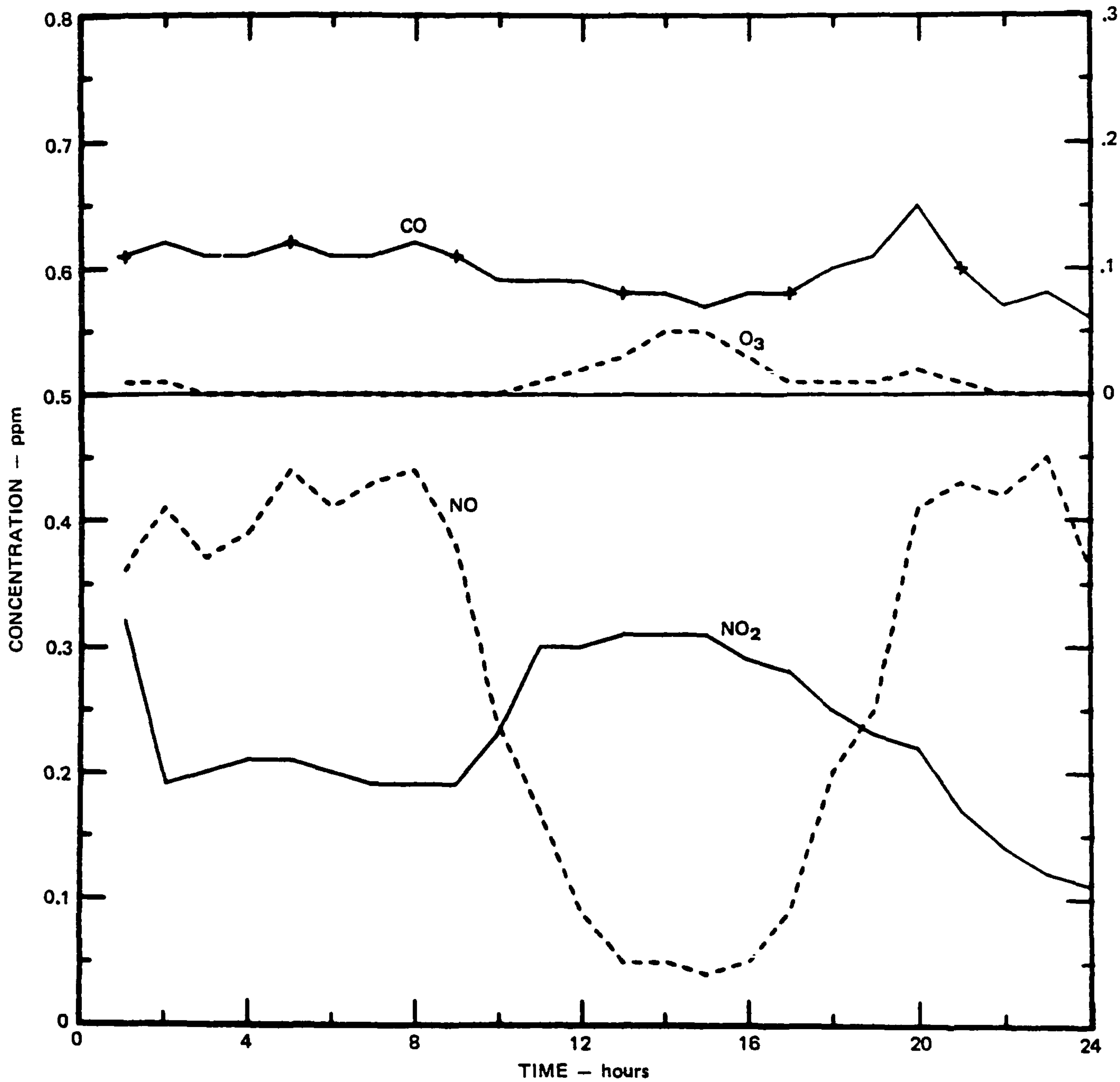


Figure 14. Example of NO_2 formation by chemical synthesis at the Temple City station on 7 December 1977.

Note the high nighttime NO_2 level carried over from previous day. CO levels are scaled by 0.01.

and Long Beach stations, so it may be related to a land/sea breeze effect.

A potential point-source effect acting jointly with chemical synthesis is shown in Figure 15 for the Whittier station. Note that the SO_2 and the NO_2 peaks coincide, and that the SO_2 concentration is substantial (this concentration is rather unusual in the Los Angeles area). The NO and NO_2 curves follow the typical synthesis pattern, but the coincidence of SO_2 and NO_2 peaks suggests that some fraction of the NO_2 concentration may be associated with a point source plume.

An example of the so-called "Sunday effect" is depicted in Figure 16, which shows pollutant histories for Sunday and Monday, 14-15 March 1976, at the Los Angeles/Westwood site. Comparison of the NO and CO curves for the two days clearly shows that mobile-source influences on Sunday differ from those on Monday. Note that the morning traffic peak is much smaller on Sunday than on Monday. Interestingly, O_3 levels are quite similar on these two days, but the O_3 peak occurs later on Sunday than on Monday, suggesting that the hydrocarbon/NO_x ratio may be lower on Sunday or that transport may be responsible. NO_2 does not seem to be affected very much by the reduced Sunday emissions, peaking at noon on both days. However, the figure shows that the NO_2 maximum on Sunday is lower than on Monday. If true in general, this would be qualitatively similar to the Sunday/weekday differences found for O_3, but the effect for NO_2 remains to be confirmed.

2. <u>Titration of NO and O_3</u>

NO_2 exceedances due to titration of NO and O_3 are portrayed in Figures 17 and 18. If the reaction $NO + O_3 \rightarrow NO_2 + O_2$ were stoichiometric, the increase in NO_2 concentration would equal the decrease in O_3 level. However, stoichiometric conditions in the atmosphere can only be approximated; the examples given are reasonable approximations. Figure 17 is a typical titration example. The San Diego/Island Avenue site is in downtown San Diego, and thus subject to traffic influences. However, 31 October 1976 is a Sunday, which accounts for the lack of pronounced CO and NO peaks during the day and for the enhanced mobile source activity that is suggested by the increase in NO and CO levels that begins around 1800. Even though it is Sunday, O_3 reaches a maximum level of 0.15 ppm (which is above the standard of 0.12 ppm). The increase in NO coincides with the decrease in O_3, and the increment in NO_2 between 1800 and 2100 is about 0.12 ppm while O_3 decreases by 0.10 ppm. Hence the titration is not stoichiometric by about 20 percent. However, it comes closer to being stoichiometric if NO_2 is reduced by 10-17 percent (see Section III for a discussion of these adjustment factors).

In the titration example shown in Figure 18 for Temple City, NO_2 levels are well above 0.20 ppm by 1600, when NO levels begin to increase. Thus, additional NO_2 produced by titration exacerbates an

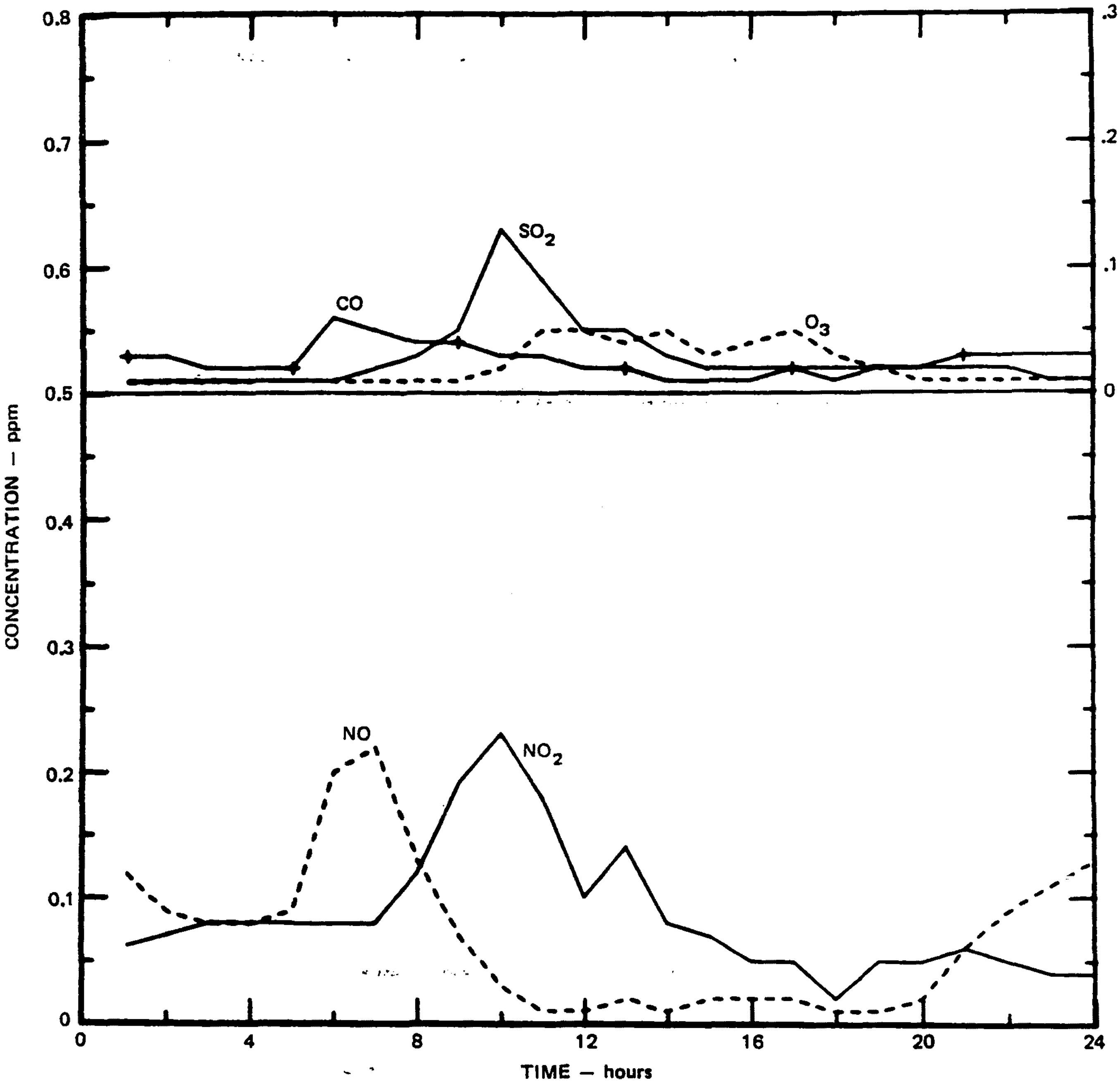


Figure 15. Example of synthesis and possible point source influence on NO_2 at Whittier on 28 August 1975.
CO levels are scaled by 0.01.

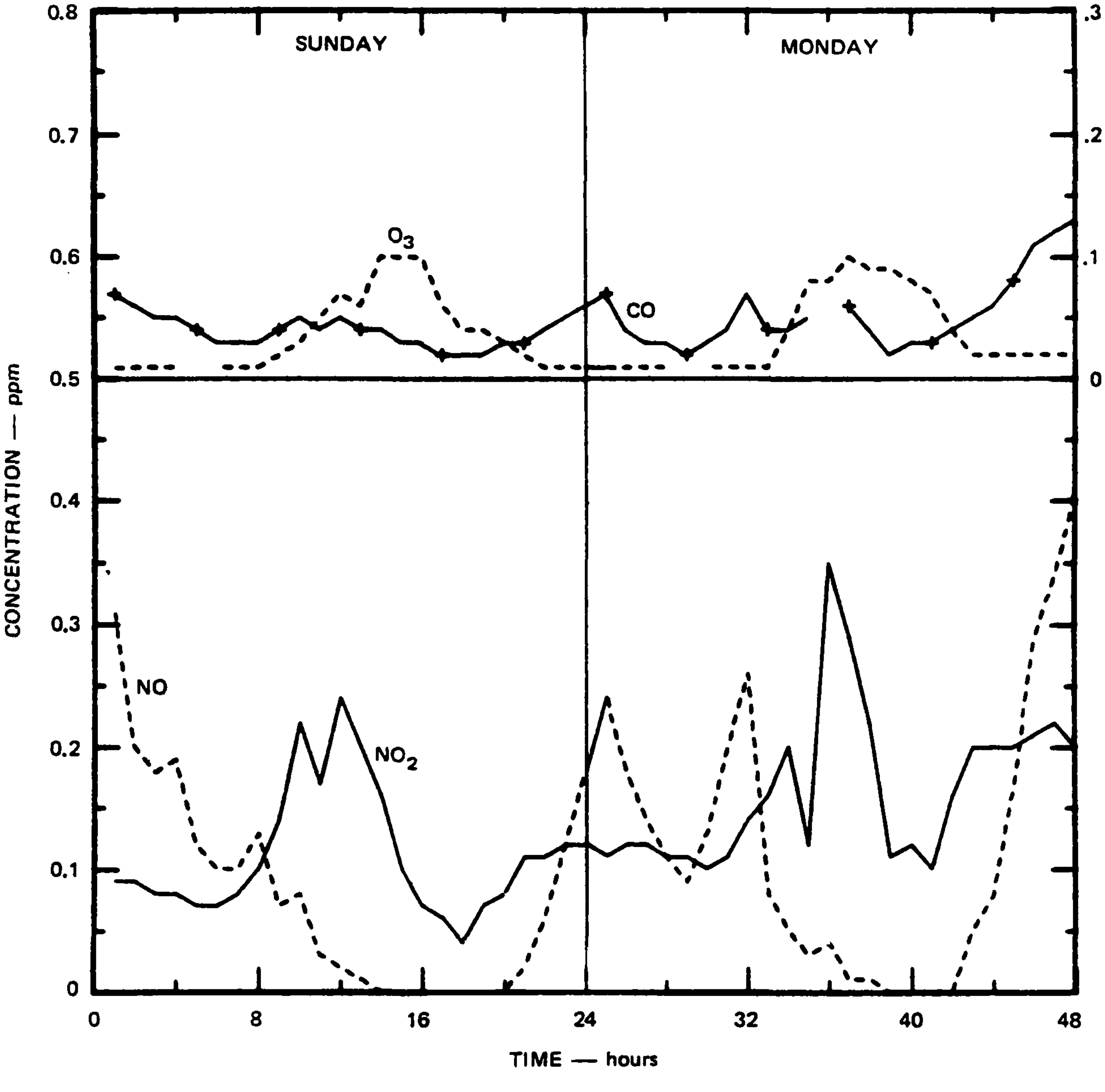


Figure 16. Example of NO_2 formation on Sunday and Monday, 14–15 March 1976, at the Los Angeles/Westwood station. CO is scaled by 0.01.

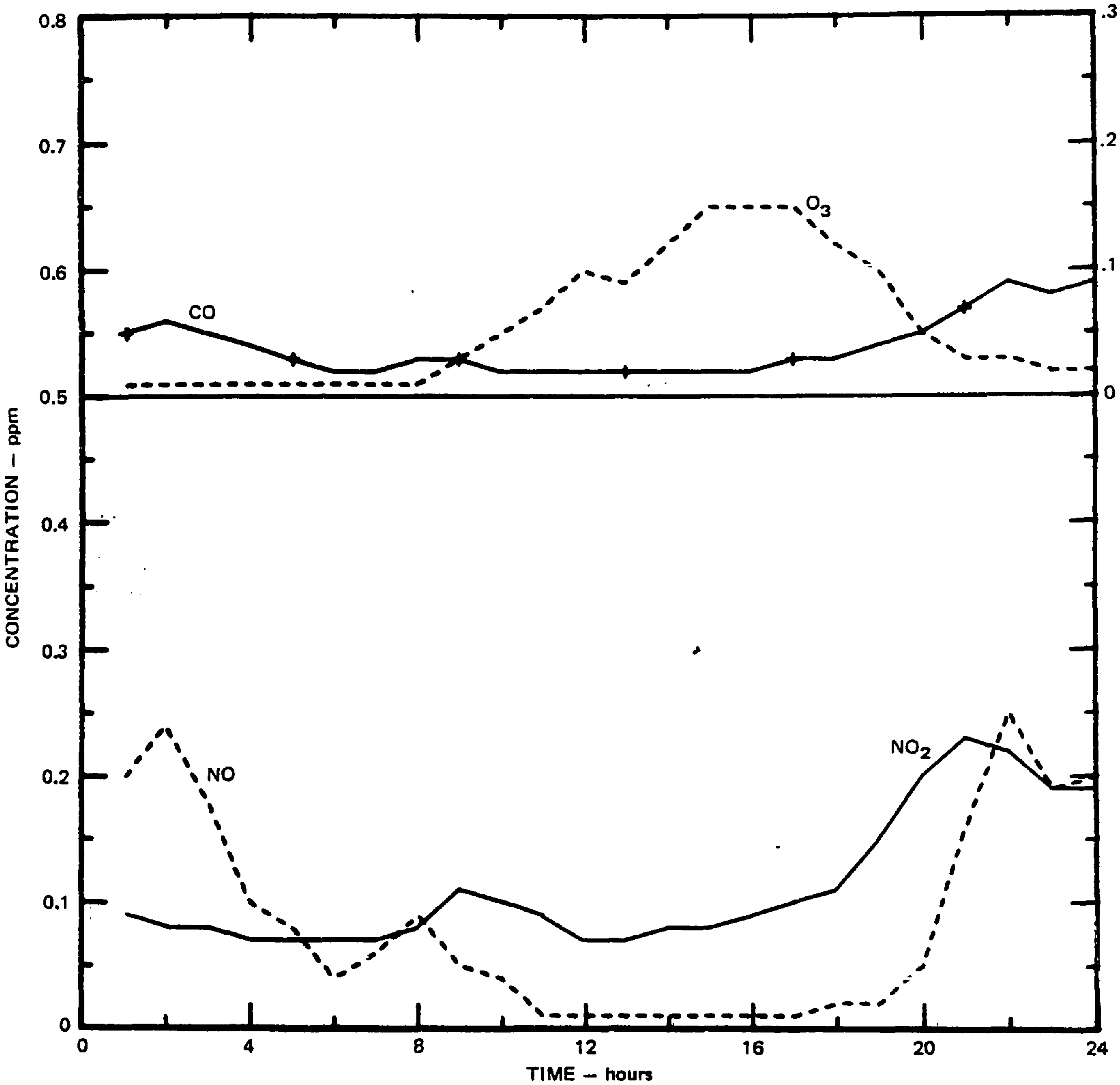


Figure 17. Example of NO_2 formation by titration at the San Diego/Island Avenue station on 31 October 1976. CO has been scaled by 0.01.

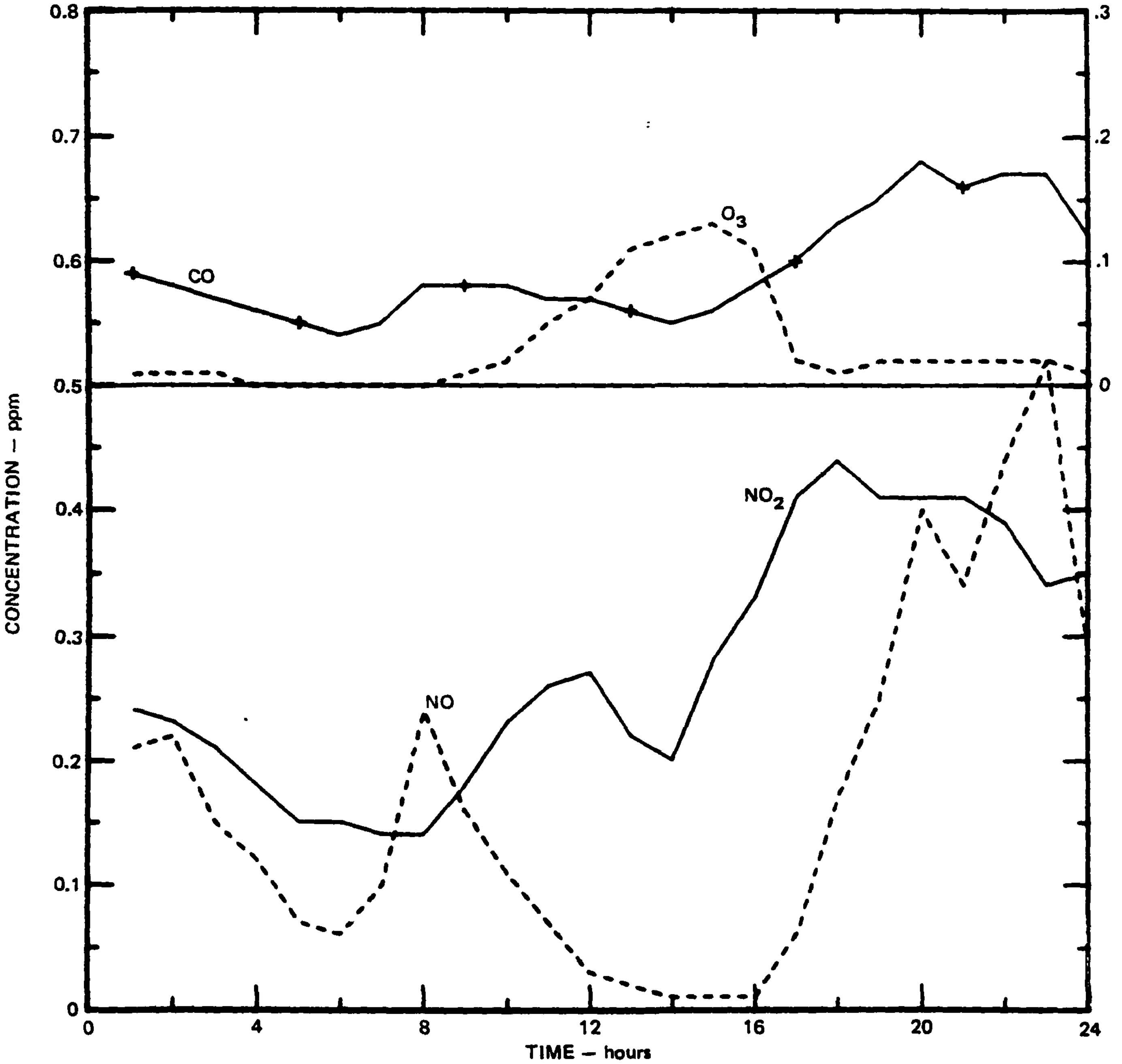


Figure 18. Example of NO_2 formation by titration at the Temple City station on 5 December 1977.
CO has been scaled by 0.01.

existing problem. From 1600 to 1800, NO_2 increases by 0.11 ppm while O_3 decreases by 0.10 ppm, which agrees closely with stoichiometric conditions. Adjusting NO_2 downward by 10 percent improves the agreement, but a 17 percent does not.

3. Transport and Point-Source Impacts

An example of NO_2 transport at the El Toro station is shown in Figure 19; the day shown is a Saturday. Note that NO_2 peaks relatively late, at 1500, and that its peak coincides with the O_3 maximum. The low NO levels indicate that most of the NO in the air mass has been converted to NO_2. The double peak in the O_3 curve often indicates transport effects: the noon peak is associated with local effects and the second peak with transport from more distant areas.

Probable point-source impacts at Long Beach and Whittier are shown in Figures 20 through 22. Figures 20 and 21 depict a Saturday/Sunday sequence at Long Beach. Figure 20 exhibits NO_2 carryover and synthesis in addition to the putative point-source effect. Note that during the day the NO_2 and SO_2 curves track each other. Both NO_2 and SO_2 show peaks of decreasing magnitude at 1200, 1500, and 1900, suggesting that a point-source plume is advecting both pollutants into the site. SO_2 concentrations are higher in Figure 21, and the NO_2 does not exceed 0.20 ppm in this case, but the NO_2 and SO_2 peaks coincide and there is no evidence of synthesis or other processes being at work. We conclude, therefore, that the NO_2 increase is most likely caused by a point source. The example in Figure 21 was chosen because it suggests an intriguing possibility: Since NO_2 did not exceed 0.20 ppm despite substantial SO_2 levels, the NO_2 contribution from point sources at this site is insufficient by itself to cause NO_2 exceedances. However, the point-source contribution could well result in NO_2 exceedances when combined with NO_2 resulting from other processes. The pattern of Figures 20 and 21 is apparent in Figure 22 for Whittier. Both SO_2 and NO_2 track each other; their peaks coincide at 1200. Evidence for other processes that form NO_2 is lacking, hence a point-source impact seems indicated. In this case, however, NO_2 exceeds 0.20 ppm. Further investigation is required to establish the relative contribution of point sources to the overall NO_2 burden when NO_2 exceedances occur.

C. Frequency and Spatial Distribution of Physical Processes

What is the relative frequency of the three physical processes associated with NO_2 exceedances? Does this frequency vary with the location of the monitoring site? Is there a statewide pattern? This section provides answers to these and other questions.

During this study, the plots of the data contained in Appendix A of this report were analyzed, and each NO_2 exceedance was assigned to one

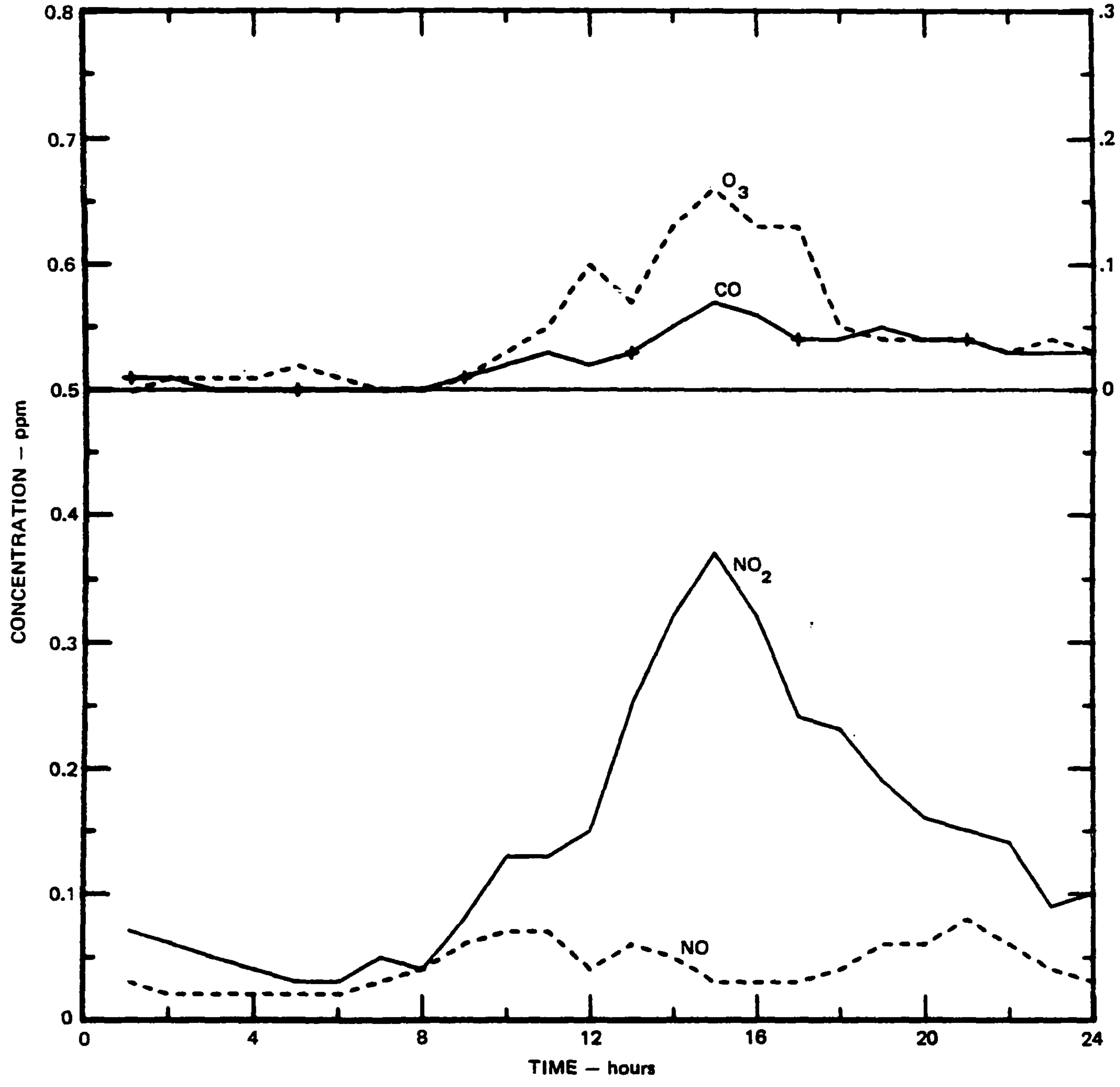


Figure 19. Example of NO_2 transport at El Toro station on 25 January 1975. CO has been scaled by 0.01

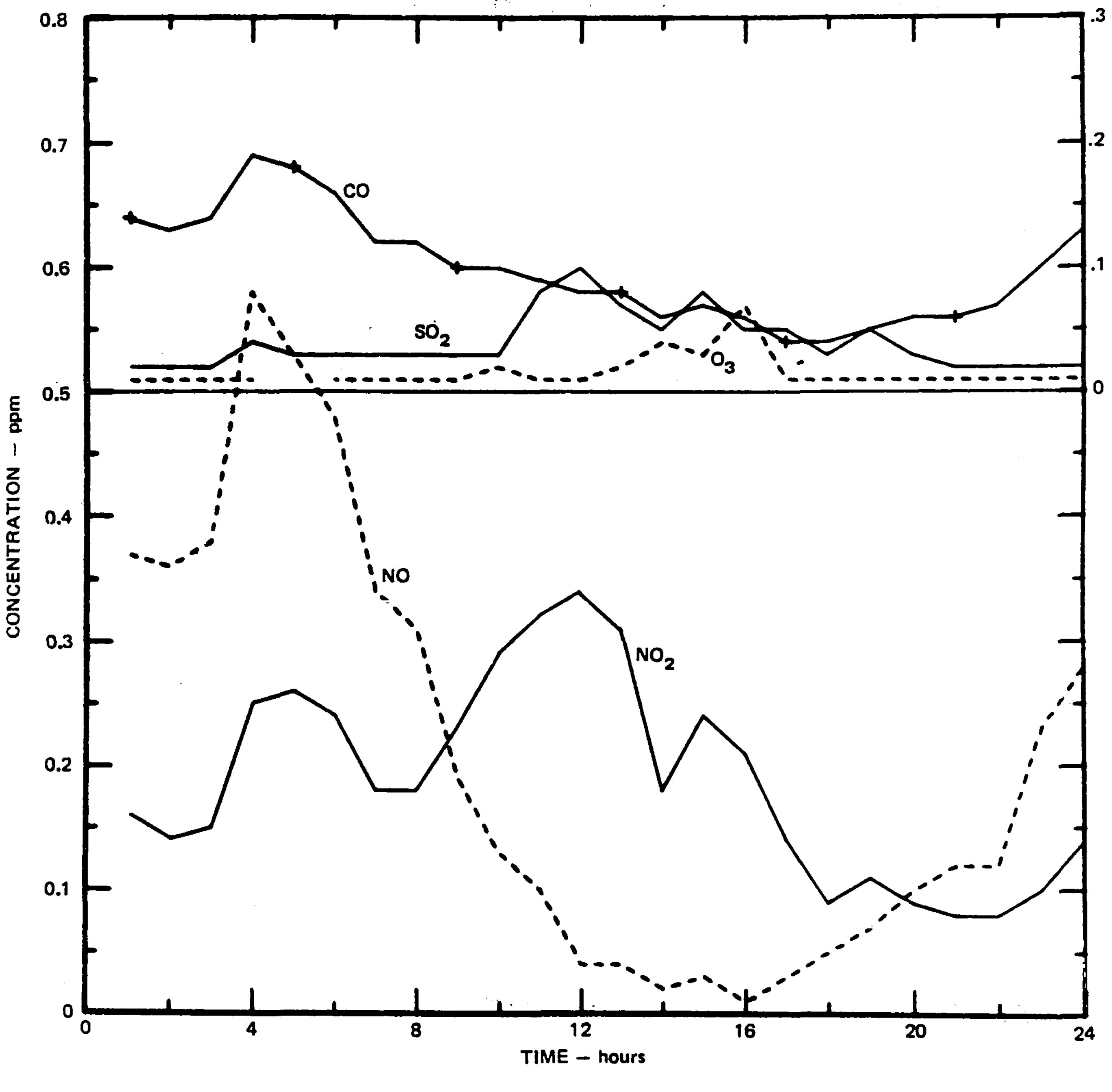


Figure 20. Example of potential point source impact at Long Beach on Saturday, 15 November 1975. CO has been scaled by 0.01.

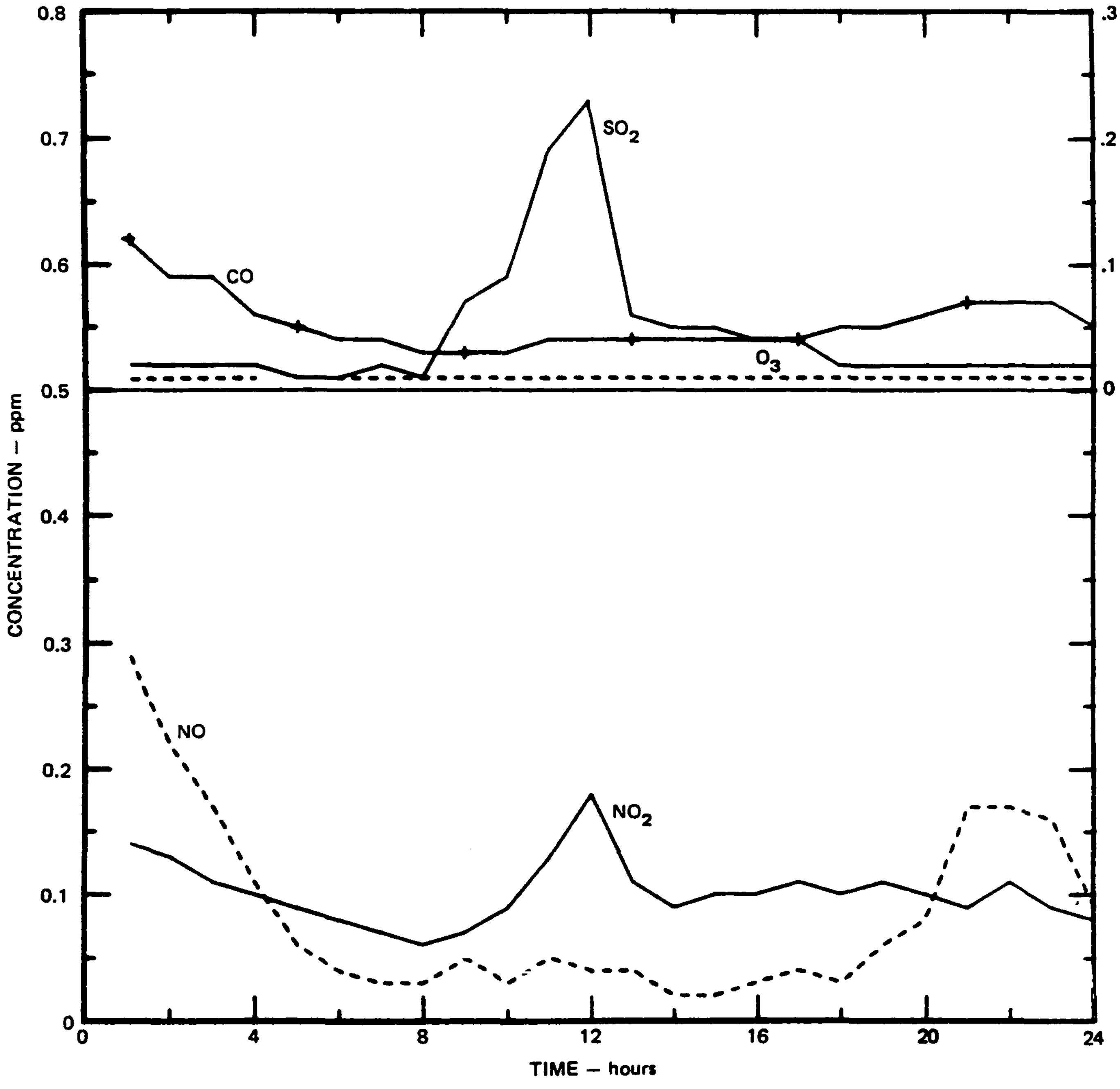


Figure 21. Example of potential point source impact at Long Beach on Sunday, 16 November 1975. CO has been scaled by 0.01.

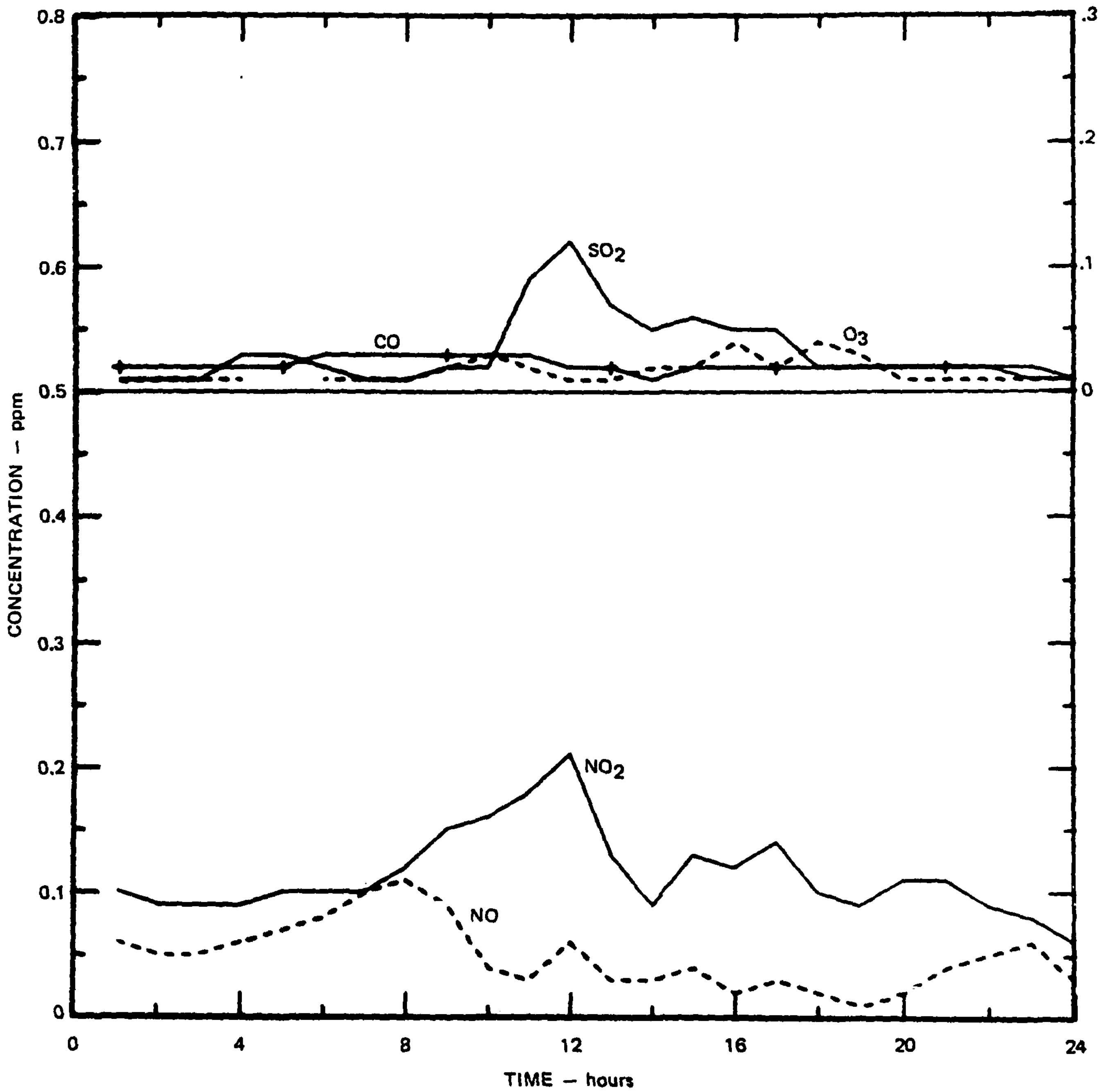


Figure 22. Example of potential point source impact at Whittier on Monday, 25 August 1975.
CO has been scaled by 0.01.

of the three categories previously defined in Section IV-A: synthesis, titration, and "other" (where the last category contains both transport and point-source effects). The resulting classification for each site is displayed in Figure 23.

Figure 23 shows both the frequency and spatial distributions of the physical phenomena. The size of each dot indicates the number of cases associated with each category (a case may consist of more than one hour): The small dot corresponds to the range 1-10 cases, the medium-sized dot to 11-50 cases, and the large dot to more than 50 cases. The order of the monitoring sites follows an approximate north/south axis, running from Sacramento in the north to Chula Vista near the Mexico-California border. Within the north/south orientation, the stations have been grouped by geograhical region, which often coincides with county boundaries. The major regions are:

- San Francisco Bay area--begins with Concord and ends with San Jose.
- The South Coast Air Basin (SCAB)
  - Los Angeles County--begins with Los Angeles/Gault St. and ends with Whittier.
  - San Bernardino County--begins with Upland and ends with Chino.
  - Riverside County--contains Riverside and Rubidoux.
  - Orange County--begins with La Habra and ends with El Toro.
- San Diego area--begins with Oceanside and ends with Chula Vista.

A small number of stations that do not belong to these three major regions are shown either separately or in small clusters.

Figure 23 indicates that in general, chemical synthesis is the predominant process associated with NO_2 exceedances. This is followed by titration and "other," in that order. Overall, synthesis is approximately 44 percent more frequent than titration, and titration is roughly eight times more frequent than transport and point-source influences. However, the relative dominance of the three categories can change drastically depending on the location of the monitoring station. These and other spatial effects are discussed below.

The spatial distribution of the NO_2 exceedances and their associated physical processes can be inferred from Figure 23. It is evident that the majority of the exceedances occur in the South Coast Air Basin, where Los Angeles County predominates. The San Diego area is second to the SCAB in number of exceedances, followed by the San Francisco Bay area. In addition to these major groupings, considerable variation exists among the various sites. Within the Bay area, Sunnyvale shows some predominance of synthesis over titration and no apparent transport or point-source effects. By contrast, Oakland shows some impact from all physical processes. Burlingame, on the other hand, shows no

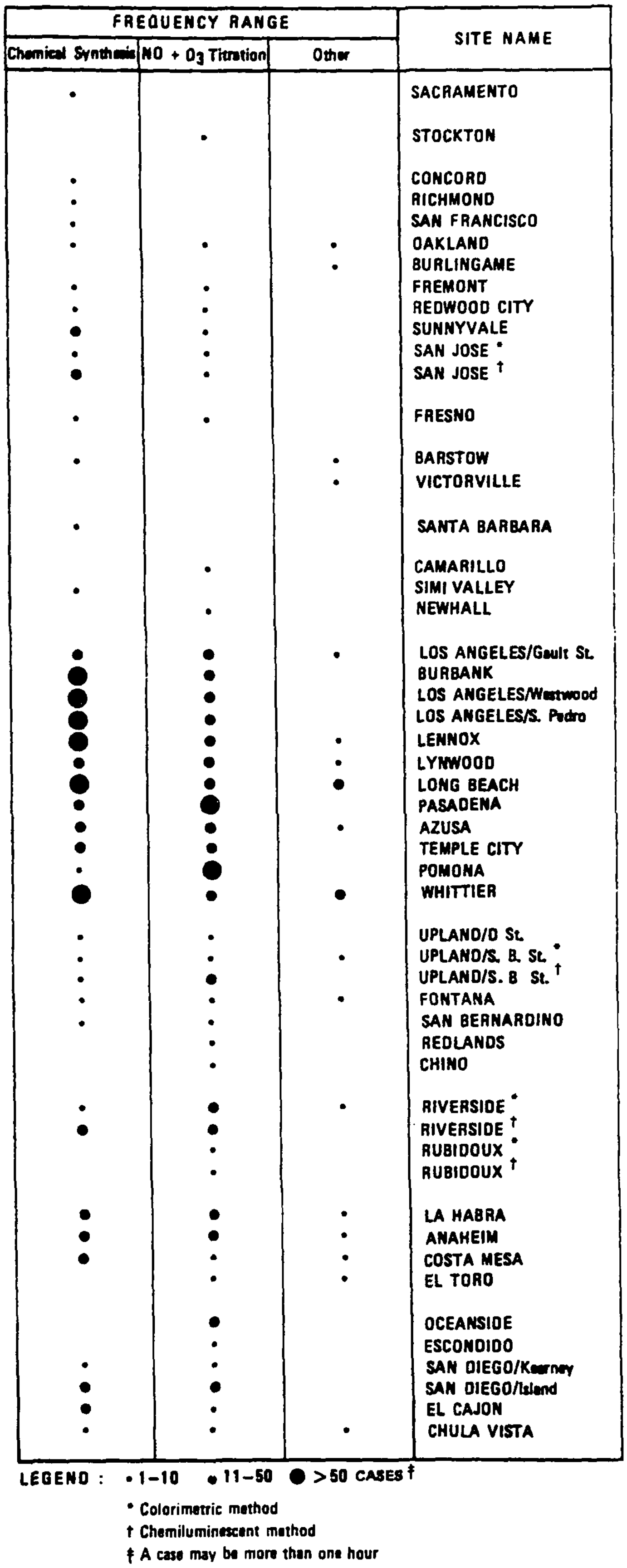


Figure 23. Physical processes in high NO_2 events classified by site.

evidence of synthesis or titration. Only synthesis is important in Concord, Richmond and San Francisco. The other sites in the Bay area are influenced by synthesis and titration, but show no transport or point-source impacts. (The San Jose station will be discussed later.)

Barstow and Victorville are located inland in relatively sparsely inhabited areas. Both are impacted primarily by transport. One possible explanation is that these sites are affected by ozone transport from urban areas, which when combined with local NO emissions yields high NO_2 levels. In this case, what appears to be transport is the result of titration. Alternatively, NO_2 transported from urban areas or from point sources could account for the exceedances. The diurnal variation of the NO_2 exceedances at these two sites (described in Section V-B) suggests transport or point-source impacts, rather than local effects. However, we were unable to identify point-source impacts because SO_2 was not monitored.

Several interesting differences are évident among the sites in Los Angeles County. Synthesis predominates at Burbank, Los Angeles/ Westwood, Los Angeles/San Pedro, Lennox, Long Beach, and Whittier. These stations are located in areas that can be considered to be source regions, i.e., areas with a high emissions density. It seems reasonable, therefore, to conclude that the prevalence of synthesis at these stations is associated with short-term effects directly related to mobile sources in their general vicinity. By contrast, the Los Angeles/Gault St. station experiences about equal influence from synthesis and titration. This station is located near a traffic corridor in the northwestern part of the country. Consequently, high NO_2 is associated both with synthesis due to short-term causes and with the titration of ozone formed during the day reacting with NO emitted by the evening commuter traffic.

Pasadena, Azusa, and Pomona are known to be recipients of ozone transported from the central basin. Thus, we expect the ozone to arrive at these sites in time to react with the evening NO peak. Accordingly, titration should play a significant role in NO_2 production. This is precisely what Figure 23 shows for Pasadena and Pomona, where titration predominates. In fact, the titration/synthesis ratio is 4/1 at Pasadena and 6/1 at Pomona. Azusa has less traffic than either Pasadena or Pomona, and the dominance of titration tends to be reduced. Although Figure 23 shows that the number of cases of synthesis and titration at Azusa fall in the same frequency range (11-50 cases), the titration/ synthesis ratio is in fact 2/1. The station at Temple City is located approximately between Azusa and Pasadena, and has appoximately a one-to-one titration/synthesis ratio: In this respect, it appears to be similar to the Los Angeles/Gault St.site.

Long Beach and Whittier are the only stations that show any significant impact from stationary sources. As Figure 23 shows, the frequency of transport/point-source effects is in the same range as the titration influence. Actually, titration occurs somewhat more frequently: the ratio of transport/titration is 0.6 at Long Beach and 0.8 at Whittier. It is not surprising that these sites show the influence of stationary sources: Section II showed that both sites are close to major clusters of stationary sources.

The San Bernardino County stations--Upland through Chino in Figure 23--are located downwind of Los Angeles County and are considered to be receptors of transported pollutants. Upland, especially, frequently exhibits some of the highest O_3 levels in the basin. However, as Section V will demonstrate, NO_2 exceedances at these sites are much less frequent than in Los Angeles County. When they occur, titration is more frequent than synthesis, as expected for ozone receptors. Chino and Redlands, in particular, experience only titration.

Data for Riverside and Rubidoux seem to be similar to that of the San Bernardino County sites. Thus, titration is the predominant effect at both sites. Riverside, but not Rubidoux, exhibits some impact due to synthesis.

La Habra and Anaheim exhibit NO_2 exceedance frequencies that are similar to those seen at Los Angeles County sites. Synthesis and titration are approximately equally important at these two stations, in keeping with their dual source/receptor character (see Section II-C for a description of wind patterns affecting these sites). Both sites also experience some minor impacts due to transport or point-source effects. The frequency of NO_2 exceedances at Costa Mesa and El Toro is much lower than at the other two sites (see Section V). Both sites are in suburban locations. The Costa Mesa station is near the coast, close to a heavily traveled highway (see Table 2): Figure 23 shows that synthesis predominates here, which is consistent with the highway influence. By contrast, the El Toro station is farther inland in an area of low population density. Titration and transport are of about equal influence at El Toro.

Two of the San Diego area sites--San Diego/Kearney and Chula Vista--are classified as suburban, and the others are in urban locations; the San Diego/Island site is downtown. Titration predominates at the suburban sites, and also at Oceanside and Escondido, but synthesis is most important at El Cajon and San Diego/Island. The prevalence of synthesis at the San Diego/Island site is consistent with similar behavior observed at source-dominated locations elsewhere. The frequency of occurrence of NO_2 exceedances at this site is also the highest of all the San Diego area stations (see Section V). The El Cajon site also seems to be located in a source-oriented area, judging by the dominance of the synthesis process.

Sites containing measurements made using both colorimetric and chemiluminescent techniques have been shown separately in Table 8. The figure clearly shows the tendency of the chemiluminescent observations to be higher than the colorimetric data, as discussed in Section III. Thus, San Jose shows a somewhat higher frequency of chemical synthesis

Table 8

DISTRIBUTION OF NO_2 EXCEEDANCES AGGREGATED FOR ALL MONITORING STATIONS, 1975-1977*

Concentration (ppm)†	Number of Hours‡	Cumulative Percentage
0.21	942	17.3
0.22	909	34.1
0.23	631	45.7
0.24	604	56.8
0.25	448	65.1
0.26	368	71.9
0.27	260	76.6
0.28	252	81.3
0.29	156	84.2
0.30	169	87.3
0.31	92	89.0
0.32	104	90.9
0.33	81	92.4
0.34	61	93.5
0.35	58	94.6
0.36	53	95.5
0.37	40	96.3
0.38	36	96.9
0.39	32	97.5
0.40	25	98.0
0.41	15	98.3
0.42	14	98.5
0.43	17	98.8
0.44	9	99.01
0.45	11	99.21
0.46	10	99.39
0.47	6	99.50
0.48	7	99.63
0.49	2	99.67
0.50	4	99.74
0.51	1	99.76
0.52	2	99.80
0.53	2	99.83
0.54	2	99.87
0.55	1	99.89
0.56	2	99.93
0.57	0	99.93
0.58	1	99.94
0.59	0	99.94
0.60	2	99.98
0.61	0	99.98
0.62	1	100.00

*Where simultaneous chemiluminescent and colorimetric measurements were made, only colorimetric data have been used in this table.

†Median = 0.24 ppm

‡Total hours = 5430

cases measured by chemiluminescence than by colorimetry. The apparent difference at Riverside is due to different lengths of the period of simultaneous measurements (see Table 5). A similar effect causes the apparent discrepancy in the titration frequency at the Upland/San Bernardino St. Station. Rubidoux does not show any apparent disagreements because the frequency of NO_2 exceedances is very low (and is below the diagram's ability to resolve it). Section V contains a further discussion of these discrepancies.

V SPATIAL AND TEMPORAL PATTERNS

Previous sections discussed some facets of the spatial variation of NO_2 exceedances. This section continues the examination of spatial patterns and considers diurnal and seasonal effects.

A. Spatial Distribution of High NO_2 Concentrations

It is useful to view the pattern of NO_2 exceedances from a statewide standpoint as well as in detail. Thus, we begin by examining the spatially aggregated frequency distribution of NO_2 exceedances, and then study their spatial distribution.

Table 8 displays the frequency distribution of NO_2 concentrations greater than 0.20 ppm, aggregated for all monitoring sites. In preparing this table, only colorimetric data were used for those sites that employed both colorimetric and chemiluminescent instruments simultaneously (see Table 5). A histogram of the distribution is shown in Figure 24. As might be expected of a tail distribution, the histogram has the shape of a decaying exponential function.

Section III-C presented the recent finding that the NO_2 data are from 10-17 percent too high. Table 8 allows us to examine the effect of adjusting the data to reflect this. The adjustment is applied using the formula $C_n = C_o/(1+a)$, where C_o = old unadjusted NO_2, C_n = new adjusted NO_2, and a = adjustment factor, $0.10 \leq a \leq 0.17$. The adjustments can be considered in either of two equivalent ways: raise the old threshold level of 0.20 ppm without altering the NO_2 data, or adjust the NO_2 data by lowering them by a factor of $1/(1+a)$ and retain the 0.20 ppm threshold. Both methods produce the same results and the choice of method is a matter of convenience. Table 9 presents the effect of the adjustment from the standpoint of the first method above. The table makes it clear that data adjustments in this range would reduce the number of exceedances between 34 and 46 percent on a statewide basis, a substantial impact. In view of this significant effect, it is apparent that regulations pertaining to an hourly NO_2 standard must specify the adjustment factor to be used.

Table 9

EFFECT OF ADJUSTING NO_2 DATA

Adjustment Factor	Old Threshold (ppm)	New Threshold (ppm)	Reduction in Exceedance Frequency (%)
0.10	0.20	0.220	34.1
0.17	0.20	0.234	45.7

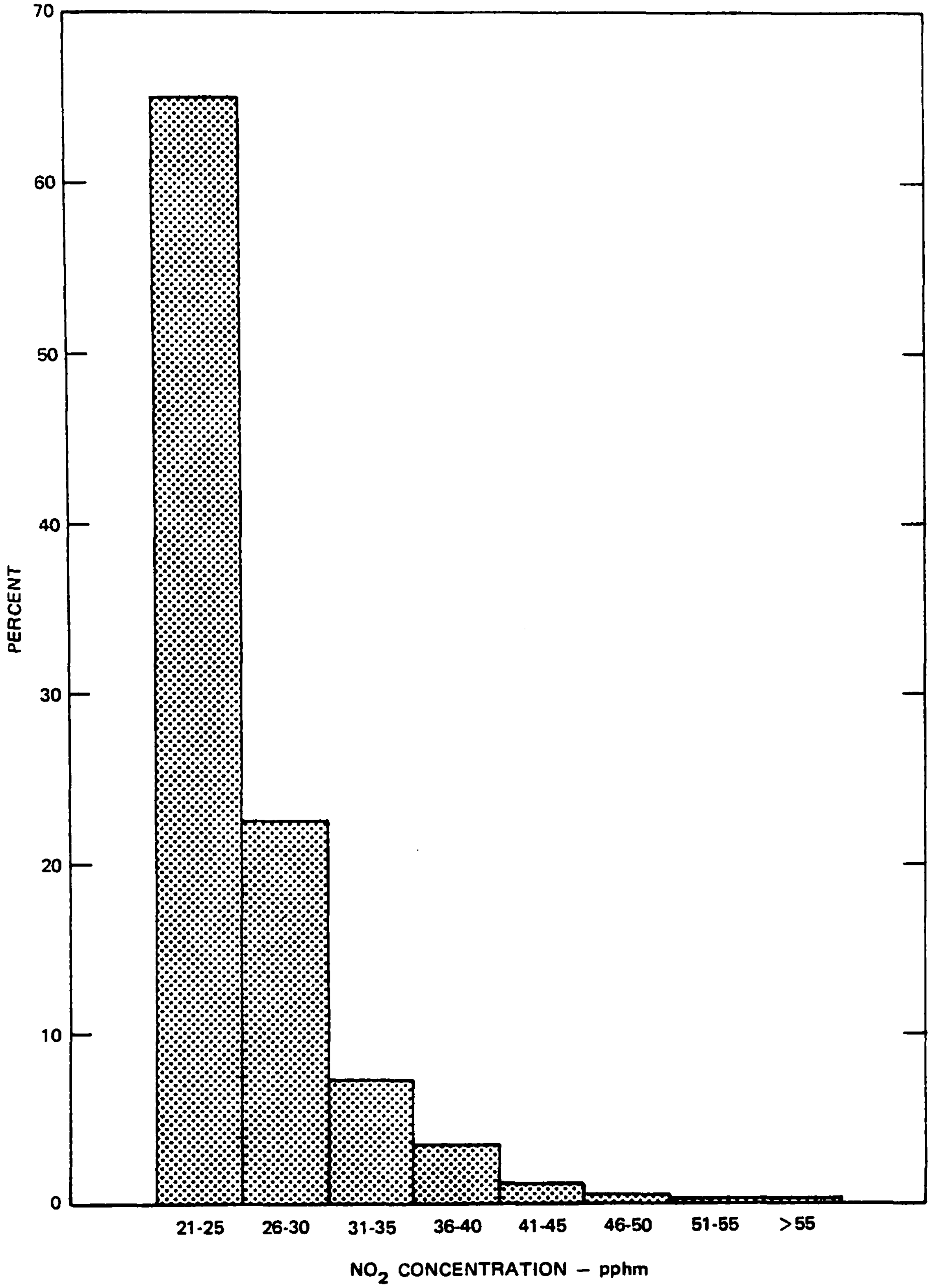


Figure 24. Histogram of the frequency distribution of NO_2 exceedances aggregated statewide.

Although Table 9 shows that data adjustments have a significant impact on a statewide basis, the effect on individual stations can be even greater. This point will be considered in the examination of the spatial distribution of NO_2 exceedances.

Figure 25 shows the range of concentrations measured at all the monitoring stations. (The figure retains the order of the sites used in Figure 23.) In addition to the concentration range, Figure 25 displays the number of hours for each site when NO_2 > 0.20 ppm (given by the number at the end of each bar). When the number of hours is greater than 10, the figure also shows the median concentration of the ensemble of NO_2 exceedances (marked by a vertical line with a dot in its center).

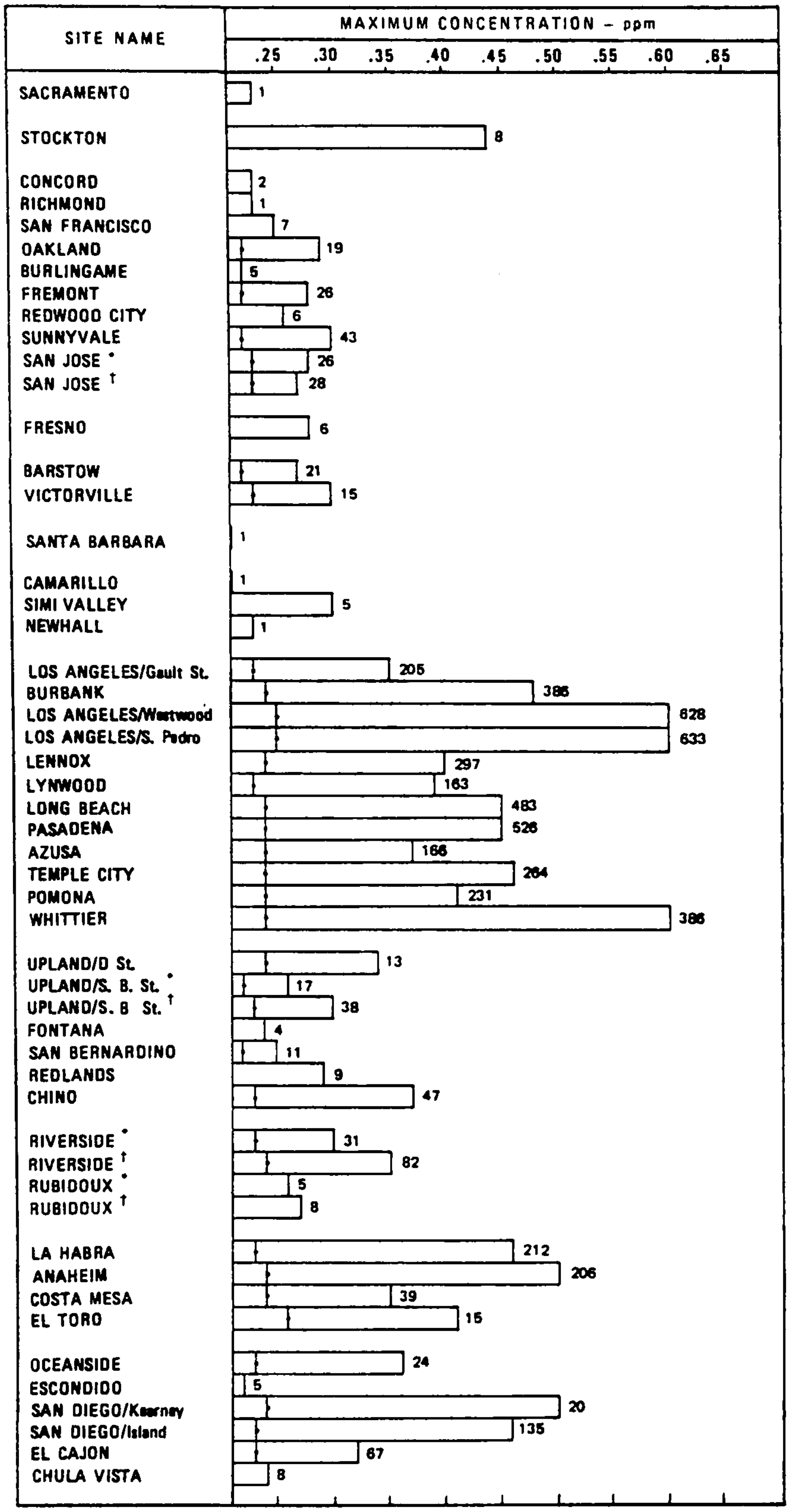
The fact that the NO_2 exceedances occur most frequently in the SCAB is clear in Figure 25. Of the 5430 total exceedances (not counting the simultaneous chemiluminescent data), 4977 are reported in the SCAB, which accounts for about 92 percent of the statewide total. Moreover, Los Angeles County alone accounts for approximately 80 percent (4368 hours) of the statewide exceedances, and for 88 percent of the SCAB's total. The Orange County sites are second to Los Angeles's with 472 hours, a 9:1 ratio in favor of the latter. It is also apparent that the sites at La Habra and Anaheim are similar to those in Los Angeles County, while the other SCAB stations differ markedly from those in Los Angeles.

A clear division exists between the northern and central California sites and those in Los Angeles and points south. The southern stations show not only a higher exceedance frequency, but also higher maximum NO_2 concentrations. Thus, except for Stockton, all the sites from Sacramento to Newhall exhibit a rather narrow range of concentrations, from 0.21 to 0.30 ppm. This range is exceeded by all twelve sites in Los Angeles County.

The stations in the San Diego area show considerable variation. Only the site located in the central business district (San Diego/Island) exhibits an exceedance frequency and a concentration range that are similar to those found in the SCAB.

It should be noted that the numerical predominance of the Los Angeles County stations is somewhat misleading because many of the sites are correlated, which results in some degree of multiple counting. More detailed investigation, which is beyond the scope of this work, is required to unravel fully the interstation dependencies. However, Section V-D presents the results of an analysis that sheds some light on this problem.

As noted earlier, adjusting the data can have a very large impact on some individual sites. For example, Figure 25 suggests that a 17 percent adjustment would eliminate several stations from among those reporting NO_2 exceedances. The percent reduction in the exceedance frequency for individual sites is listed in Table 10 for both 10 and 17



* Colorimetric method
† Chemiluminescent method

Figure 25. Spatial distribution of NO_2 concentrations exceeding 0.20 ppm. Number at end of bar indicates hours exceeding 0.20 ppm. Vertical line with a dot marks the location of the median concentration.

Table 10

REDUCTION OF NO_2 EXCEEDANCE FREQUENCY
AT INDIVIDUAL STATIONS AFTER DATA ADJUSTMENT

Site Name	Ajustment Factor	
	10%	17%
Sacramento	0	100
Stockton	25	38
Concord	50	100
Richmond	0	100
San Francisco	43	57
Oakland	53	68
Burlingame	100	100
Fremont	58	65
Redwood City	50	83
Sunnyvale	58	67
San Jose*	46	65
San Jose†	36	57
Fresno	50	67
Barstow	62	71
Victorville	40	67
Santa Barbara	100	100
Camarillo	100	100
Simi Valley	0	40
Newhall	0	100
Los Angeles/Gault St.	42	58
Burbank	36	49
Los Angeles/Westwood	23	32
Los Angeles/San Pedro	25	35
Lennox	38	49
Lynwood	42	56

Site Name	Adjustment Factor	
	10%	17%
Long Beach	33	42
Pasadena	32	43
Azusa	39	49
Temple City	31	42
Pomona	34	47
Whittier	33	46
Upland/D St.	23	31
Upland/San Bernardino St.*	53	76
Upland/San Bernardino St.†	50	58
Fontana	50	75
San Bernardino	55	91
Redlands	22	33
Chino	40	60
Riverside*	45	65
Riverside†	38	49
Rubidoux*	40	60
Rubidoux†	63	63
La Habra	40	54
Anaheim	37	49
Costa Mesa	36	49
El Toro	0	13
Oceanside	38	54
Escondido	100	100
San Diego/Kearney	30	30
San Diego/Island	46	56
El Cajon	61	76
Chula Vista	63	88

*Colorimetric method

†Chemiluminescent method

percent adjustment factors. The table shows that a 17 percent adjustment eliminates nine sites, whereas the 10 percent factor eliminates four. For the San Francisco Bay area stations, it is apparent that either adjustment would mitigate considerably the magnitude of the high NO_2 problem. The same applies to other sites outside the SCAB, as well as to the stations in San Bernardino and Riverside counties. Thus, adjusting the data to improve its accuracy has the effect of further limiting the occurrence of high NO_2 levels to the SCAB in general and to Los Angeles County in particular.

Figure 25 provides further evidence of the high incidence of NO_2 exceedances that is associated with source-dominated areas. As mentioned in Section IV-C, Burbank, Los Angeles/Westwood, Los Angeles/San Pedro, Lennox, Long Beach, and Whittier are areas with high traffic density, where chemical synthesis is the most common mechanism leading to NO_2 exceedances. Figure 25 shows that these sites also have some of the highest exceedance frequencies and experience a wide range of concentrations. Pasadena is the only other site that is in the same class with respect to number of exceedances, and it is a hybrid which combines the characteristics of both source and receptor sites. The association between high exceedance frequency, NO_2 levels, and source density is also apparent at La Habra, Anaheim and San Diego/Island. By contrast, those sites which are located beyond areas of high source density, e.g., Azusa, Riverside, Chino, and El Cajon, show lower exceedance counts and NO_2 concentrations.

However, differences in emissions density alone cannot explain the statewide pattern of high NO_2 events. The Bay area sites are located in high traffic-density areas, yet the incidence of NO_2 exceedances and the maximum NO_2 levels reached are well below those for Los Angeles. Clearly, the north-south differences are heavily influenced, if not controlled, by the marked variation in climate encountered in these two parts of the state. The north is generally cooler, windier, and has cleaner air: the south, of course, has a warmer climate, and more smog.

Figure 25 shows differences in exceedance frequency and in maximum concentration at those sites where both colorimetric and chemiluminescent measurements were obtained. We caution, however, that the discrepancy in exceedance frequency at Upland/San Bernardino St., Riverside, and Rubidoux is explained by the fact that one instrument operated three years, and the other two (see Table 5). The two techniques were used for three years at San Jose; there is a slight difference in the exceedance frequency as well as in the maximum NO_2 concentration reached at this site.

B. Seasonal and Diurnal Variations

The analysis presented here seeks to answer the following questions:

- How does the NO_2 exceedance frequency change with season and with time of day?
- Do the concentrations of NO_2 that exceed 0.20 ppm vary with time of day? If so, what is the variation?

The seasonal and diurnal fluctuations of NO_2 exceedances should provide some indications about the forcing function, i.e., the emissions, that drives the source/atmosphere system. They should also furnish evidence about the links between the physical processes discussed in Section IV and the exceedance frequency. The clues obtained from the study of seasonal variations prompted the investigation of seasonal patterns in stationary-source emissions in the SCAB which is described in Section V-C.

The second question is aimed at determining the relative strength of the various physical processes leading to NO_2 exceedances. What differences, if any, exist between the NO_2 concentrations associated with synthesis, titration, and other influences such as transport? This is studied by comparing the distribution of NO_2 levels that exceed 0.20 ppm stratified for three time intervals, on the assumption that the various physical processes follow some regular pattern of diurnal variation. This analysis is conducted at several selected stations, because the assumption is more likely to be satisfied at those sites and because the respective data bases are extensive.

Seasonal and diurnal changes in the NO_2 exceedance frequency are displayed for all the sites in Figure 26, where the order of the monitoring stations is the same as in Figure 23 (Section IV-C). The seasonal fluctuations are shown in the right side of Figure 26. Note that each column corresponds to a month, and that the calendar has been arranged so that December and January appear next to each other in the center of the panel. The figure shows that NO_2 exceedances have a strong seasonal component; the exceedances occur most frequently during November-February. It is clear that the phenomenon occurs statewide, although the effect is less pronounced outside southern California owing to the lower exceedance frequency. Meteorological conditions are largely responsible for the seasonal variation, since it is well known that the mixing layer is shallower in the winter, thereby leading to higher levels of nitrogen oxides (NO_x). However, it is possible that higher NO_x emissions from increased space heating and other sources contribute to the problem in the winter months. Since this may be important for regulatory purposes, Section V-C examines the seasonal component of NO_x emissions in the SCAB.

Diurnal fluctuations in the exceedance frequency are displayed in the left side of Figure 26. The columns of the panel correspond to the

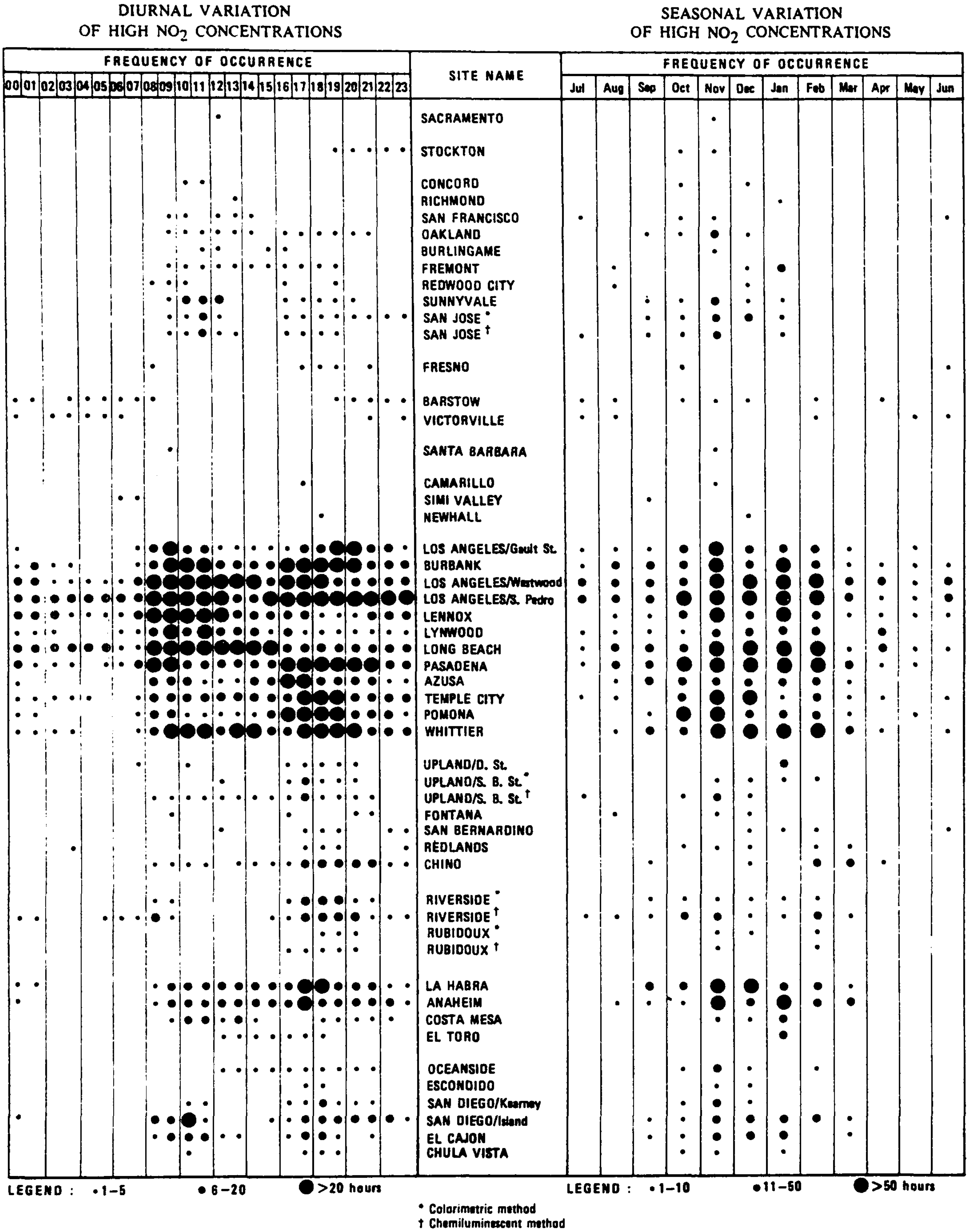


Figure 26. Diurnal and seasonal variation of NO_2 exceedance frequency.

24 hours of the day, running from 0 to 23, one pair of hours to a column. The figure shows some clustering for the hours 0800-1300 and 1600-2000. In general, sites where synthesis predominates have clusters in the morning hours; stations where titration is dominant have clusters in the 1600-2000 period. The Bay area stations contain several examples of the morning-clustering effect, as do Lennox and San Diego/Island in the south. Pasadena, Azusa, Temple City, and Pomona display clusters during the evening, in keeping with the fact that titration is important at these sites. The hybrid source/receptor character of Pasadena is evident in the double cluster it exhibits: one cluster for 0800-0900 corresponding to synthesis and one for 1600-2100 corresponding to titration.

Many other similar patterns can be observed. Comparing Figure 26 with Figure 23 yields more insights about the diurnal variation of the various physical processes.

Figure 26 shows that the NO_2 exceedances recorded in Stockton, Barstow, and Victorville occur only at night. This suggests that transport or point sources or both are probably responsible for the high NO_2 observed at these locations. Examination of the plots of NO_2 concentration for these two sites (see Appendix A) reveals that many exceedances are sudden pulses of short duration, which is an attribute commonly found in point-source impacts. However, such occurrences cannot be confidently attributed to point sources because SO_2 was not monitored.

Are NO_2 levels associated with synthesis greater, smaller, or equal to those linked to titration or other physical causes? To answer this question, we divided the calendar day into three 8-hour intervals (0-0500 and 2200-2300,* 0600-1300, and 1400-2100) and compared the frequency distributions of NO_2 levels corresponding to each time interval. The rationale for this approach is that synthesis is generally a morning phenomenon, titration usually occurs in the afternoon and early evening, and other processes are more common at night. Consequently, we associate synthesis with the period 0600-1300, titration with the interval 1400-2100, and other factors with the hours 0-0500 and 2200-2300. Although this approach is only an approximation, it is a practical means for tackling this problem, since the volume of data precludes an hour-by-hour classification of each NO_2 exceedance.

Nine monitoring stations were selected for the analysis because each has an extensive data base and because the correspondence between physical processes and time of day is likely to be satisfied in the majority of cases. The nine sites are: Anaheim, Azusa, Lennox, Long Beach, Los Angeles/San Pedro St., Los Angeles/Westwood Blvd., Pasadena,

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*The first interval is designated and 0-0500 and 2200-2300, rather than 2200-0500, to emphasize that there is no crossover between calendar days.

Whittier, and San Diego/Island Avenue. The first eight stations are in the SCAB and the last is in the city of San Diego. The prevalence of various physical processes among the stations is another criterion for selecting these stations.

The frequency distributions of NO_2 levels for the three time intervals were tested statistically for homogeneity. The test is based on the chi-square statistic and indicates any statistically signficant differences between the distributions (c.f. Dixon and Massey, 1957). The distributions are said to be homogeneous if no statistically significant difference can be detected. The null hypothesis is that the distributions are homogeneous, and the alternative hypothesis is that they are not. The null hypothesis is rejected or not depending on the value of the chi-square statistic. If the null hypothesis is not rejected (i.e., if it is "accepted"), the implication is that the physical processes at work at various times of day yield NO_2 concentrations that are similar. Conversely, if the null hypothesis is rejected, we infer that significant differences exist in the NO_2 levels associated with the various time intervals (and by assumption, with the physical factors corresponding to those intervals).

The frequency distributions for the nine stations and corresponding chi-square statistics are shown in Table 11. In several instances, all three distributions could be compared simultaneously, but in some cases only the 0600-1300 and 1400-2100 distributions could be compared because certain technical assumptions of the chi-square test were not satisfied when the night distribution was included (see Dixon and Massey, 1957). Table 11 shows that the night distribution was excluded from the comparison at Anaheim, Azusa, Whittier, and San Diego/Island Avenue. This may in itself be significant, since it suggests that the processes operating at night at these sites differ qualitatively from the daytime and early-evening processes.

It can be seen in Table 11 that the homogeneity hypothesis is rejected for the 0600-1300 and 1400-2100 distributions at Anaheim and Los Angeles/Westwood Blvd. NO_2 exceedances are more common during 1400-2100 than during 0600-1300 at Anaheim, while the opposite is true at Los Angeles/Westwood Blvd. However, at both sites there are more high values (>32 pphm) during the period 0600-1300, suggesting that synthesis yields more high NO_2 levels than titration at these two sites.

No statistically significant difference (with significance level of 0.05) was detected among the three distributions at Lennox, Los Angeles/San Pedro St., and Pasadena. Thus, at these three sites the various physical processes yield statistically indistinguishable NO_2 concentrations, although the frequency of occurrence differs substantially among the three time intervals.

Long Beach and Los Angeles/Westwood Blvd. exhibit significant differences when all three distributions are considered. However, the homogeneity hypothesis cannot be rejected at Long Beach for the periods

Table 11

COMPARISON OF FREQUENCY DISTRIBUTIONS OF NO_2 LEVELS
OCCURRING IN DIFFERENT TIME INTERVALS

Site Name/ Time Interval (PST)	Hours in Specified Concentration Range					Total Hours	Statistical Analysis		
	21-23 pphm	24-26 pphm	27-29 pphm	30-32 pphm	> 32 pphm		Chi-Square	Degrees of Freedom	Homogeneity* Hypothesis
Anaheim									
0-0500 and 2200-2300	9	2	0	0	0	11	†		
0600-1300	26	13	6	6	10	61	10.30	4	1
1400-2100	66	34	21	7	6	134	10.30	4	1
Azusa									
0-0500 and 2200-2300	4	5	0	0	0	9	†		
0600-1300	14	9	6	2	0	31	2.37‡	3	2
1400-2100	64	41	12	3	6	126	2.37‡	3	2
Lennox									
0-0500 and 2200-2300	33	13	4	1	5	56	7.66	8	2
0600-1300	85	54	25	8	13	185	7.66	8	2
1400-2100	28	15	5	5	3	56	7.66	8	2
Long Beach									
0-0500 and 2200-2300	47	20	9	7	4	87	15.69	8	3
0600-1300	101	71	37	31	36	276	7.43	4	3
1400-2100	54	33	17	10	6	120	7.43	4	3
Los Angeles/San Pedro St.									
0-0500 and 2200-2300	52	32	12	12	17	125	13.63	8	2
0600-1300	94	75	39	34	68	310	13.63	8	2
1400-2100	73	50	31	19	25	198	13.63	8	2
Los Angeles/Westwood Blvd.									
0-0500 and 2200-2300	25	19	14	3	0	61	29.48	8	4
0600-1300	114	99	59	33	81	386	13.97	4	4
1400-2100	63	46	40	15	17	181	13.97	4	4
Pasadena									
0-0500 and 2200-2300	21	16	4	1	0	42	12.83	8	2
0600-1300	54	30	21	7	9	121	12.83	8	2
1400-2100	153	94	46	27	43	363	12.83	8	2
Whittier									
0-0500 and 2200-2300	15	10	1	0	0	26	†		
0600-1300	87	41	17	16	25	186	6.02	4	2
1400-2100	74	52	22	11	15	174	6.02	4	2
San Diego/Island Ave.									
0-0500 and 2200-2300	10	4	0	0	0	14	†		
0600-1300	24	14	7	4	3	52	7.74	4	2
1400-2100	42	18	8	1	0	69	7.74	4	2

*Notes: α = significance level, 1 = rejection with $\alpha = 0.05$; 2 = acceptance with $\alpha = 0.05$; 3 = rejection for all three distributions but not for 0600-1300 and 1400-2100 with $\alpha = 0.05$; 4 = rejection for all three distributions and for 0600-1300 and 1400-2100, $\alpha = 0.05$.

†Distribution excluded.

‡Last two concentration ranges combined for comparison purposes.

0600-1300 and 1400-2100. This indicates that nighttime conditions at Long Beach differ quantitatively, and possibly qualitatively, from those that exist at the other time intervals. Recalling that Long Beach is situated in an area with a high density of stationary sources, it is possible that the difference revealed in Table 11 may be caused by the predominance of mobile sources during the day and early evening and of stationary sources at night. We saw earlier that at Los Angeles/ Westwood Blvd. the homogeneity hypothesis was rejected for the 0600-1300 and 1400-2100 distributions. Thus, all three distributions differ significantly at this station, which indicates that the physical processes operating here are well-differentiated with time of day: This is the only station that showed this feature.

Azusa, Whittier, and San Diego/Island Avenue did not exhibit any statistically significant differences between the 0600-1300 and 1400-2100 distributions. Evidently, the physical processes operating during these periods yield similar NO_2 levels.

C. Seasonal Emissions Patterns in the South Coast Air Basin

The previous section discussed the strong seasonal component in the frequency of NO_2 exceedances. Specifically, it was noted that the exceedance frequency increases during the period November through February. This phenomenon was most strongly manifested at the SCAB stations. Here we examine seasonal effects in NO_x emissions in the SCAB to see whether they follow a pattern similar to that of the NO_2 exceedances.

NO_x emissions from stationary sources have been studied in detail by Bartz et al. (1974). Figure 27 shows the estimated monthly variation in NO_x emissions for the period July 1972-June 1973. Note that the emissions reach a maximum in December and January, which coincides with part of the period when the number of NO_2 exceedances increases. Most of the December-January peak is due to increased emissions from residential, small commercial, and small industrial sources rather than to the large point sources. This may pose some problems in the formulation of strategies for controlling high NO_2 levels.

The top curve of Figure 27 also shows monthly emission factors normalized to mean monthly emissions. For example, June shows a factor of 0.98, which means that in June emissions are 98 percent of the monthly mean. Thus, December and January respectively contain 129 and 139 percent of mean monthly emissions.

The next step is to include the effect of mobile sources, since they contribute between 60 and 70 percent of total NO_x emissions on an annual basis. The seasonal component of mobile-source emissions was estimated from the literature for both light- and heavy-duty vehicles (Goodman et al., 1977; Arledge and Tan, 1978). Unfortunately, the available seasonal data for mobile sources were not given for each

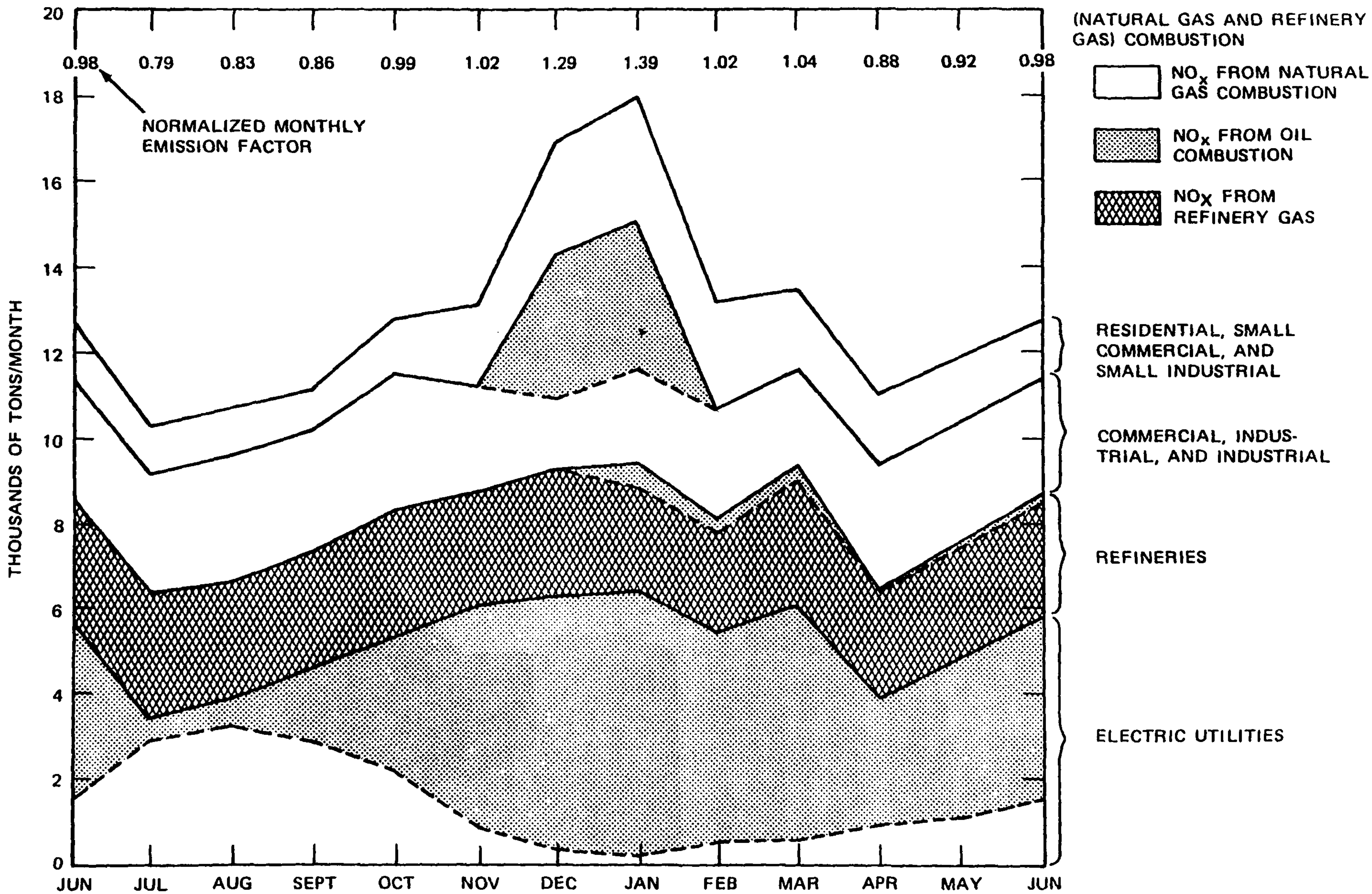

Figure 27. Monthly variation of NO_x emissions for the period July 1972–June 1973 for the South Coast Air Basin. (Adapted from Bartz, et al., 1974)

month, but were instead aggregated by quarter. The stationary-source data were similarly aggregated, and the quarterly factors for the three source categories are given in Table 12 and compared in Figure 28. Note that mobile-source emissions are out of phase with the stationary sources. This enhances the impact of the latter in the winter months.

To estimate the composite effect of stationary and mobile sources, we obtained emission estimates for the SCAB for 1976, applied the quarterly emission factors, and computed for each quarter: (1) the composite factor for total NO_x emissions; (2) the ratio of stationary to total emissions; (3) the ratio of stationary to mobile-source emissions. The estimated mean NO_x emissions for the three source types are given in Table 13. Items (1)-(3) above are contained in Table 14. The fourth column of Table 14 shows that emissions during January-March are about 5 percent higher than mean levels. It is apparent from the second and third columns of the table that this slight enhancement is due to stationary sources. The table also indicates that two of the other quarters exhibit hardly any change, and that there is a decrease of 5 percent during July-September that is also driven by stationary sources.

The evidence points to enhanced NO_x emissions driven by stationary sources during the winter months. It is probable that the increase would have been greater than 5 percent had the months been treated individually or been aggregated differently, e.g., by keeping December and January together. Unfortunately, we were constrained to use the quarterly aggregation used for the mobile sources. While 5 percent does not seem significant, this is an average figure for the entire basin that masks the impact at individual stations. Since the emissions are not distributed uniformly, it is quite possible that certain areas of the SCAB, particularly those with high residential and commercial density, may experience wintertime increases in NO_x emissions that are greater than 5 percent.

More research is needed to elucidate the role of enhanced NO_x emissions in inducing high NO_2 levels. The analysis described above provides a qualitative indication that the seasonal component of the emissions is compatible with its counterpart for the NO_2 exceedances.

D. Association Between NO_2-Monitoring Stations in the South Coast Air Basin

Are NO_2 exceedances reported in the SCAB linked to individual stations, or are they a manifestation of a regional phenomenon? This section attempts to answer this question by investigating the degree of association between various stations.

Fifteen stations were selected for the analysis: Anaheim, Azusa, Burbank, La Habra, Lennox, Long Beach, Los Angeles/San Pedro St., Los Angeles/Gault St., Los Angeles/Westwood Blvd., Lynwood, Pasadena, Pomona, Temple City, Riverside, and Whittier. The sites were selected

Table 12

QUARTERLY FACTORS FOR NO_x EMISSIONS
IN THE SOUTH COAST AIR BASIN

Period	Stationary Sources*	Light-Duty Vehicles†	Heavy-Duty Vehicles‡
Jan-Mar	1.15	1.00	0.93
Apr-Jun	0.93	1.04	1.03
Jul-Sep	0.83	1.01	1.07
Oct-Dec	1.10	0.95	0.97

*Estimated from Bartz et al. (1974)

†Estimated from Goodman et al. (1977)

‡Estimated from Arledge and Tan (1978)

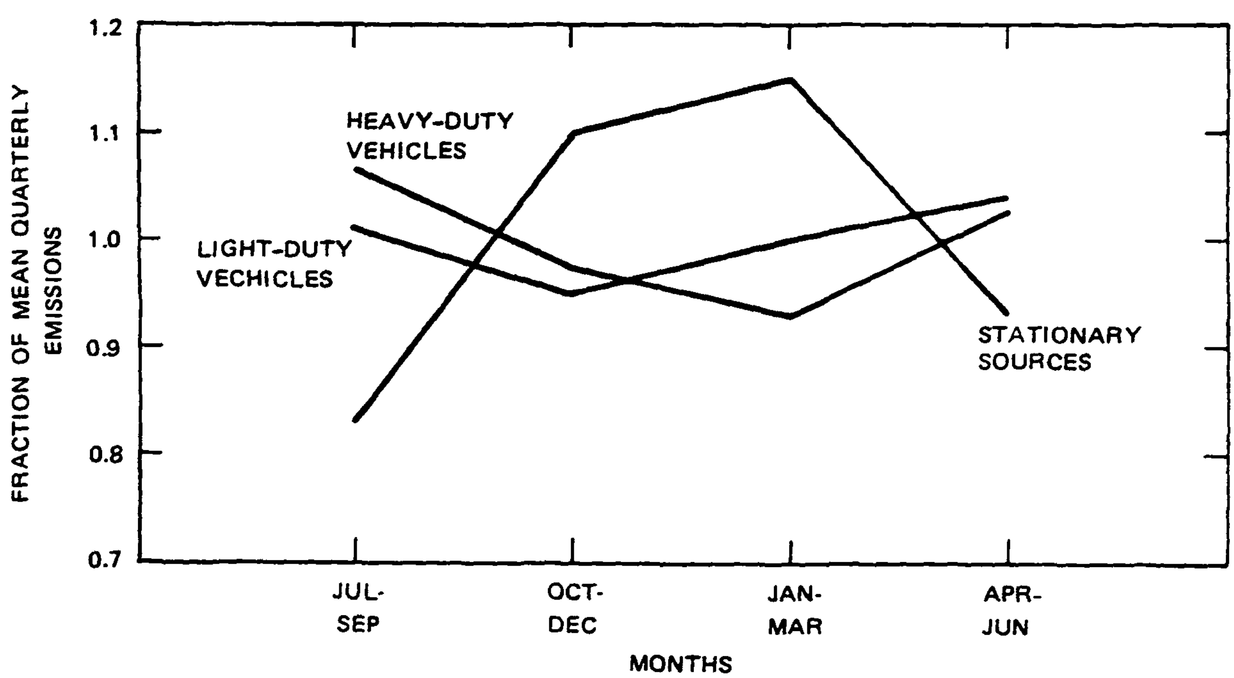

Figure 28. Quarterly variation of NO_x emissions in the South Coast Air Basin of California.

Table 13

ESTIMATED 1976 NO_x EMISSIONS
IN THE SOUTH COAST AIR BASIN

Source Category	Emissions (tons/day)
Stationary	460*
Light-duty vehicles	600†
Heavy-duty vehicles	180†

*Estimated from Bartz et al. (1974)

†California Air Resources Board, personal communication, 18 May 1979.

Table 14

QUARTERLY VARIATION OF NO_x EMISSIONS
IN THE SOUTH COAST AIR BASIN FOR 1976

Period	Stationary/Total Emissions Ratio	Stationary/Mobile Emissions Ratio	Composite Quarterly Factor
Jan-Mar	0.41	0.68	1.05
Apr-Jun	0.34	0.53	1.00
Jul-Sep	0.32	0.48	0.95
Oct-Dec	0.41	0.68	1.01
Annual	0.37	0.59	--

on the basis of spatial coverage, their locations relative to prevailing wind flows (see Figure 7), and quantity of data available.

The analysis begins by examining the pattern of occurrence of two or more stations reporting at least one NO_2 exceedance the same day. The degree of association between certain pairs of stations is then estimated.

NO_2 exceedances were reported at one or more of the fifteen sites on 351 different days during 1975-1977, which is 32 percent of the total number of days in the three-year period. Some of these days had more than one station recording an exceedance the same day. This is illustrated in Table 15, which lists the number of days when one or more stations reported an exceedance. The table shows that single-station exceedances were reported on 105 days. Hence, multiple-station exceedances occurred about 70 percent of the time (i.e., 246 days). Thus, multiple reports of exceedances are more common than single-site reports by a ratio of 2:1. Table 15 also shows that, as expected, the frequency of multisite reports generally decreases, but the overall decrease is somewhat erratic, showing increases when the number of sites

Table 15

DISTRIBUTION OF 15 SELECTED STATIONS
IN THE SOUTH COAST AIR BASIN
RECORDING NO_2 EXCEEDANCES THE SAME DAY

Number of Stations	Number of Days
1	105
2	58
3	33
4	40
5	19
6	19
7	15
8	15
9	13
10	12
11	16
12	5
13	0
14	1
15	0

is 4 and 11. The five days when 12 sites recorded exceedances are: 25 January 1975, 4 November 1975, 17 December 1975, 16 March 1976, and 14 February 1977. The day when 14 of the 15 sites reported exceedances was 23 November 1976. Note that these six days occur in the fall and winter, which suggests that regional episodes of high NO_2 levels are confined to this time of year. However, further analysis revealed that days with single-site exceedances are frequent during the winter as well, with 53 of 105 days falling during the months November through March. This is, of course, a reflection of the seasonal pattern discussed in connection with Figure 26. It would be of interest to study these six days to examine the weather patterns that resulted in so many stations reporting NO_2 exceedances the same day, but we must leave this for a future study.

Table 16 shows how frequently the various sites reported exceedances on the same day as at least one other site; the table also contains the total number of days when each site reported an exceedance. It is evident that most of the sites reported exceedances in combination with one or more stations. Only the sites at Los Angeles/Westwood Blvd., Los Angeles/San Pedro St., Pasadena, and Temple City reported more than ten days each when the exceedance did not coincide with any of the other 14 stations. Thus, a significant degree of dependence among the sites is apparent.

In connection with the question of which sites are most closely associated, we examined the correlation between pairs of sites using 2x2 contingency tables as shown below.

2 X 2 CONTINGENCY TABLE FOR SITES A AND B

		SITE B	
		E	$\bar{E}$
SITE A	E	a_{11}	a_{12}
	$\bar{E}$	a_{21}	a_{22}

The symbols E and $\bar{E}$ respectively denote the presence or absence of an exceedance on a given day. The entry a_{11} represents the number of days when both sites A and B recorded an exceedance the same day, and entry a_{22} contains the days when neither site recorded an exceedance the same

Table 16

NO_2 EXCEEDANCES RECORDED
AT TWO OR MORE SOUTH COAST AIR BASIN SITES

Site Name	Number of Days with Multisite Exceedances	Total Days
Los Angeles/Westwood Blvd.	144	167
Los Angeles/San Pedro St.	140	161
Pasadena	142	158
Long Beach	129	134
Whittier	113	118
Burbank	111	117
Lennox	99	106
Pomona	71	73
Los Angeles/Gault St.	68	70
Lynwood	63	65
Temple City	44	59
Azusa	58	58
La Habra	53	54
Anaheim	47	47
Riverside	14	14

day. Entries a_{12} and a_{21} contain the number of days when one site, but not the other, reported an exceedance.

Of the 105 possible site pairs, 22 were selected for study based on their locations relative to the typical wind flows shown in Figure 7. Contingency tables were obtained for the 22 pairs and tested for independence using a standard chi-square test with one degree of freedom (c.f. Mosteller and Rourke, 1973; Dixon and Massey, 1957). Another measure of association revealed whether knowledge about the reported exceedances at Site A gave information about exceedances at Site B. In other words, given that Site A is in state E, what is the probability that Site B is in state E, and vice versa? This measure of association is denoted by M, and is defined as follows:

$$M = P_{11}/P_1 P_2$$

where

$$P_{11} = a_{11}/N$$

$$P_1 = (a_{11} + a_{12})/N$$

$$P_2 = (a_{11} + a_{21})/N$$

$$N = a_{11} + a_{12} + a_{21} + a_{22}$$

Thus, M is the ratio of the probability that both A and B are in state E, to the product of the probabilities that either site is in state E. If Sites A and B are independent, then $M = 1$. If they are negatively correlated, then $M < 1$, and if positively correlated, then $M > 1$. However, chance alone may cause M to exceed 1. Hence, for each contingency table we computed a value f such that if the observed $P_{11} > f$, then we can say that P_{11} is not due to chance with a confidence level of 95 percent or better. (This is known as Fisher's test, see Langley, 1970.) The computation of f was performed while holding P_1 and P_2 constant. We also calculated a "bond coefficient" defined by:

$$\text{bond coefficient} = 100 \times (P_{11} - f)/f$$

The bond coefficient measures the information gained about the probability of one site being in state E, given that the other is in state E. The higher the bond coefficient, the higher the association between the two sites. If the bond coefficient is zero or negative, then knowing that one site is in state E yields no information about the state of the other site.

Results are shown in Table 17, which contains the entries a_{ij} of the contingency tables, the chi-square statistic, the coefficient M, and the bond coefficient. In the table, the station pairs are arranged in descending order of the bond coefficient. Regarding the chi-square statistic, note that for one degree of freedom the null hypothesis of independence is rejected at a 95 percent confidence level if chi-square is greater than 3.84.

Table 17 shows that the chi-square statistic leads to rejecting independence for 20 of the 22 station pairs. Thus, Los Angeles/San Pedro St. and Los Angeles/Gault St. appear to be independent, as do Lynwood and Temple City. Note that the bond coefficient for each of these two pairs of sites is zero and negative, respectively. By and large, the bond coefficient, M, and the chi-square statistic agree on the presence of some association, but the bond coefficient quantifies it best.

Table 17

CONTINGENCY TABLES AND MEASURES OF ASSOCIATION BETWEEN SELECTED STATIONS IN THE SOUTH COAST AIR BASIN

Site A	Site B	Contingency Table Entries (Number of Days)				Bond Coefficient (%)	M	Chi-Square
		a_{11}	a_{12}	a_{21}	a_{22}			
La Habra	Whittier	39	13	74	220	70	2.30	47.65
Long Beach	Anaheim	39	94	7	210	63	2.23	46.94
Pasadena	Azusa	51	107	7	187	55	1.96	49.95
Lynwood	Whittier	43	20	74	213	54	2.04	39.98
Azusa	Lynwood	24	33	41	255	50	2.29	23.55
Burbank	Los Angeles/Gault	44	73	26	209	47	1.89	32.90
Long Beach	Whittier	74	58	42	174	42	1.68	47.80
Burbank	Pasadena	84	31	74	162	40	1.62	52.62
Los Angeles/Westwood	Lennox	80	85	26	154	36	1.58	45.28
Los Angeles/San Pedro	Azusa	40	121	16	171	25	1.54	15.81
Los Angeles/San Pedro	Lynwood	43	119	18	167	23	1.51	15.71
Lennox	Lynwood	31	74	32	210	19	1.63	12.02
Burbank	Los Angeles/San Pedro	72	46	89	142	14	1.32	15.00
Pasadena	Temple City	36	122	21	172	13	1.40	8.20
Los Angeles/Westwood	Pasadena	94	74	62	118	12	1.25	15.39
Los Angeles/San Pedro	Long Beach	76	82	55	132	12	1.27	11.92
Los Angeles/San Pedro	Pasadena	92	71	68	119	11	1.23	13.35
Los Angeles/Westwood	Los Angeles/Gault	44	123	24	154	10	1.35	8.65
Los Angeles/Westwood	Azusa	35	132	21	160	6	1.30	4.96
Los Angeles/San Pedro	Los Angeles/Westwood	86	72	77	107	2	1.14	4.90
Los Angeles/San Pedro	Los Angeles/Gault	39	121	30	157	0	1.23	3.25
Lynwood	Temple City	13	52	46	241	-19	1.19	0.35

The two sites most closely associated are La Habra and Whittier, followed by Long Beach and Anaheim. Figure 7 demonstrates the plausibility of the associations since La Habra (Site 18) and Whittier (Site 51) are close to each other and on the path of the same air trajectory, as are Long Beach and Anaheim (although the association is less obvious). Similar associations can be seen in Figure 7 for Pasadena (Site 27) and Azusa (Site 2), Lynwood (Site 24) and Whittier (Site 51), and Azusa (Site 2) and Lynwood (Site 24). The lack of association between Los Angeles/San Pedro (Site 21) and Los Angeles/Gault (Site 23) is also evident in Figure 7, since the typical flows do not pass over both sites. In general, the plausibility of all the associations quantified in Table 18 is confirmed by Figure 7.

It is interesting to note that upwind sites such as Los Angeles/Westwood (Site 22) show only a weak association with downwind locations such as Pasadena (Site 29) and Azusa (Site 2). This report has shown that the latter are dominated by titration, whereas synthesis is most frequent at the upwind sites; this suggests that NO_2 transport from upwind to downwind sites is relatively unimportant in causing exceedances at the downwind stations.

VI ANALYSIS OF PEAK/MEAN RELATIONSHIP

A. Introduction

The current national ambient air quality standard for NO_2 is based on the annual mean concentration. In considering an hourly standard, it would be useful to know whether any relationship exists between extreme values (such as the annual maximum) and the mean.

This section investigates the functional dependence between the annual maximum and mean NO_2 using regression methods. The data used in the analysis were obtained from publications issued by the CARB (1976; 1977a,b). All 51 original stations were considered in the analysis, but some stations were excluded for individual years because of missing data. The analyses were performed for individual years during 1975-1977 and for the three years combined.

B. Peak/Mean Relationship

The correlation between peak and mean values was calculated, and linear regression equations were obtained for the peak as a function of the mean. Table 18 contains the parameters of the regression. Scatter diagrams of the calculated values are shown in Figures 29 through 31 for the individual years and in Figure 32 for the pooled data.

Table 18

PARAMETERS OF PEAK/MEAN REGRESSION

Year	Correlation Coefficient*	Regression Line† A	Intercept B (ppm)	Intercept Significance	Number of Points	Standard Error of Estimate (ppm)
1975	0.85	6.1	0.04	$p < 0.05$	49	0.07
1976	0.80	4.6	0.08	$p < 0.002$	47	0.06
1977	0.83	5.8	0.02	None	41	0.08
1975-1977	0.82	5.5	0.05	$p < 0.002$	137	0.07

*Significant for $p < 0.0001$

†Regression line is Peak = A * Mean + B, where A = slope and B = intercept.

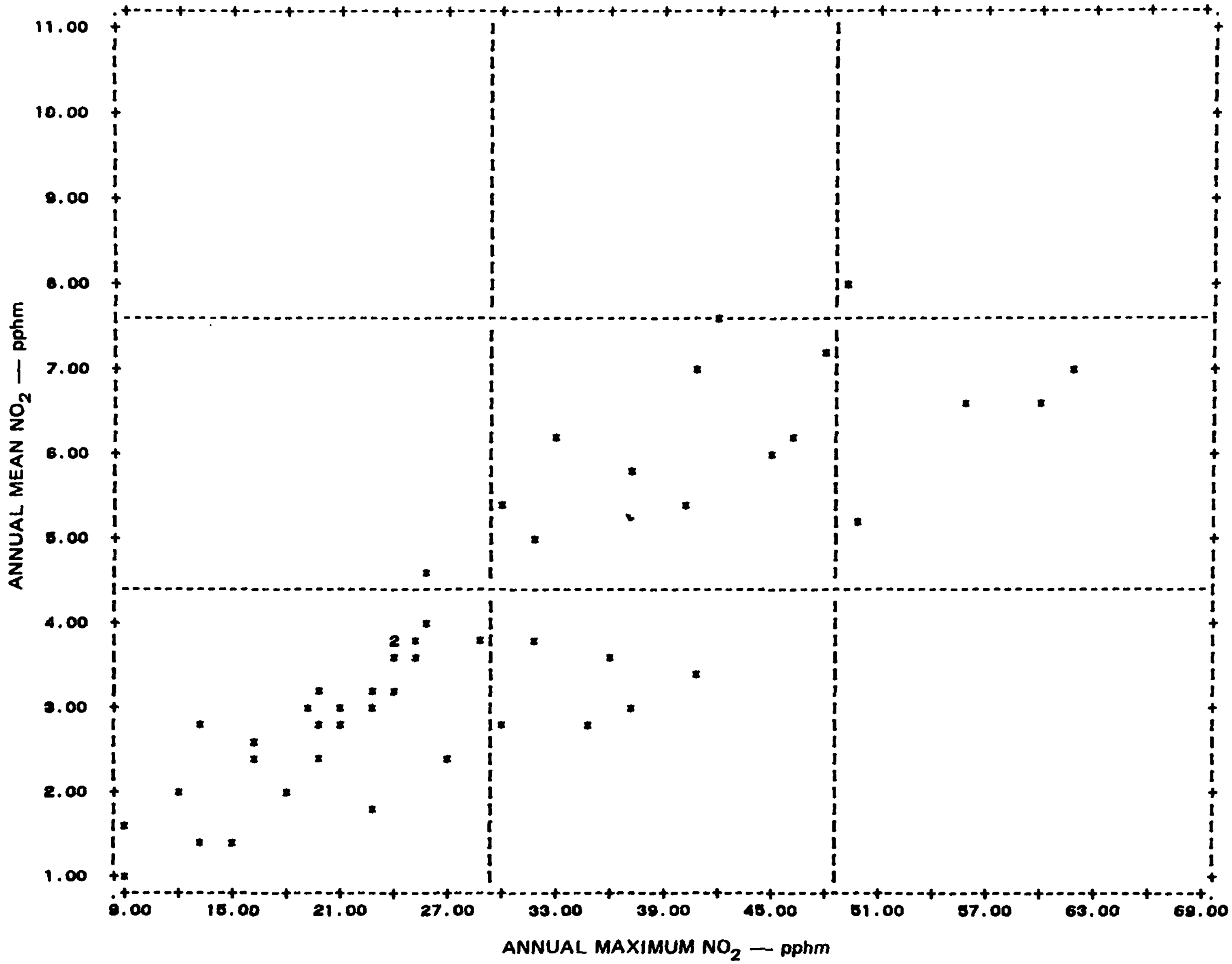

Figure 29. Scatter diagram of annual mean as a function of maximum NO_2 for selected California sites in 1975. Number of points plotted is 49.

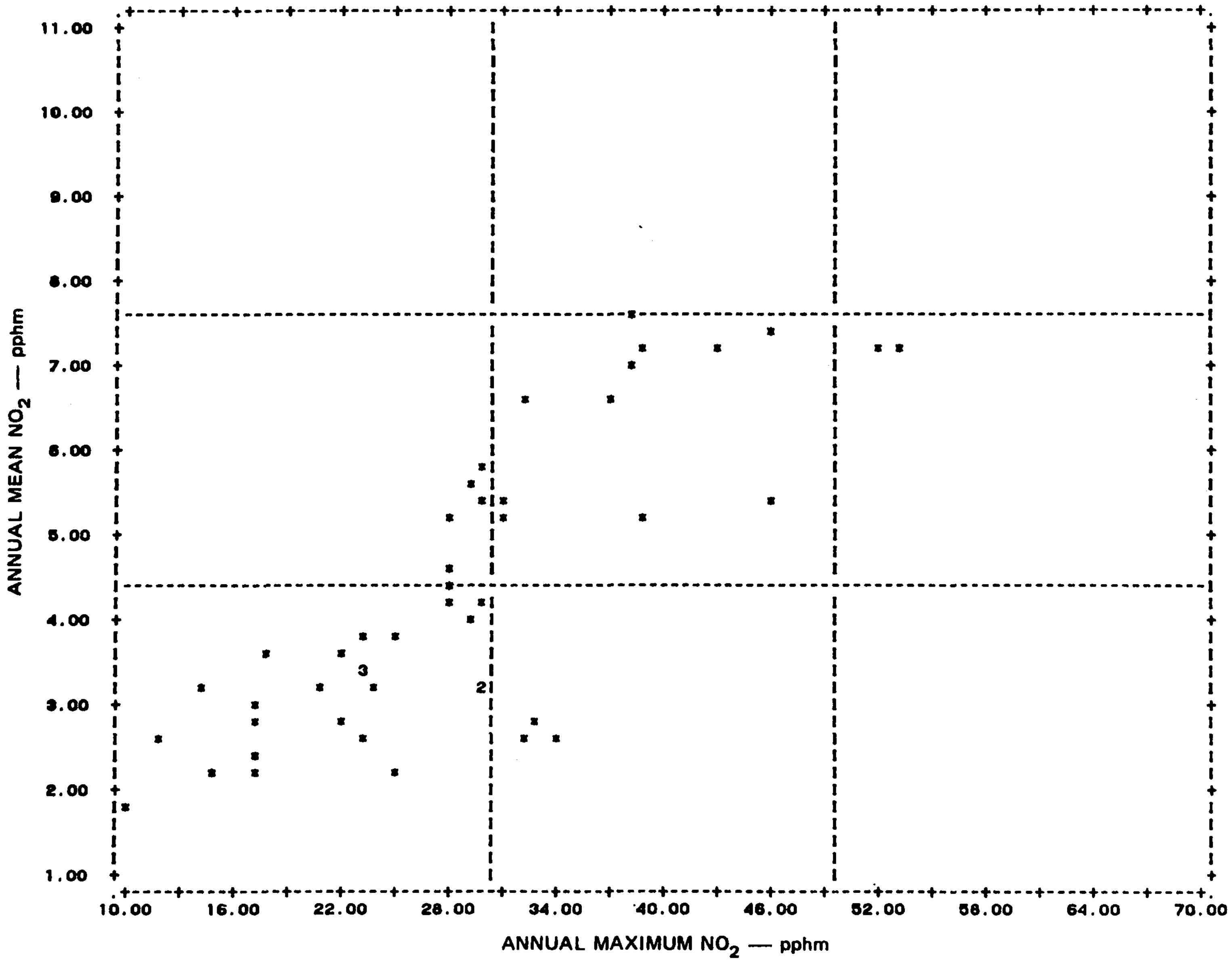

Figure 30. Scatter diagram of annual mean as a function of maximum NO_2 for selected California sites in 1976. Number of points plotted is 47.

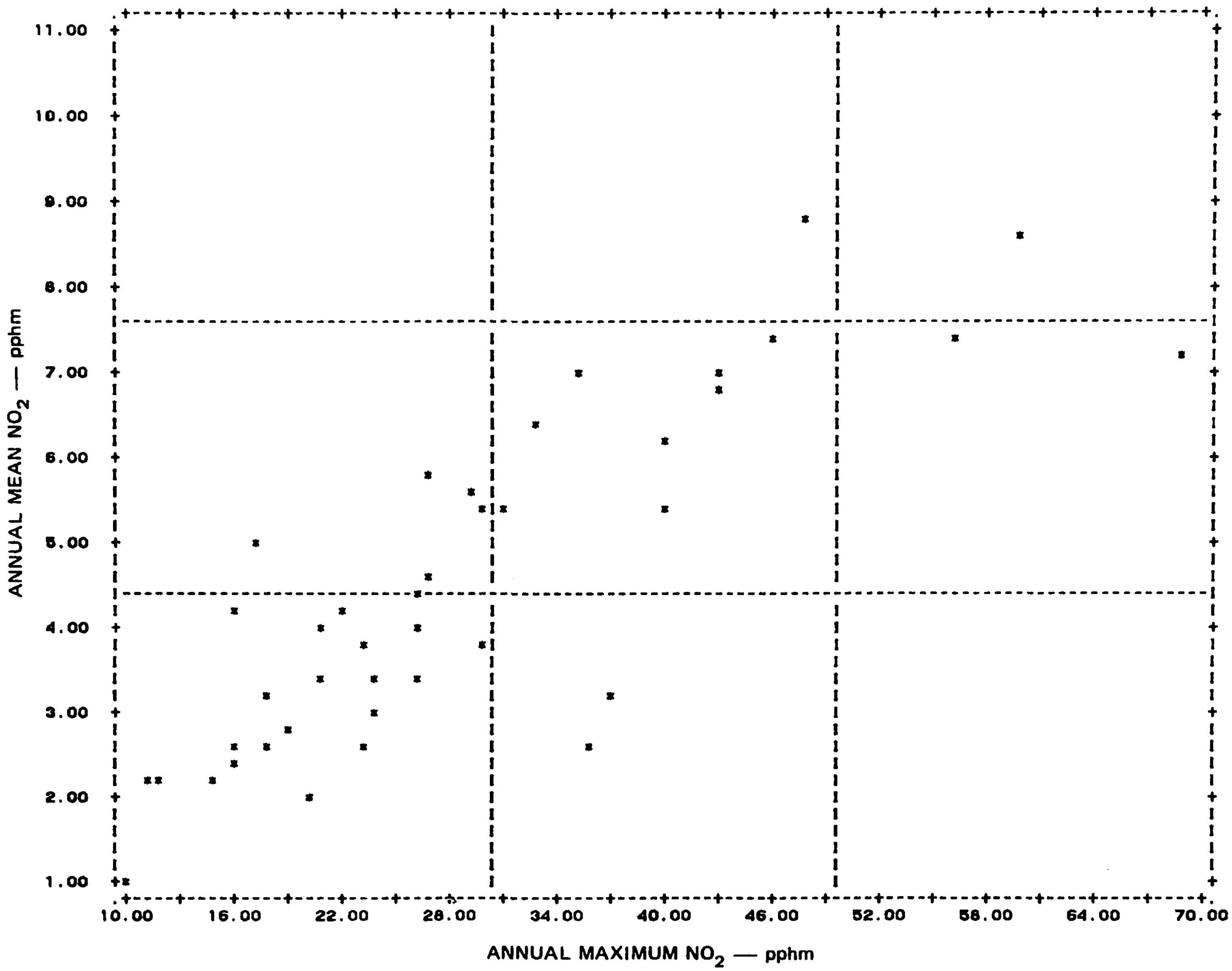

Figure 31. Scatter diagram of annual mean as a function of maximum NO_2 for selected California sites in 1977. Number of points plotted is 41.

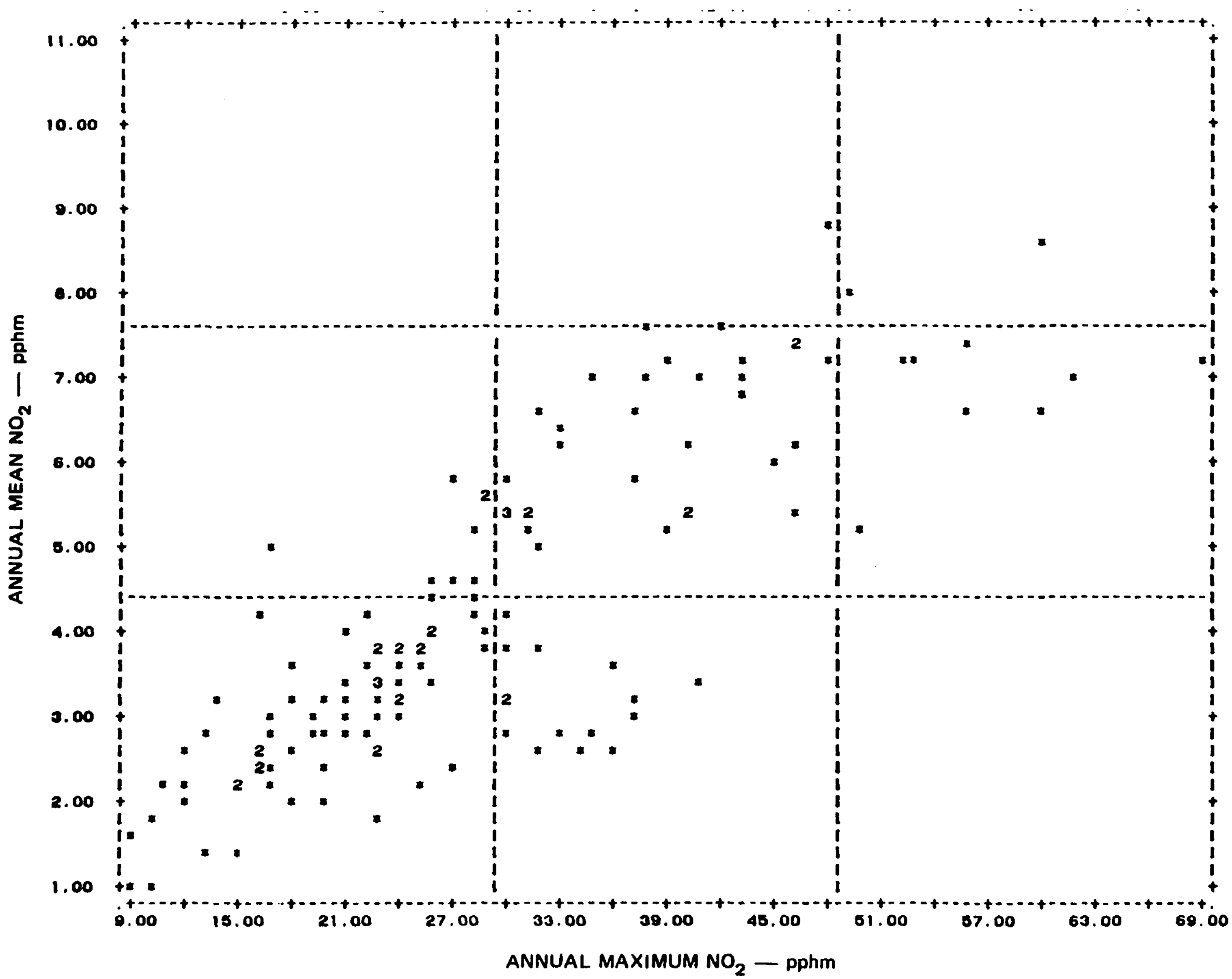

Figure 32. Scatter diagram of annual mean as a function of maximum NO_2 for selected California sites, 1975–77. Number of points plotted is 137.

It is evident from the scatter diagrams that a strong linear relationship links the peak and the mean. As Table 18 shows, the correlations for individual years range from 0.80 in 1976 to 0.85 in 1975, and for the pooled data it is 0.82. The narrow range of correlations and slopes for the individual years indicates that the variability of the data is small, so it appears to be reasonable to pool the annual data to obtain an overall regression.

A question might be raised about the effect of data adjustments on the regression. The correlation coefficient and the slope will not be affected if the same adjustment factor were applied to all the data, but the intercept and the standard error of estimate will be scaled by the adjustment factor. On the other hand, if different adjustments are applied to individual peak/mean pairs, the correlation coefficient and the regression line will be affected. We cannot tell in general what effect such nonuniform data adjustment might have on the regression: The effects of nonuniform adjustments can be evaluated only by recomputing the regression after the data have been adjusted.

Using the derived regression equation for the pooled data, if the mean equals the national air quality standard of 0.05 ppm, the estimated peak value will be 0.33 ± 0.07 ppm, apparently violating the California hourly standard of 0.25 ppm, a limit not to be equalled or exceeded. Thus, in California the hourly standard of 0.25 ppm is more restrictive than the annual norm of 0.05 ppm, since satisfying the latter does not imply compliance with the hourly limit. Adjusting the regression parameters by 10 or 17 percent changes the predicted peak value only slightly to 0.32 ± 0.06 ppm, assuming that the 0.05 ppm mean value used in the calculation represents an accurate measurement.

In assessing the utility of the regression function relating peak and mean NO_2 concentration, whose output is in essence an average, it is useful to examine the variability of the peak/mean ratio observed in the data. Figure 33 shows a digital histogram of the ensemble of peak/mean ratios for the pooled data. The ratios range from 3.3 at Bakersfield to 12.9 at Oceanside, with a median ratio of 6.3. The figure shows that the ratios cluster tightly about a ratio of 6, with 96 of 137 ratios ranging from 5.0 to 7.6.

For a mean value of 0.05 ppm, the regression equation relating peak and mean NO_2 yields an expected peak/mean ratio of 6.5 ± 0.6; the uncertainty is computed from the standard error of the coefficients of the regression equation. How does the estimated ratio compare with the observed values? Examination of the data revealed that there are 11 peak/mean ratios where the mean is in the interval $0.045 \leq \text{mean} \leq 0.054$ ppm. These ratios are: 3.3, 5.2, 5.4, 5.6, 5.7, 5.8, 5.8, 6.2, 6.2, 7.4, and 9.3. Comparison of the estimated and observed peak/mean ratios shows that the estimates, which are in the range 5.9 to 7.1, lie at the upper end of the set of observed ratios. This implies that for a mean

NO_2 PEAK TO MEAN RATIO	DECIMAL DIGIT OF RATIO		Row Count
3	3 6	Bakersfield, Fresno	(2)
4	2 4 5 6 6 7 9 9 9		(9)
5	0 0 0 0 1 1 1 1 2 2 3 3 3 3 4 4 4 4 5 5 5 5 5 6 7 7 7 7 8 8 8 8 8 8 8 9 9 9 9		(39)
6	0 0 0 0 0 1 1 2 2 2 2 2 2 2 2 2 2 3 [3] 3 3 4 4 4 4 4 5 5 6 7 7 8 8 8 9 9		(36)
7	0 0 1 1 1 1 1 1 1 2 2 3 3 4 4 4 5 5 5 5 6		(21)
8	0 2 2 2 4 4 5 6 7 8 8		(11)
9	1 1 1 3 4 5 5		(7)
10	3 4 4 9		(4)
11	0 4 5 7 7 9		(6)
12	6 9	Costa Mesa, Oceanside	(2)
		Total	(137)

Figure 33. Frequency distribution of peak/mean ratio of NO_2 for selected California sites, 1975–1977.

Interpretation: 12|6 9 corresponds to ratios of 12.6 and 12.9 at Costa Mesa and Oceanside, respectively. Similarly, 3|3 6 stands for ratios of 3.3 and 3.6 at the sites listed. Sites are not shown for other rows. The boxed digit corresponds to the median ratio of 6.3

of 0.05 ppm the regression equation may tend to overestimate the peak since the majority of the observed peak/mean ratios are lower than the estimates. This conclusion applies only when the mean is 0.05 ppm, and could change if another mean value were used.

VII SUMMARY OF SPECIFIC FINDINGS

The study analyzed NO_2 concentrations exceeding 0.20 ppm recorded in California during 1975-1977. Principal findings in the major investigative topics of the project are presented in the following sections.

A. Monitoring Site Features

Fifty-one monitoring stations originally reported NO_2 exceedances during 1975-1977. This number was reduced to 48 after the data were reviewed. All the sites are located in urban and suburban areas. Half the stations are in the South Coast Air Basin.

Mobile-source emissions predominate at most monitoring sites. Potentially significant local point sources such as power plants and heavy industries were few in number. Probable effects from a steel mill were identified at one site (Fontana). Probable source-receptor links between stationary sources of NO_x located outside the immediate vicinity of the sites and several monitoring stations in the South Coast Air Basin were identified. The sites at Long Beach and Whittier showed the most pronounced stationary-source impacts.

B. Data Quality

The NO_2 data were found to contain very few anomalies. The data for only 62 of approximately 1800 site-days were considered to be anomalous and were eliminated from the data base. Based on the low incidence of data errors noted above, data quality can be considered to be good. However, according to a recent study by the California Air Resources Board, the NO_2 levels are from 10 to 17 percent lower than the measurements indicate.

Comparison of simultaneous colorimetric and chemiluminescent NO_2 measurements at three sites revealed correlations of 0.71 and 0.86 at Riverside and Upland, respectively, but no correlation at San Jose. The colorimetric/chemiluminescent comparison also revealed a tendency for the latter data to be higher than the colorimetric observations.

C. Physical Processes Linked to NO_2 Exceedances

NO_2 synthesis is the most common mechanism leading to high NO_2 in densely urbanized areas. NO + O_3 titration also causes NO_2 exceedances, but is about 2/3 as frequent as synthesis. Titration appears to be ozone-limited, rather than NO-limited. NO_2 exceedances due to titration are especially important at downwind sites where transported ozone reacts with NO emitted by local sources. Pasadena and Pomona are examples of this type of site.

Transport and point-source effects related to NO_2 exceedances were relatively infrequent. Long Beach and Whittier exhibited the best examples of stationary source impacts.

D. Spatial and Temporal Variation of NO_2 Exceedances

On a statewide basis, NO_2 levels exceeding 0.20 ppm ranged from 0.21 to 0.62 with a median concentration of 0.24 ppm. Over 5,400 site-hours exceeding 0.20 ppm were recorded statewide during 1975-1977. About 92 percent of the NO_2 exceedances were recorded in the South Coast Air Basin, with Los Angeles County accounting for 80 percent of the statewide total.

However, it was determined that between 34 and 46 percent of the exceedances would be eliminated statewide if the NO_2 data were adjusted downward to compensate for the 10-17 percent bias. Such an adjustment often has a much greater impact on individual stations.

NO_2 exceedances have a strong seasonal component, occuring most frequently during the period November through February. The seasonality is evident statewide. Seasonal patterns of NO_x emissions in the South Coast Air Basin showed increased contributions from stationary area sources during the winter months.

NO_2 concentrations occurring during the time interval 0-0500 and 2200-2300 differs quantitatively from the distributions that prevail at other times at six of nine sites examined. The NO_2 levels were lower during 0-0500 and 2200-2300. Seven of nine stations tested showed no statistically significant differences between the distribution of NO_2 exceedances occurring during 0600-1300 and that for 1400-2100.

The diurnal variation of NO_2 exceedances appears to be associated with the traffic cycle in the more densely urbanized areas.

Analysis of 15 selected stations in the South Coast Air Basin revealed that the incidence of exceedances recorded at two or more sites on the same day surpasses that of single-site exceedances by better than a 2:1 margin. As a corollary to the preceding finding, a widespread pattern of interstation correlations was found among the selected stations in the South Coast Air Basin. The correlations are consistent with the typical flows that occur in the Basin.

E. Peak/Mean Relationship

Annual maximum and mean NO_2 were found to be correlated. The correlation coefficient is 0.82 and is highly statistically significant. The peak/mean ratio ranged from 3.3 to 12.9, with a median ratio of 6.3.

VIII CONCLUSIONS

High NO_2 concentrations seem to be primarily an urban phenomenon. This conclusion is reached bearing in mind that NO_2 monitors are clustered in urban areas, which raises the possibility that high NO_2 levels in rural areas may go undetected. Nevertheless, the pattern of NO_2 exceedances throughout California strongly suggests that a high density of emissions of NO_x and hydrocarbons are required for synthesis to result in NO_2 exceedances. Furthermore, since NO_2 exceedances due to titration require high levels of both NO and O_3, titration effects will probably be insignificant in rural areas where either NO or O_3 or both tend to be low. In fact, although titration-related exceedances in urban areas generally are ozone-limited, they would tend to be NO-limited in rural areas. NO_2 transport from urban areas and from point sources is thus the sole remaining mechanism that could lead to NO_2 exceedances in rural areas.

The evidence of this study suggests that NO_2 from urban areas is not transported over long distances, certainly not over distances as long as those associated with ozone transport. Examples of this situation are found in southern California when one considers well-known ozone receptors such as Upland, Riverside, and Palm Springs. Upland and Riverside show relatively few NO_2 exceedances, and Palm Springs shows none, yet all are heavily impacted by ozone transport from the Los Angeles area. Point sources of NO_x in rural areas could help to promote NO_2 exceedances if the NO-rich plume from the point source encounters an ozone-laden urban plume, thereby producing NO_2 by titration of NO and O_3. However, being conditioned on the vagaries of meteorological conditions, such an occurrence is likely to be infrequent. Nevertheless, it remains a distinct possibility whose chances would be enhanced if point sources of NO_x were to proliferate in rural areas. On balance, however, the evidence examined indicates that high NO_2 concentrations are essentially confined to urban areas and their immediate surroundings.

A second item of interest from a regulatory standpoint is the seasonality of the frequency of NO_2 exceedances. The seasonal pattern was apparent on a statewide basis, consisting of an increased exceedance frequency during the period November-February. Although the more stagnant conditions that prevail in California during these months are certainly a contributing factor, the possibility exists that the high NO_2 levels may be enhanced by increased NO_x emissions from space heating using natural gas. Analysis of seasonal patterns of NO_x emissions in the South Coast Air Basin, where the seasonality of the NO_2 exceedances is most pronounced, tends to support this hypothesis. However, more research is needed to define better and to quantify the relationship between seasonal fluctuations of NO_x emissions and NO_2 concentrations. Recommendations in these areas are given in the next section.

Few anomalies were found in the data base; only about 3 percent of the site-days containing exceedances were rejected on the basis of suspected errors. Thus, in this respect the data is of good quality. It is strongly recommended that data-screening procedures employing graphical methods such as were used in this study continue to be applied in the future, since this increases the confidence in the results obtained.

More important than the presence of anomalous data is the recent discovery by the California Air Resources Board that NO_2 levels in the state are between 10 and 17 percent lower than indicated by the measurements. On a statewide basis, adjusting the data by these factors eliminates between 34 and 46 percent of all the exceedances. It also has the effect of further confining the problem of high NO_2 levels to the South Coast Air Basin in general and to Los Angeles and Orange Counties in particular. Thus, any contemplated regulatory actions must specify the adjustment factor to be applied to the data.

A disturbing result of the data quality assessment was discovered in the comparison of simultaneous colorimetric and chemiluminescent measurements. The analysis indicated that the correlation was 0.71 at Riverside and 0.86 at Upland, which is respectable but perhaps not quite as high as one might expect. One site, San Jose, showed no significant correlation between the measurements. More serious is the fact that, in general, the chemiluminescent measurements tended to be greater than the colorimetric observations, which leads one to ask which one is correct. The question cannot be answered from the data available to us, but it is imperative that an answer be obtained in view of the regulatory implications of the choice of measurement method.

Pursuant to federal regulations (Federal Register, 10 May 1979), NO_2 measurements in California as of January 1980 will be performed using chemiluminescent instruments only. (All states must discontinue using colorimetric methods for NO_2, but the compliance dates vary.) The discrepancies between colorimetric and chemiluminescent measurements noted above suggest that these two types of data may not be strictly comparable. Since implementation plans are based on analyses of historical data, lack of data comparability makes it difficult to monitor progress toward compliance with ambient NO_2 standards. Thus, additional efforts must be devoted to establishing the degree of correspondence between colorimetric and chemiluminescent NO_2 measurements.

The comparison of the distributions of NO_2 concentrations for various times of day revealed that NO_2 levels observed during the hours 0-0500 and 2200-2300 (PST) were significantly different from concentrations measured during 0600-2100. In general, the nighttime levels were lower than the daytime values. The lower concentrations that exist at night indicate that NO_2 has a short lifetime, further evidence pointing to the relative lack of importance of NO_2 transport from urban areas as a contributor to elevated NO_2 in rural areas.

The interstation correlation with respect to same-day NO_2 exceedances between various pairs of sites in the South Coast Air Basin suggests that short-term effects dominate the formation and transport of high NO_2 levels. Moreover, the correlation indicates that area sources, rather than point sources, are the principal proximate causes of the elevated NO_2 levels in the Basin.

The derived linear-regression equation relating annual maximum and mean NO_2 implies that the current California hourly standard of 0.25 ppm is more restrictive than the national annual standard of 0.05 ppm, since meeting the annual standard does not necessarily guarantee satisfying the hourly limit. Consequently, if a national hourly standard equal to California's 0.25 ppm were established, then the hourly rather than the annual standard would become the controlling factor in abatement efforts, assuming that the annual standard remains unchanged. Thus, in setting a national hourly NO_2 standard, it is necessary to consider the relationship between peak and mean NO_2 to ensure that the two standards reinforce each other.

IX RECOMMENDATIONS FOR FURTHER RESEARCH

In addition to the specific results reported in the previous section, this study revealed other areas that should be the subject of further investigation:

- A more detailed investigation of the relationship between seasonal emissions of NO_x and elevated NO_2 levels is required. In particular, it could be fruitful to attempt to relate degree-days and NO_2 levels, correlate degree-days with NO_x emissions, and compare the two.
- Regional-scale episodes of elevated NO_2 levels occurred in the South Coast Air Basin on six days that are identified in the text of the report. Meteorological patterns on these days should be investigated to identify the weather conditions that led to such episodes.
- About a third of all the NO_2 exceedances reported in the South Coast Air Basin were associated with single stations. It would be of interest to examine a sample of these cases to establish why the elevated NO_2 was observed at a given station, and at no other station, on a given day.
- The data suggest that there may be weekend/weekday or Sunday/weekday differences in NO_2 analogous to those found for ozone. It is recommended that this topic be investigated further.
- Several cases of high NO_2 related to point sources were identified at Whittier and Long Beach. Such instances often combined synthesis and point-source effects. It is recommended that attempts be made to establish the relative contributions of the various processes to the overall NO_2 level in order to isolate point-source effects.
- More analyses and comparisons of simultaneous colorimetric and chemiluminescent measurements of NO_2 should be made at the high end of the concentration range and under field, rather than laboratory, conditions.
- The frequency distributions of NO_2 levels exceeding 0.20 ppm occurring in summer and winter should be compared to determine whether significant differences exist between them. Further study is also required to establish the seasonal variation, if any, of physical processes such as chemical synthesis and titration.
- A more extensive investigation should be undertaken of peak/mean relationships for NO_2. Such an investigation should include data from other states.

REFERENCES

Arledge, K.W. and R.L. Tan, 1978: "A Heavy-Duty Vehicle Emission Inventory System," Final Report, Contract No. A6-051-87, TRW Environmental Engineering Division, Redondo Beach, California (March)

Bartz, D.R., K.W. Arledge, J.E. Gabrielson, L.G. Hays, S.C. Hunter, 1974: "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin of California," Report No. KVB-5800-179, KVB Inc., Tustin, California, NTIS No. PB-273688 (September).

California Air Resources Board, 1976: "Summary of 1976 Air Quality Data--Gaseous Pollutants," Annual Summary, Vol. VIII.

California Air Resources Board, 1977a: "Three-Year Summary of California Air Quality Data, 1973-1975" (January).

California Air Resources Board, 1977b: "Summary of 1977 Air Quality Data--Gaseous and Particulate Pollutants," Annual Summary, Vol. IX.

California Air Resources Board, 1979: "California Air Quality Data," Vol. IX, No. 1.

De Marrais, G.A., G.C. Holzworth, and C.R. Hosler, 1965: "Meteorological Summaries Pertinent to Atmospheric Transport and Dispersion Over Southern California," Technical Paper No. 54, U.S. Weather Bureau, Washington, D.C.

Dixon, W.J. and F.J. Massey, 1957: Introduction to Statistical Analysis, 2nd edition, McGraw-Hill Book Company (New York, New York).

Federal Register, 1979: Vol. 44, No. 92, pp. 27558-27604 (10 May).

Goodman, H.S., G.E. Abercrombie, K.W. Arledge, and R.L. Tan, 1977: "A Mobile Source Emission Inventory System for Light Duty Vehicles in the South Coast Air Basin," Final Report, Contract No. ARB 4-1236, TRW Environmental Engineering Division, Redondo Beach, California (February).

Hunter, S.C. and N.L. Helgeson, 1976: "Control of Oxides of Sulfur from Stationary Sources in the South Coast Air Basin of California," Report No. KVB-5802-432, KVB, Inc., Tustin, California (June), NTIS No. PB 261754.

Langley, R., 1970: Practical Statistics, Dover Publications (New York, New York).

Mosteller, F. and R.E.K. Rourke, 1973: Sturdy Statistics, Addison-Wesley Publishing Company (Reading, Massachusetts).

Thuillier, R.H. and W. Viezee, 1978: "Air Quality Analysis in Support of a Short-Term Ambient Air Quality Standard for Nitrogen Dioxide," Final Report, SRI Project 6780, EPA Contract 68-02-2835, SRI International, Menlo Park, California (February).

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-450/4-79-034a		

4. TITLE AND SUBTITLE
Analysis of High NO_2 Concentrations in California, 1975-1977

5. REPORT DATE
August 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. R. Martinez and K. C. Nitz

8. PERFORMING ORGANIZATION REPORT NO.
6780-12 and -13

9. PERFORMING ORGANIZATION NAME AND ADDRESS
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-2835

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

EPA Project Officer - Harold G. Richter

16. ABSTRACT

During the period 1975-1977, 51 monitoring stations in California collectively recorded about 1,800 site-days in which hourly nitrogen dioxide (NO_2) concentrations exceeded 0.20 ppm. This work investigates potential causes of these high NO_2 events, the physical phenomena involved in their occurrence, and their spatial and temporal patterns. In addition, the potential association between emission sources and the frequency and magnitude of high NO_2 levels at the various locations is analyzed using detailed site-description data compiled in this study. The relationship between annual maximum hourly levels and annual mean concentration is explored, and the quality of the NO_2 data is evaluated.

Appendix A (unpublished) is a compilation of data curves used in the analysis. Appendix B (unpublished) is a compilation of descriptions of the sites from which the data came. Neither of these is required to understand the basic report text.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Nitrogen Dioxide California Short-Term Standard NO_2, Spatial and Temporal Variations NO_2, Causes of High Concentrations		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	108
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

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