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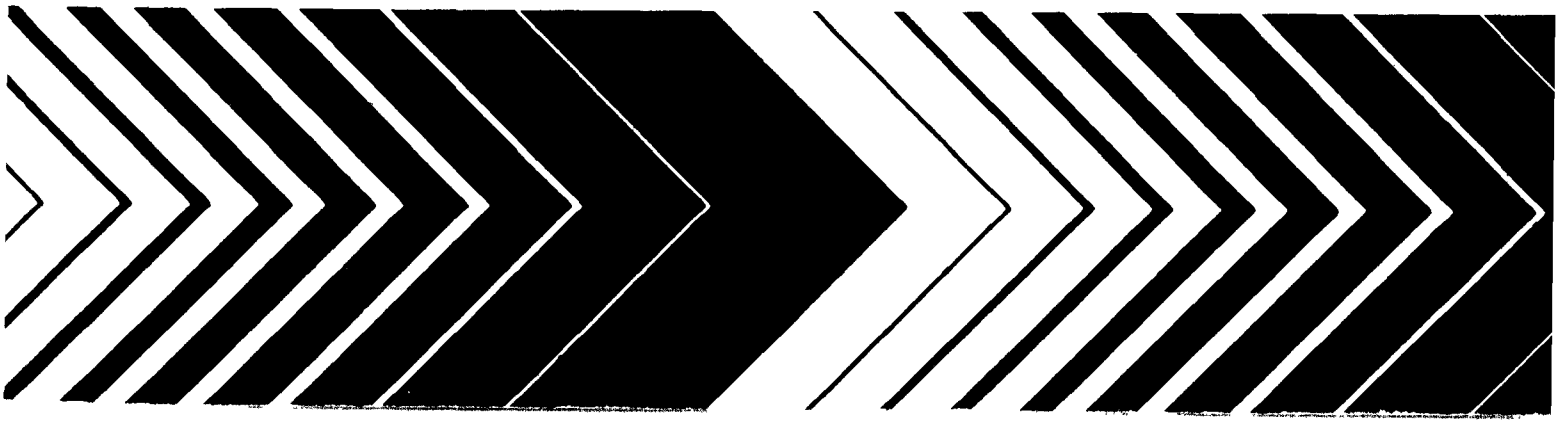
Survey for Airborne Nitrosamines



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SURVEY FOR AIRBORNE NITROSAMINES

by

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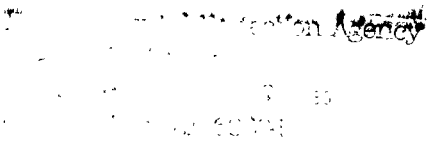

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

This report contains the results of a survey for airborne volatile nitrosamines in Los Angeles and Contra Costa Counties, and at a rocket fuel plant near Hollister, California. Temporal patterns showed morning and evening maxima and suggested photolysis in midday sun. No clear indication of significant point sources was found.

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Acting Director
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ABSTRACT

A survey for airborne volatile nitrosamines was carried out in Los Angeles and Contra Costa Counties and at a rocket fuel plant near Hollister, California. A mobile sampling unit with ambient aqueous KOH bubblers was used, followd by extraction, concentration, and analysis by gas chromatography with thermal energy analysis detection. The detection is based on decomposition of nitrosamines to NO which gives chemiluminescence upon reacting with ozone. Low levels of dimethyl and diethylnitrosamine were observed sporadically at numerous locations but gave no clear indication of significant point sources. Most samples were below 0.03 $\mu g/m^3$ while the highest reached 1.0 $\mu g/m^3$. Temporal patterns showed morning and evening maxima and suggested photolysis in midday sun. No relationship between airborne nitrosamine levels by area and incidence of several human cancers is apparent.

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Acknowledgements

The computerized maps of cancer incidence in Los Angeles were derived by Herman Menck (Public Health Analyst, Pathology Department, USC School of Medicine) from the computer files of the Los Angeles Cancer Surveillance Program directed by Thomas Mack, M.D., M.P.H. (Associate Professor of Community and Family Medicine and Pathology, USC School of Medicine).

This project was supported in part under contract No. NO1 CP 53500 within the Virus Cancer Program of the National Cancer Institute, National Institutes of Health.

This report was submitted in fulfillment of ARB contract No. A6-096-30, "Survey of Airborne Nitrosamines" by the School of Medicine of the University of Southern California under the partial sponsorship of the California Air Resources Board. Work was completed as of June 1978.

I. CONCLUSIONS

No evidence for any specific point emission source for volatile nitrosamines was observed. Part of the sampling was concentrated in areas of chemical industry in Los Angeles and Contra Costa Counties and near the rocket fuel plant outside Hollister. A systematic county-wide survey of Los Angeles was also carried out. The majority of all samples were below detection limits (about 0.03 $\mu g/m^3$ for dimethylnitrosamine, DMN). Several samples reached 0.3 $\mu g/m^3$ DMN or higher, up to a maximum of 1.0, but later repeat samples were always lower. Positive samples occurred more frequently in winter. A diurnal pattern was suggested, with maxima around 0800 and 1800. Diethylnitrosamine was found less frequently than DMN but at similar concentrations, and a few samples had traces of a third, less volatile component, unidentified. Computer-derived maps of airborne nitrosamine levels by area show no apparent correlation with incidence of various human cancers.

RECOMMENDATIONS

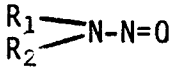
The sources of sporadic low levels of airborne nitrosamines remain to be identified. No particular geographic concentration has been observed. Therefore further sampling might be carried out at existing monitoring sites, although mobile sampling is easy. The sampling is simple but work-up is time-consuming and would be the limiting factor in further studies. Samples can be held (frozen) for at least a week before processing, making it convenient to send them to a central location for analysis. The rather costly analyzer has already been acquired.

To test whether there is a vehicle source, samples might be taken of auto and diesel exhaust at the ARB El Monte facility. Exhaust sampling procedures would need to be validated.

II. INTRODUCTION

The class of N-nitroso compounds is large. Although no verified cases of human cancer have been attributable yet to nitrosamines, the evidence in animals is extensive. Of about fifty nitrosamines tested, all but seven were carcinogenic. Moreover, there have been examples of cancer caused in almost every organ among the numerous animal species tested with one or another nitrosamine. No species tested has been found to be resistant to all nitrosamines, suggesting that man is not likely to be an exception (1).

The general formula for nitrosamines is



where R_1 and R_2 may be alkyl or aryl groups, but not hydrogen. If one R group is acyl (R'CO-) the compound is a nitrosamide, many of which are also carcinogenic. This report will not distinguish between nitrosamines and nitrosamides except to note that the latter are much less volatile as a class, and may be formed and decomposed more rapidly.

Nitrosamines are formed in solution by direct reaction of nitrous acid with secondary amines, and by a more complex sequence, with tertiary amines. Primary amines are also nitrosated but the nitroso products are unstable and have not been isolated. The nitrosation rates are maximum at a pH usually between 3 and 4 but varying with the basicity of the amine (i.e. low enough for high proportion of molecular nitrous acid and high enough for some free amine to be present). In the vapor phase with oxides of nitrogen (NO_x) volatile amines may be nitrosated. In photochemical smog systems both the presumed reactant nitrous acid and the nitrosamine are photolyzed by ultraviolet light. From laboratory rates it has been predicted that in the atmosphere the nitrosamine might be found in the morning (2). In artificial smog systems the yield of nitrosamine is quite low and the much more stable nitramine, R_2NNO_2, is formed in larger amounts (3).

Nitrosamines have been found in certain foods (bacon, sausage, cheese), cutting oils, cosmetics, tobacco smoke, and in air (4). The possibility of *in vivo* formation from nitrate and various amines in foods or drugs has been shown, as well as the presence in the body of bacteria able to reduce nitrate to nitrite (5). This has led to recent restrictions on use of nitrate and nitrite as foods preservatives. The presence of

nitrosamines in air has in a few cases been traced to direct emission from an industrial source. but there have been other findings of low levels of nitrosamines not near any known source (6).

The possibility of nitrosamines in community air in California either as a result of direct emission or as a result of atmospheric reactions involving oxides of nitrogen has been of concern to the Air Resources Board. The recent commercial availability of a highly specific and sensitive analyzer for nitrosamines and development of suitable methods of air sampling made an air survey practical.

Following calibration and validation of collection and analysis procedures and some local air sampling, the project was carried out in several phases. For most of the work a mobile battery-powered set-up was operated in a passenger car or wagon. The phases were as follows:

Los Angeles industrial areas: Known chemical plants were plotted on a map and the major clusters showed at Vernon-Commerce and Carson-Wilmington. Sampling was concentrated in these areas.

Contra Costa industrial areas: The belt of chemical and petroleum industry runs along the waterfront from Richmond to Antioch. Samples were taken near individual plants all along the belt.

Hollister rocket fuel plant: The McCormick-Teledyne-Selph plant outside Hollister was scheduled to begin full-scale production of fuel, using a nitrosamine intermediate. Air samples were taken outside the plant before and after the start-up date.

Los Angeles census areas survey: Systematic sampling was done throughout the southern half of the County at about 150 locations for comparison with cancer incidence data, and as a check on possible unsuspected emission sources.

Diurnal pattern: At a fixed local site samples were collected during all the various hours of the day and night to test for a diurnal pattern

Following tha data collection the results were examined for indication of specific emission sources, with follow-up sampling in some cases. Correlations were tested wtih cancer incidence, nitrogen oxide data from the South Coastal Air Quality Management District, and with season or time of day.

III. EXPERIMENTAL METHODS

A. Air Sampling:

Typically an air sample of about 60 l was drawn at one l-min^{-1} through a 100 ml glass bubbler containing 50 ml of 1 N-KOH (7). For field sampling from an automobile a Teflon inlet tube was extended out the window and two small battery-powered diaphragm pumps (Spectrex AS-120) were used in parallel. A rotameter for air flow rates was checked periodically by wet test meter. During the sampling period wind, temperature, and weather conditions were noted. The wind direction and velocity were estimated by use of a vane, compass, and hand-held anemometer. The KOH solution was made up using water taken directly from an all glass/Teflon still. The bubbler was protected from light by aluminum foil. After sampling the solution was transferred to a polyethylene bottle. Unless the sample was to be processed the same day it was frozen on dry ice or placed in the freezer until work-up. Replicate samples stored for various times showed no loss over at least two weeks.

B. Sample Processing (8):

The KOH samples including a blank control were thawed, if necessary, and extracted in a 125 ml separatory funnel with 3 x 8 ml portions of dichloromethane (Burdick and Jackson glass-distilled). The extracts for each sample were combined over sodium sulfate, then decanted into a 25 ml Kuderna-Danish tube with an ebullation tube and Vigreaux-type condenser. Then 0.5 ml 2,2,4-trimethylpentane was added as keeper and the extract was evaporated to approximately 0.5 ml on a block heater at 65°. After cooling, the residual volume was read by the graduations on the narrow tip of the evaporator tube and transferred to a Teflon-capped culture tube. The concentrated extract was usually analyzed the same day, but if not, it was stored in the freezer. Repeat analyses of such stored extracts showed no discernible changes over at least two weeks cold storage.

C. Analysis by GC-TEA:

The analytical instrumentation consisted of a gas chromatograph (GC) connected by a tape-heated exit tube to the entry of the Thermal Electron Analyzer (TEA). The GC was an isothermal unit (Varian Aerograph 940). Three different columns were used during the project, all with satisfactory results during their lifetimes. Argon carrier gas was passed through a molecular sieve cartridge into the GC. Flow rates were measured at the GC exit by a soap bubble tube. The columns and conditions used were:

1. Carbowax 20 M on Chromosorb W, 12' x 1/8" stainless steel; column 180°, injector 190°, carrier flow 20 cc-min^{-1}. (This column was supplied with the TEA, and full details are not available.)

2. FFAP 15% on 80/100 mesh acid-washed, DCMS-treated Chromosorb W, 21' x 1/8" stainless steel; column 210°, injector 225°, carrier flow 30 cc-min^{-1} (Varian Instruments).

3. Carbowax 20 M, 10% on 80/100 mesh acid-washed DCMS-treated Chromosorb W, 6' x 1/8" stainless steel; column 150°, injector 160°, carrier flow 20 cc-min^{-1} ("Quik-Col", Applied Science Laboratories).

The TEA operates as follows (9). The GC effluent enters a catalytic furnace (controlled at a temperature up to 500°C, in our case 450°) and is drawn through a stainless steel loop cold trap into a small reactor chamber under partial vacuum. The cold trap temperature is controlled by use of coolant and solvent; usually this is a slush of isopentane and liquid nitrogen, but for our purposes the liquid nitrogen alone was quite satisfactory. A metered flow of oxygen gas passes through a glow discharge tube for partial conversion to ozone, and is drawn into the reactor chamber, where ozone reacts with any nitric oxide present in a chemiluminescent reaction emitting light in the near infrared. The reactor has a window with a suitable filter facing a refrigerated photomultiplier tube. The amount of light emitted by the reacting gases is indicated by the photomultiplier tube output and is recorded on a strip chart.

A portion of the sample in dichloromethane (usually 10 µl) is introduced into the GC. It contains anything scrubbed from the air into the KOH solution and extractable in the solvent. The column is selected for efficient separation of volatile nitrosamines. Sample components, including solvent, leave the GC and enter the furnace where nitrosamines are decomposed to yield nitric oxide and organic pyrolysis products; other organics pyrolyze but do not yield NO. The cold trap retains most of the condensable materials found, but not nitric oxide. In the reactor only nitric oxide can react with ozone to cause emission of light at the wavelength passed by the filter to the detector. Thus the unit is highly specific towards nitrosamines and a very few other compounds capable of decomposing to form nitric oxide. The GC distinguishes among various nitrosamines and other nitric oxide generators. Spectra are shown in Figures 3.1 and 3.2.

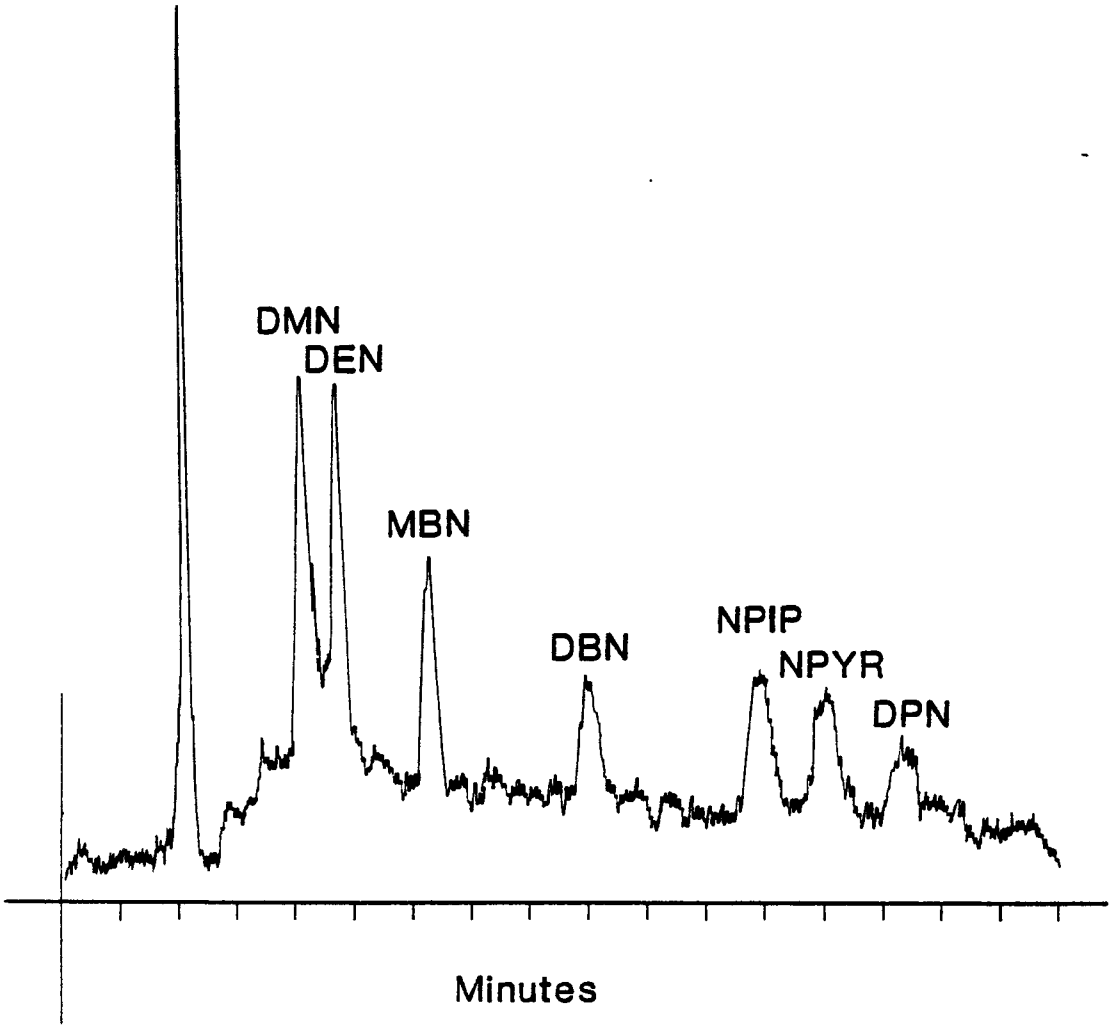
D. Calibration

Commercial dimethylnitrosamine (DMN; K&K) and diethylnitrosamine (DEN; Eastman) were used as interim reference standards until certified samples of seven pure nitrosamines were received from the National Cancer Institute Chemical Repository at Illinois Institute of Technology. DMN and DEN from the two sources were indistinguishable under the conditions used. The seven reference nitrosamines were run repetitively at realistic levels on column #2 with the results given in Table 3.1 and Figure 3.1.

Two sets of recovery runs are summarized in Table 3.2. In each case a batch of 1 N-KOH was spiked by adding DMN in dichloromethane (20 ng/µl). In the first set 15 µl was added to 500 ml KOH, in the second 10 µl was added. 50 ml portions of the spiked KOH were used. Some were air-blown by drawing charcoal-filtered air through them. All were then extracted and evaporated, then run in duplicate on the GC-TEA. There was no significant difference between airblown and non-aerated samples, and losses of 7% and 6% from theoretical probably arise during the later processing and are comparable to the repeatability of the GC at this level.

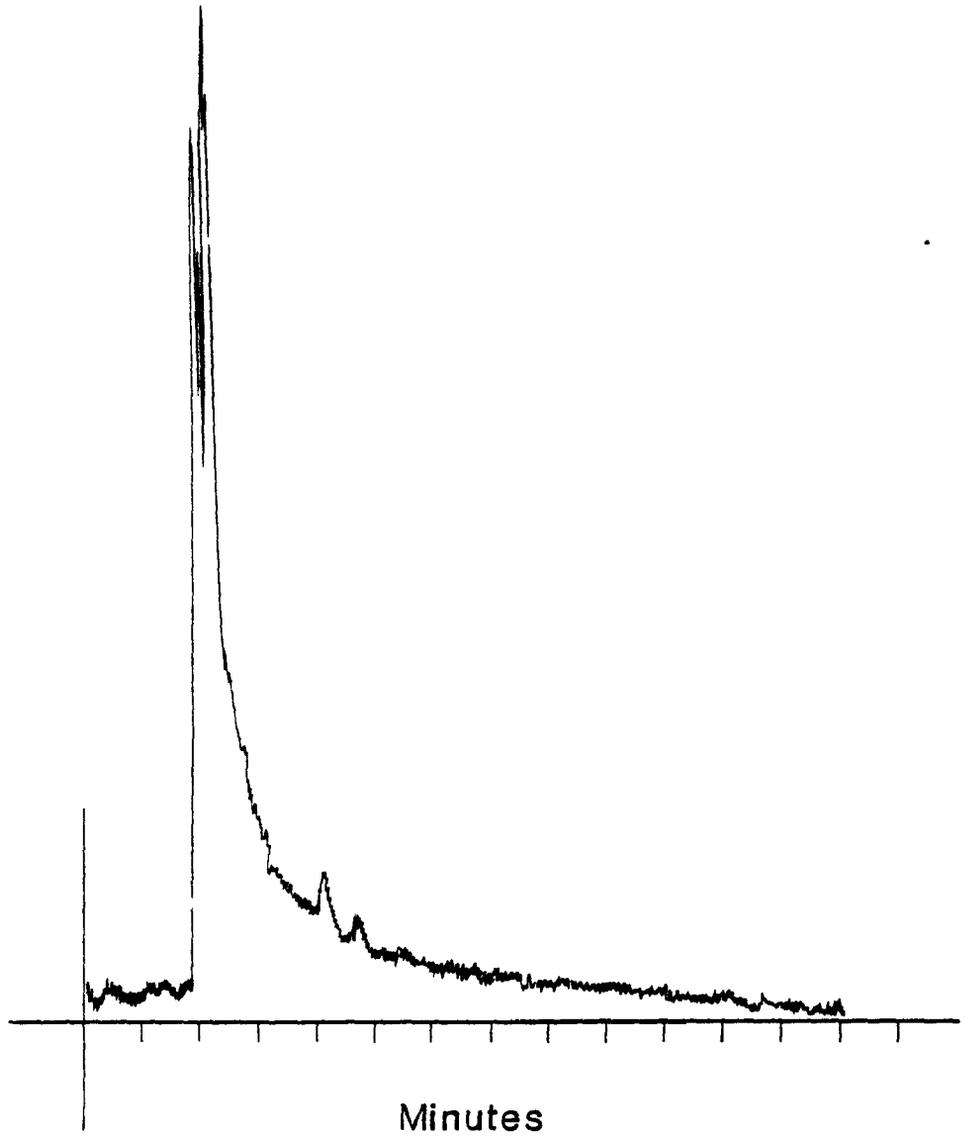
Initially there was no problem with blank controls, but from about December on there began to be sporadic positive blanks. These have always been low level and in the extreme corresponded to what would have been an air concentration of about 0.05 $\mu g/m^3$. Most are less than half that, or just about at the detectability limit. We have

FIGURE 3.1



GC-TEA trace of seven-component reference blend. Identities of peaks given in table 3.1

FIGURE 3.2



GC-TEA trace of air sample extract with 0.17 ng DMN and 0.14 ng DEN

TABLE 3.1

REFERENCE NITROSAMINE DATA

Nitrosamine	Sensitivity[a] (div/ng)	Retention Time, t_r (sec)	Relative[b] t_r
Dimethylnitrosamine (DMN)	26.6 ± 0.23[c]	249 ± 1.0[c]	(1.00)
Diethylnitrosamine (DEN)	23.4 ± 3.1	283 ± 1.0	1.14
Methylbutylnitrosamine (MBN)	14.3 ± 1.3	378 ± 2.1	1.52
Dibutylnitrosamine (DBN)	7.2 ± 1.0	547 ± 3.1	2.20
Nitrosopiperidine (NPIP)	9.2 ± 0.73	729 ± 3.0	2.92
Nitrosopyrrolidine (NPYR)	8.8 ± 0.25	798 ± 3.5	3.20
Dipentylnitrosamine (DPN)	4.6 ± 0.64	878 ± 5.6	3.53

a. With 0.5 ng samples.

b. Relative to DMN.

c. Standard deviation, 4 replicates.

TABLE 3.2

DIMETHYLNITROSAMINE RECOVERY CHECKS

Sample	Charcoal Filtered Air volume, l		Ng DMN Found	
Set 1:				
A	72		24.9	
			28.7	
B	78		26.4	
			30.8	
C	75		27.6	
			29.5	
D	0		27.1	
			27.3	
		mean	27.9	theory 30 ng loss 7%
Set 2:				
A	0		20.4	
			24.5	
B	75		20.1	
			19.6	
C	0		18.2	
			19.9	
D	75		19.0	
			18.5	
E	0		14.0	
			15.1	
		mean	18.9	theory 20 ng loss 6%

been unable to pin down the source of this. Often with a positive blank there will be negative air samples from the same batch of reagents handled the same way. It seems unlikely that exposure to nitrosamines in laboratory air could be the cause, because many positive blanks show both DMN and DEN, whereas only DMN is used on most days for calibration. In any case the calibration solutions are only 50 ng/ml and are opened only long enough to charge the injection syringe. The injected samples are, of course, destroyed in the TEA furnace. Positive blank values are subtracted from all samples treated in the same batch. Nevertheless their occurrence introduces additional uncertainty in low level samples, and in effect makes the detection limit higher than it would otherwise be. The problem of artifacts in nitrosamine analysis was reviewed recently (10).

A matching retention time on the GC-TEA is not by itself sufficient to demonstrate the presence of a specific nitrosamine. This was done for DMN by a separate determination using liquid chromatography on silica (Partisil 20/400). The column was 3 x 500 mm, the solvent was diethyl ether or 5% acetonitrile in dichloromethane, and an Altec ultraviolet detector at 254 nm was used. With a flow rate of 1.5 cc/min at 300 psi, 5 μg each of the nitrosamines was readily detected, DEN soon after the injection pulse, and DMN 10 minutes later. Since atmospheric samples contained too little nitrosamine for ultraviolet detection, a reference mixture was run immediately before the sample, then fractions were collected at the indicated volumes, and after reconcentration into dichloromethane were run on the GC-TEA. The fractions gave TEA responses at retention times for DEN, DMN, or no response, as predicted from volumes observed in the reference silica chromatogram. The elution order of DMN and DEN was reversed from that on the GC.

E. Dimethylnitramine synthesis and properties:

Because it had been shown (3) that dimethylnitramine, $(CH_3)_2NNO_2$, is a major product in the photochemical reaction of dimethylamine and NO_x, we synthesized it by a reported procedure (11). The crude product was obtained in 35% yield by adding 5.3 ml (0.069 mol) dimethylformamide in 40 ml acetic anhydride slowly with stirring to 22 ml 70% nitric acid chilled in dry ice. After one hour addition 50 ml more acetic anhydride was added and the mixture let stand for two hours. The mixture was then poured into

ice water and neutralized with 50% NaOH, cooled, extracted with 2 x 50 ml dichloromethane, dried over Na_2SO_4 and the solvent evaporated. The crude product (melting 50-55° corr.) was chromatographed on 70-200 mesh silica (deactivated with 5% water) in a 1 x 25 cm column with dichloromethane eluent, taking 5 ml fractions. The nitramine appeared in cuts 3-7, cut 13 smelled of dimethylformamide, cut 15 smelled aromatic (resembling benzaldehyde), and some colored residue remained on the column. The infrared spectum of the nitramine was run on a Beckman IR 18A, and matched the literature (12), as shown in Table 3.3. The melting point was 57-8° corr, as compared to 54-6° (11) and the ultraviolet spectrum in methanol showed maxima at 346 and 239 and a minimum at 217 nm. When run on the GC-TEA the signal intensity was about a third less than that of DMN and the retention time about the same as that of methylbutylnitrosamine or dipropylnitrosamine. Recovery checks showed that it is retained like DMN in the 1 N-KOH bubbler.

IV. SURVEY OF EMISSION SOURCES

A. Literature Leads:

Several sources of information were scanned in the attempt to locate specific sources of amines and nitrosamines. EPA on request sent a report on nitrosamines prepared for them by Mitre Corporation, which lists only one amine manufacturer in California (in Martinez), and a computer listing of 28 chemical producers (not necessarily of amines) in California. We ourselves have a computerized file of 5000 emission sources in Los Angeles County which was derived from a print-out from the EPA National Air Data Branch. Since it includes the Standard Industrial Code, we searched the file for organic chemical and similar related industries and located almost 100 more possible chemical sources (not necessarily of amines). Further searching in Commercial Directories located a few more amine sources, although these are not clearly differentiated between manufacturers and distribution sites. The total of potential chemical sources situated in Los Angeles is about 160 to date. These have been located by street map grid squares and plotted on a chart to show which areas would be most heavily dotted with sources, and thus the most likely places to begin sampling.

TABLE 3.3

DIMETHYLNITRAMINE INFRARED MAXIMA IN CCl_4

Observed, cm^{-1}	Literature[a], cm^{-1}
	2975 m
2935 m[b]	2941 m
1530 vs	1527 vs
1485 s	1475 s
1460 s	1464 s
	1450 s
1415 s	1403 m
1315 vs	1304 vs
1270 s	1260 sh
1140 m	1129 m
1055 m	1045 m
1005 s	998 ms
620 m	625 m (film)
	612 m (vapor)

a. Reference (12).

b. v = very; s = strong; m = medium; sh = shoulder.

B. Industrial Areas in Los Angeles County:

The map plot of known chemical and related industry showed the highest density to be in the Vernon-Commerce area (just south and southeast of central Los Angeles) followed by the Carson-Wilmington-Torrance area in the southern part of the county. The mobile unit was used to sample throughout these two areas plus a few other locations. We attempted to sample near most plants as close to downwind as practical. The types of industry included chemical, petroleum, rubber, and meat or fish packing plants. Locations are shown in Figures 4.1 and 4.2. Samples were taken during July, August and September, 1977. Most samples were negative and the few positives were mostly around 0.1 $\mu g/m^3$. One exceeded 0.3 $\mu g/m^3$ but was not that high during later resampling. Individual sample results are given in the Appendix.

C. Rocket Fuel Plant:

The Teledyne-McCormick-Selph plant, located outside Hollister, was scheduled to start full production of rocket fuel on October 25, according to EPA advisers. The production of the fuel (dimethylhydrazine) involves nitrosation of dimethylamine to DMN, followed by reduction. The mobile unit was used to sample air downwind of the plant from October 24 to 27.

The plant is located about three miles WSW of the city of Hollister. On Figure 4.3 it is in the lower left corner running about 0.6 miles along Union Road and enclosing an artificial reservoir. There is a posted fence along the road and a second fence about 300 feet in. The surrounding area is pasture and farmland and the only house nearby is just outside the eastern plant boundary. Public roads border only the northern and part of the western plant boundaries; the rest of the perimeter appears to be inaccessible by automobile except a short way along the neighbor's track east of the plant. Union Road is paved and curbed with no shoulders and is fairly heavily traveled The west side road is unpaved dirt. The terrain is hilly except to the west, varying from 240 feet in elevation on the flat to about 600 feet at some hill tops.

The weather Monday and Tuesday was clear and warm with winds mostly southerly. On Wednesday broken overcast appeared with winds still southerly until a midday shift to northwesterly, where they remained for the most part.

There was light rain in the late afternoon Wednesday. The wind directions allowing most nearly downwind sampling were south to southwest, and these occurred Monday p.m. through Wednesday a.m. Thereafter the winds were unfavorable. Sample sites are shown on the map. Results are given in Table 4.1.

D. Contra Costa County:

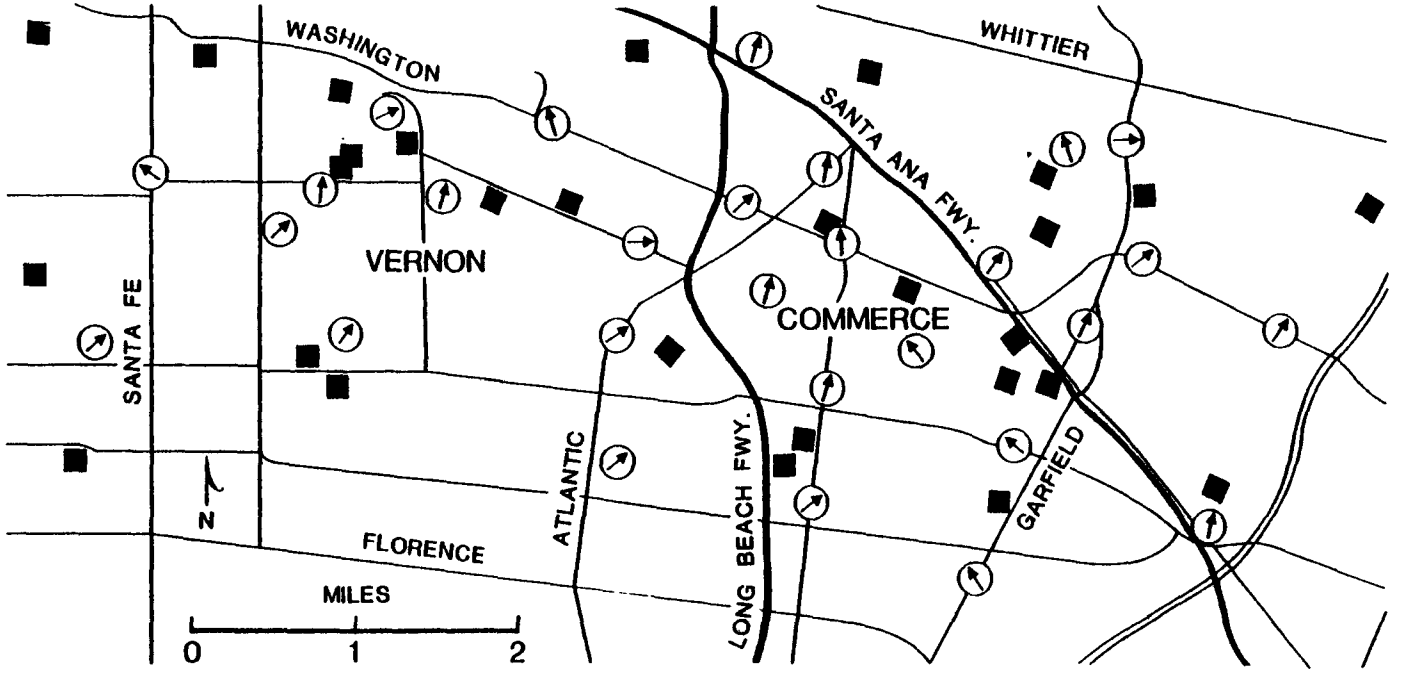
There is a belt of chemical and petroleum industry in Contra Costa County running along the shore of San Pablo Bay, Carquinez Straits, and up the river past Antioch, where the San Joaquin and Sacramento rivers meet. This belt was surveyed with a mobile sampling unit during the week of April 10-14, 1978. One hour samples of 40-60 l air were bubbled through 50 ml of N-KOH, protected from light. The bubbler contents were immediately frozen on dry ice and kept frozen until they were brought back to Los Angeles and placed in a freezer for subsequent work-up and analysis. Blank controls were also taken along.

During the week the weather was quite uniform. Winds were all southwest to northwest, mostly at 5-10 mph. There were occasional clouds or thin overcast, and temperatures varied 16-25°C. The uniform wind direction made it impossible in some cases to get close to downwind of industrial plants where roads did not run along the side wanted.

Figure 4.4 shows the survey area with locations of eastern samples lettered. The crosshatched rectangles are areas shown on a larger scale in figures 4.5 to 4.7. In Figure 4.7 the higher density of samples is partly because of the chemical plant of Shell Oil, the only known producer of volatile amines in California. Samples E, F, H and U are just east of this plant.

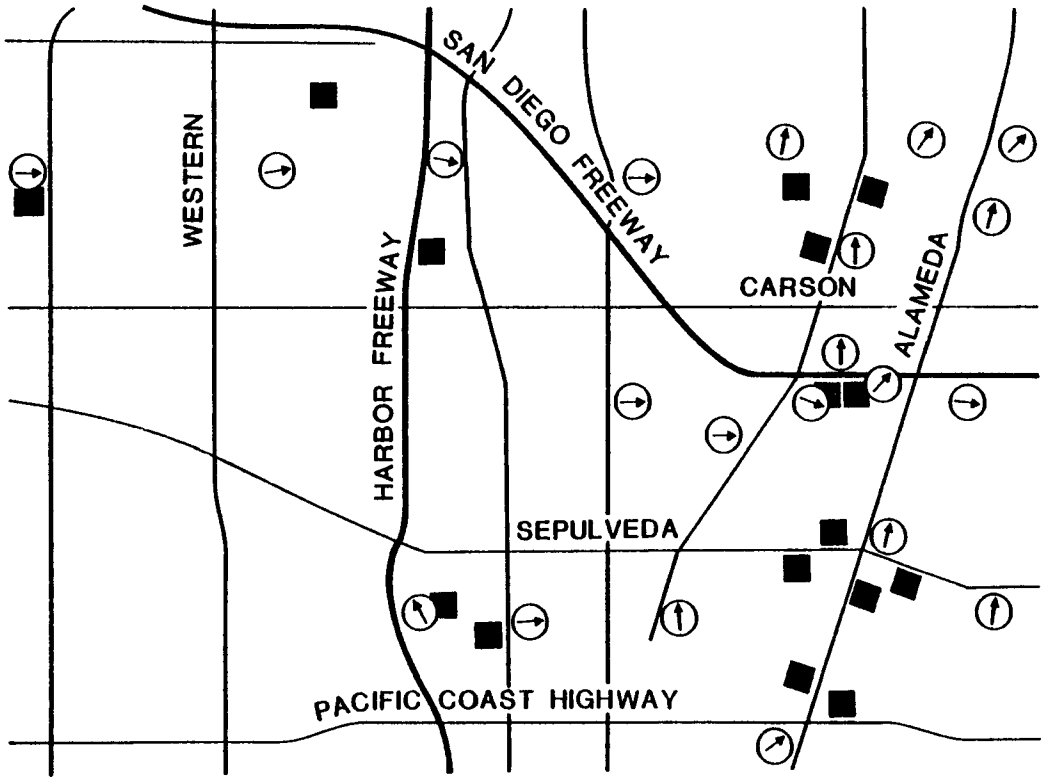
Sample data are given in Table 4.2. Two samples were mistakenly given the same label, and unfortunately one of these showed the highest level of dimethylnitrosamine (1.0 or 1.1 $\mu g/m^3$) along with diethylnitrosamine and materials with retention times corresponding approximately to dipropylnitrosamine and nitrosopiperidine. The two locations confused (C and G) were in northwest Richmond and east of Martinez, respectively. Another sample (U), close to Shell Chemical, showed 0.34 $\mu g/m^3$ DMN. All other samples were below 0.1 $\mu g/m^3$ DMN. A follow-up set of samples at the two confused sites was collected on May 30 and June 2, with results as shown in Table 4.2. Two of the three values at site (G) of 0.08 and 0.10 $\mu g/m^3$ DMN are in line with many others at various locations. Site (C) showed nothing.

FIGURE 4.1



Air sampling sites in the Vernon-Commerce area (shown by circles). Arrows indicate wind direction. Squares are chemical or meat processing plants

FIGURE 4.2



Air sampling sites in the Torrance-Carson-Wilmington area (shown by circles). Arrows indicate wind direction. Squares are chemical or petroleum plants

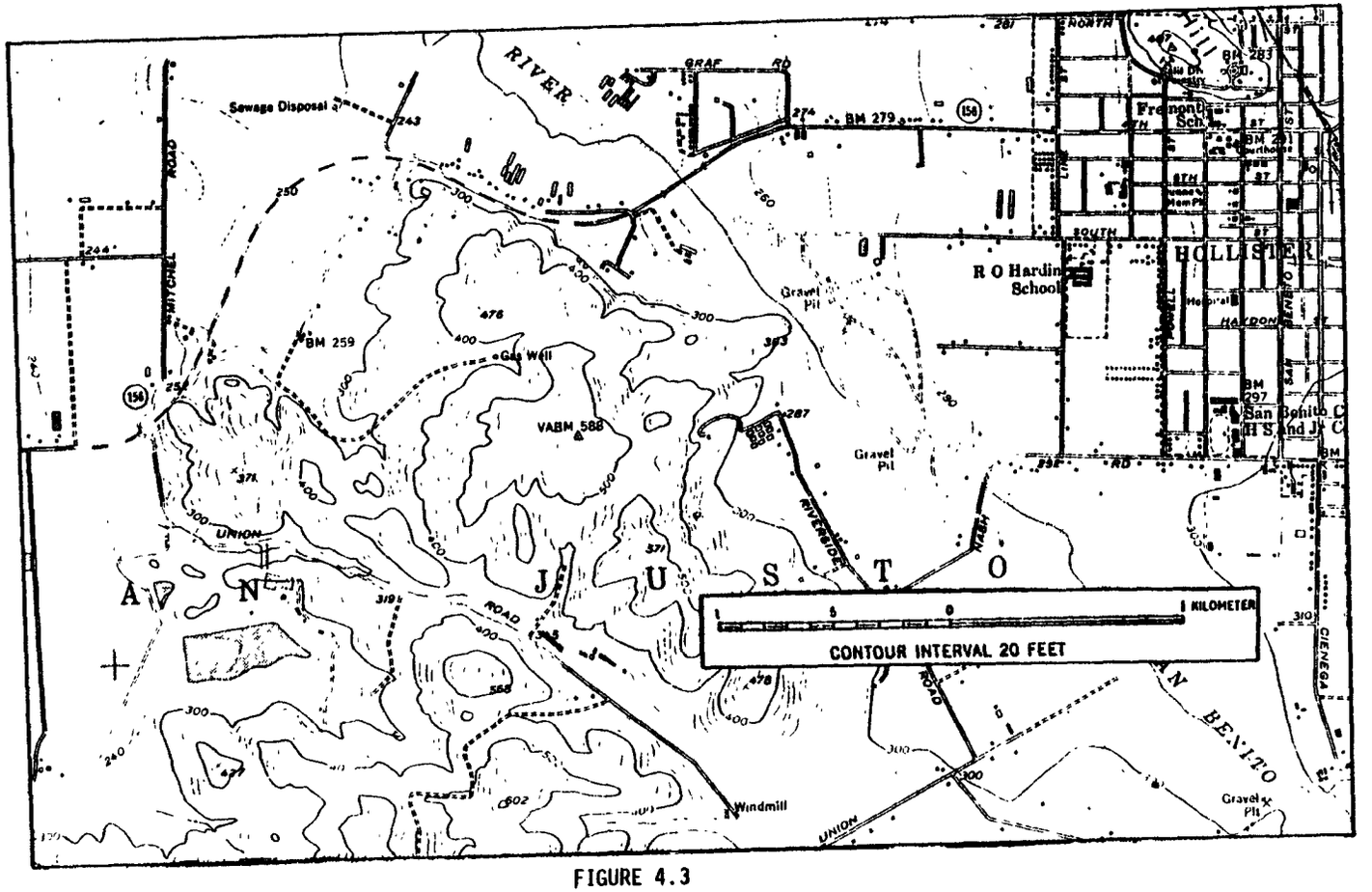


FIGURE 4.3

Map of Hollister area. Rocket fuel plant is at lower left around artificial lake.

TABLE 4.1

HOLLISTER AIR SAMPLES

Collected along Union Road north of Teledyne Plant

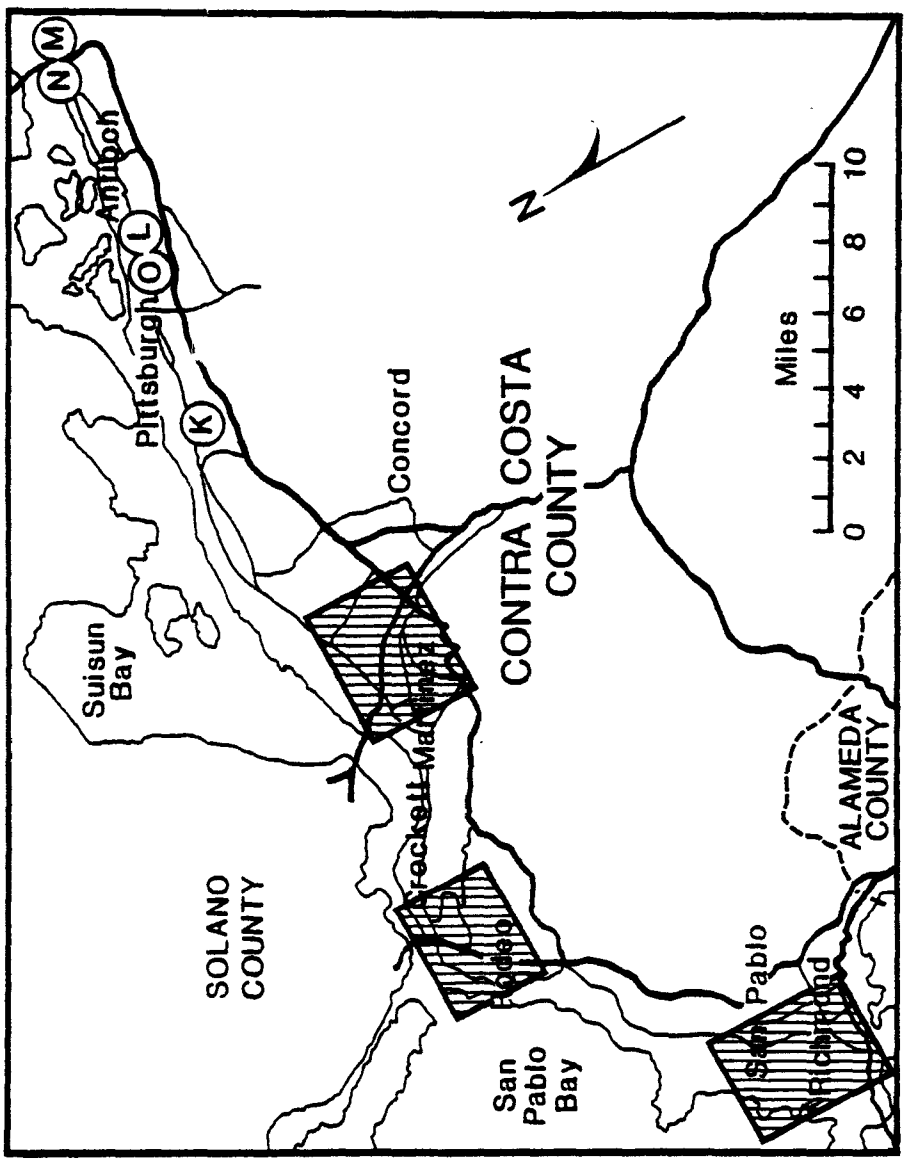
Sample Date	Time	Average Wind Estimates		Average Temp.	DMN* $\mu g/m^3$	
		° True	mph	° C		
10-24	1332 - 1432	180	~ 1	31	0.11	Clear
	1433- 1532	200	1 - 2	31	nd	Clear
	1545 - 1645	150	5 - 8	31	nd	Clear and gusty
10-25	0810 - 0910	180	2 - 4	18	nd	Clear
	0911 - 1011	220	1 - 2	22	0.25	Clear
	1045 - 1145	170	2 - 4	25	0.11	Clear
	1146 - 1246	160	4 - 6	26	nd	Clear
	1327 - 1427	190	2 - 6	32	nd	Clear; wind veering last 10 min.
	1444 - 1544	330	7 - 10	31	nd	Clear
10-26	0806 - 1006	160	2 - 6	19	0.19	Partial overcast
	1007 - 1137	160	2 - 9	21	0.13	Partial overcast; wind starts to veer
	1302 - 1402	310	2 - 6	26	0.03	Partial overcast
	1403 - 1503	300	4 - 10	24	0.04	Total overcast
	1605 - 1705	250	1 - 3	22	nd	Light rain
10-27	0816 - 0916	200 - 360 variable	4 - 6	14	0.11	Partial overcast
KOH control					nd	

*DMN - dimethylnitrosamine

nd - not detected

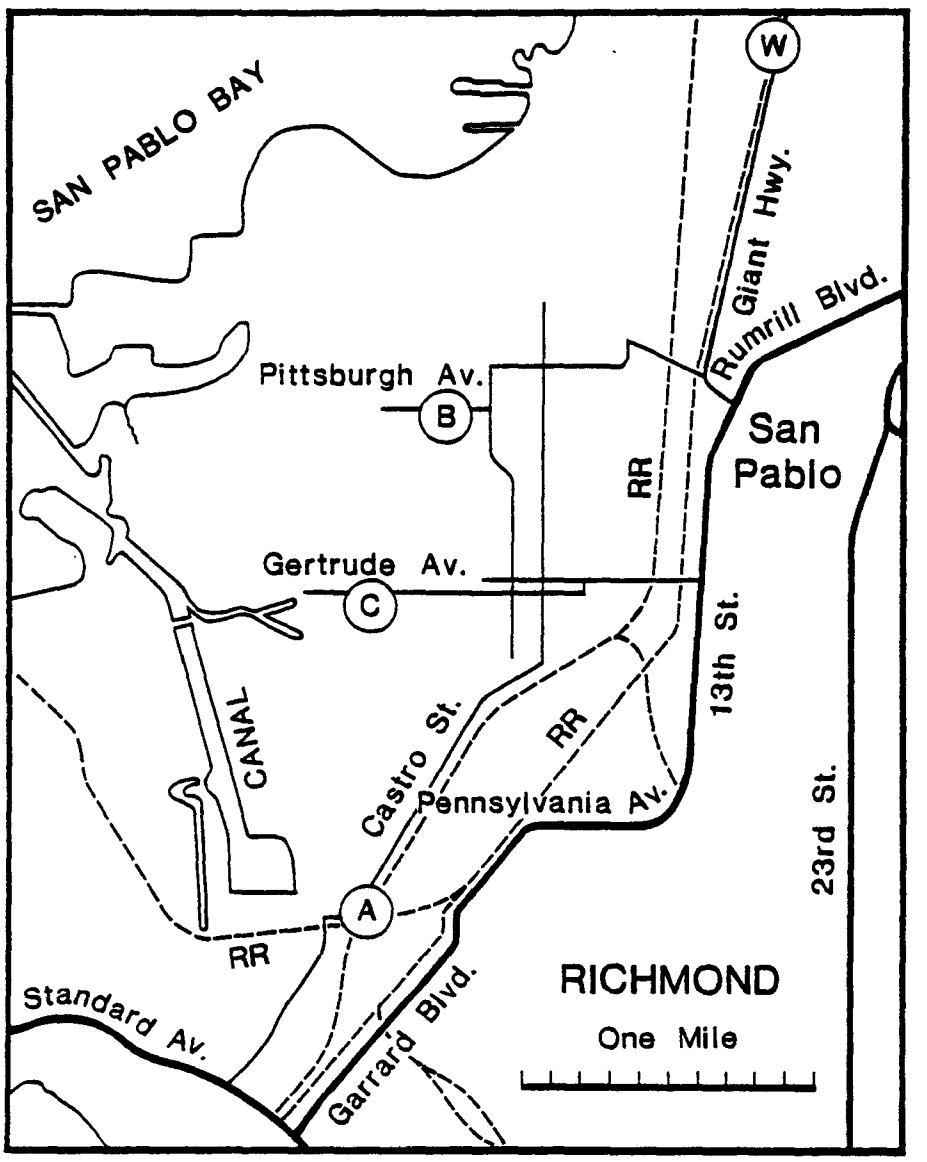
Tentative recovery factor (0.94) not used.

FIGURE 4.4



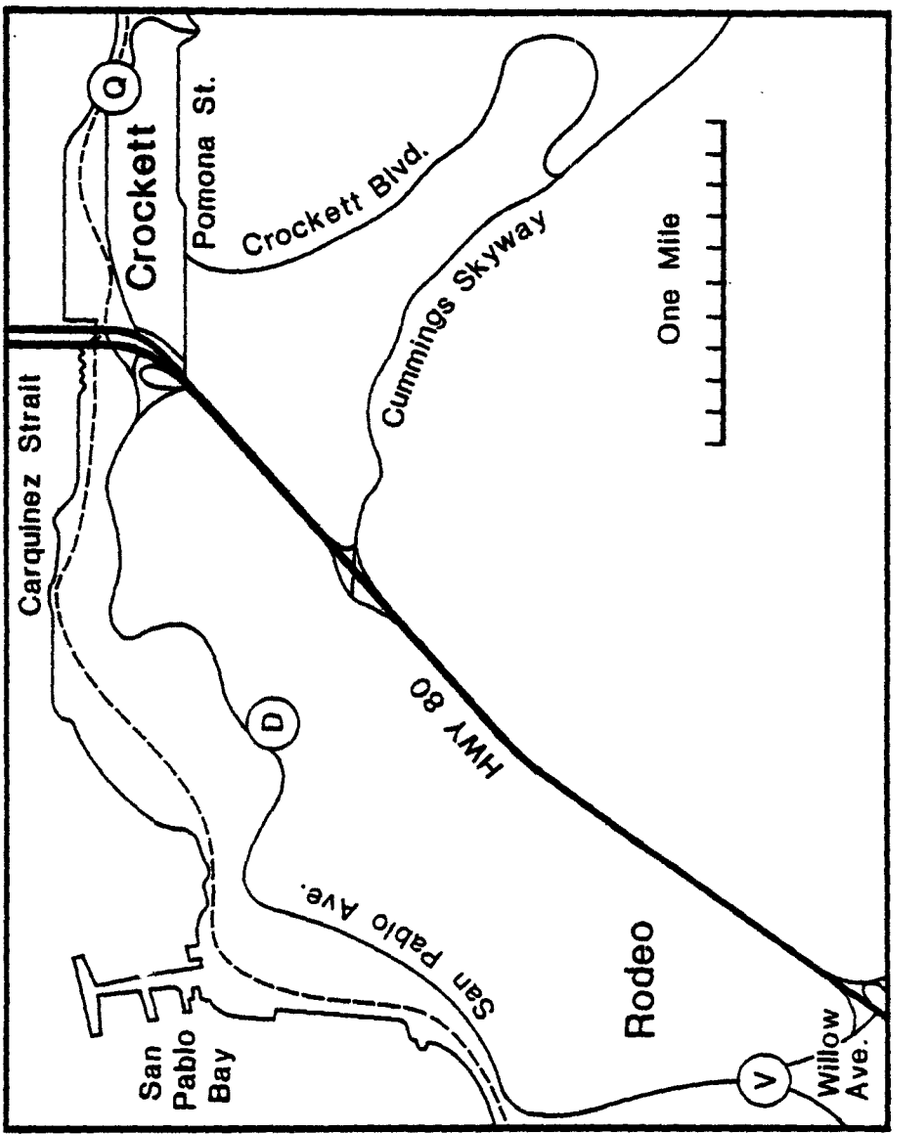
Map of west Contra Costa County. Cross-hatched areas are shown in larger scale in three following figures. Circles are coded air sample sites described in table 4.2

FIGURE 4.5



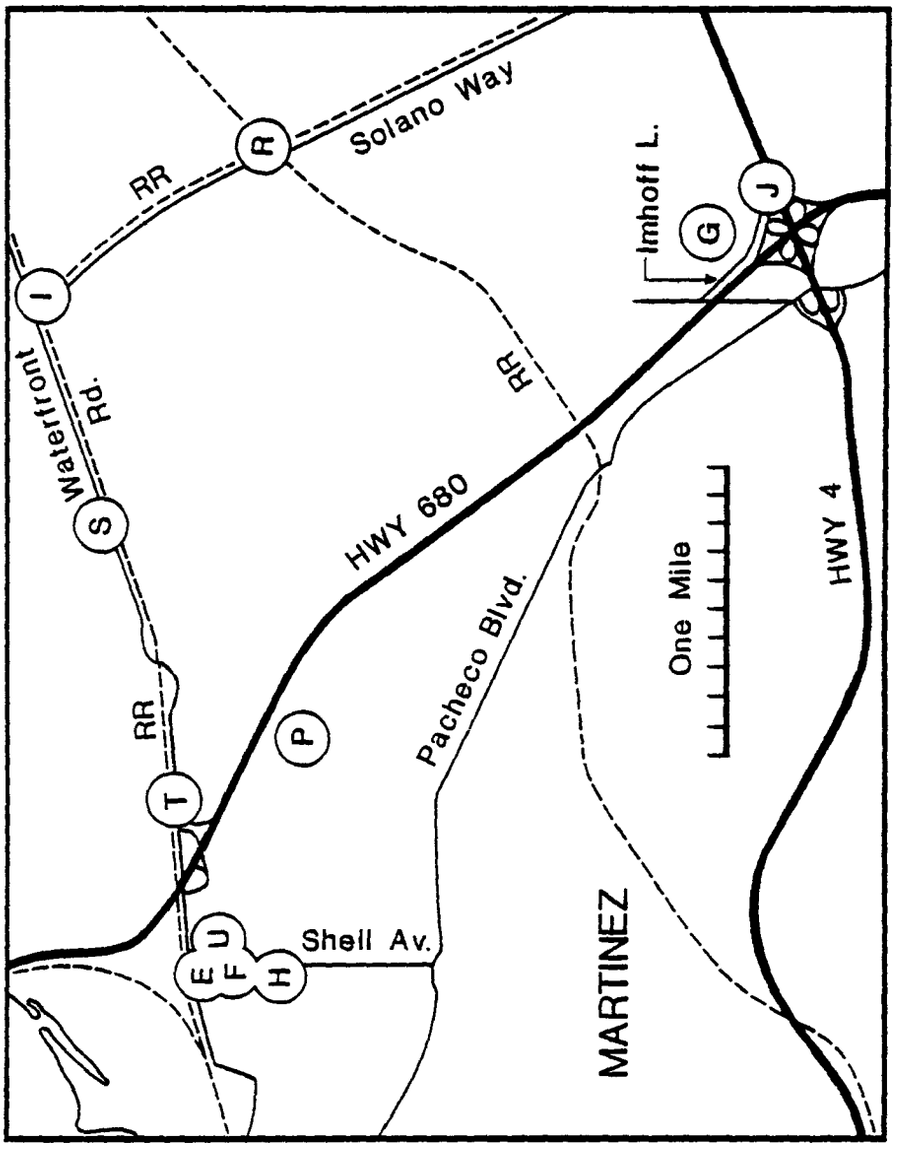
Map of North-west Richmond area. Circles are coded air sample sites described in table 4.2

FIGURE 4.6



Map of Rodeo-Crockett areas. Circles are coded air sample sites described in table 4.2

FIGURE 4.7



Map of east Martinez area. Circles are coded air sample sites described in table 4.2

TABLE 4.2

DATE	TIME	CODE	LOCATION	AV. WIND: DIRECTION °true	VELOCITY mi/hr	AV °c	WEATHER	SAMPLE VOLUME, l	DMN, µg/m³	NEARBY INDUSTRY
4-10	1100-1200	A	Castro St. opposite end of San Pablo Canal, Richmond	215	5½	22	Sun	39.5	n*	Standard Oil and others
	1320-1420	B	Pittsburgh Ave, 0.2 mi W. of Central St, NW of Richmond	205	6	21	Sun	45.6	0.06	Standard Oil and others
	1430-1540	C	Gertrude Av, 0.4 mi. W. of York St, N. of Richmond	200	6	20	Sun	45.3	0.05 or 0.98†	Standard Oil and others
	1615-1635	D	Oil Country Rd., NE of Rodeo	230	3½	22	High thin clouds	48.1	0.05	Union Oil Refinery
4-11	0800-0900	E	Shell Av., E. of Martinez	275	5	20	Overcast, cleared	41.9	0.09	Shell Oil (Chemical plant)
	0905-1005	F	S. of previous E	270	6	22	Sun	38.4	n	Shell Oil (Chemical plant)
	1050-1150	G	0.2 mi NE of Imhoff Dr. near junction 4 and 680	280	8	23	Sun	40.8	0.06 or 1.09†	Industrial waste treatment
	1315-1415	H	Shell Av., S. of F	330	5	25	Sun	29.7	n	Shell Oil (Chemical plant)
	1430-1530	I	Waterfront Rd. & Solano Way, E. of Martinez	280	7	23	Sun	35.4	0.02	Phillips/Lion Oil Refinery
	1615-1715	J	Imhoff Dr., E. end near 4-11-C	275	5	23	Sun	26.7	0.08	Contra Costa Sanitation
4-12	1010-1110	K	Willow Pass Rd., W. of Bailey Rd., West Pittsburgh	305	6	20	Scattered high thin clouds	42.6	n	Hysol (Div. of Dexter)
	1138-1238	L	West 10th, 0.2 mi E. of California Av., E. of Pittsburgh	265	7	22	Mostly high thin overcast	41.6	n	Dow, Allied, U.S. Steel
	1345-1445	M	E. 18th St., 0.6 mi E. of 4, E. of Antioch	285	8	23	Mostly high thin overcast	44.5	n	Dupont and others
	1505-1605	N	Wilbur Rd , 0.5 mi. W of 4, E. of Antioch	295	11	22	Mostly high thin overcast	42.9	0.01	Fibreboard, Crown Zellerbach
	1630-1730	O	Loveridge Rd. & California Ave., E Pittsburgh	285	10	19	Mostly high thin overcast	40.5	n	Union Carbide

TABLE 4.2 (continued)

DATE	TIME	CODE	LOCATION	AV. WIND: DIRECTION ^{0}true	VELOCITY mi/hr	AV ^{0}C	WEATHER	SAMPLE VOLUME, l	DMN, μg/m^3	NEARBY INDUSTRY
4-13	0817-0917	P	Road to sanitation plant, W. of 680, E. of Martinez	265	7	18	Scattered clouds	40.2	n	Shell Oil (Refinery)
	1011-1113	Q	Winslow St. & Vallejo St., Crockett	270	4	18	Scattered clouds	38.3	n	C & H
	1324-1424	R	Solano Way, N. of Monsanto Rd., E. of Martinez	210	6	21	Scattered clouds	39.3	0.01	Lion Oil
	1434-1547	S	Waterfront Rd., 0.8 mi W. of Solano Way, E. of Martinez	220	9	24	Scattered high clouds	37.2	n	Landfill, marine terminals
	1614-1714	T	Waterfrond Rd., E of 680	240	9	18	Scattered high clouds	40.4	0.01	Shell Oil
4-14	0811-0911	U	Shell Av., E. of Martinez	260	4	16	Mostly overcast	60.6	0.34	Shell Oil (Chemical)
	0944-1044	V	San Pablo Ave. at Willow Rd., Rodeo	250	3	18	Mostly overcast	59.8	0.02	Pacific Refining
	1114-1214	W	Giant Highway N. of Miner Av., N. Richmond	240	5	17	Mostly over-	56.4	n	Koppers, Witco
5-30	1420-1520	C	Resample previous site	280	5	37	Sunny	84.6	n	
	1615-1715	G	Resample previous site	030	7	34	Sunny	83.4	n	
6-02	0735-0835	G	Resample previous site	265	7	12	Broken clouds	81.6	0.08	
	0836-0936	G	Resample previous site	255	5	14	Scattered clouds, clearing	79.2	0.10	
	1041-1141	C	Resample previous site	085	2	23	Sunny	84.0	n	
	1142-1242	C	Resample previous site	070-260	2½	24	Sunny	77.4	n	

* n = not detected

† These two samples were erroneously given the same label.

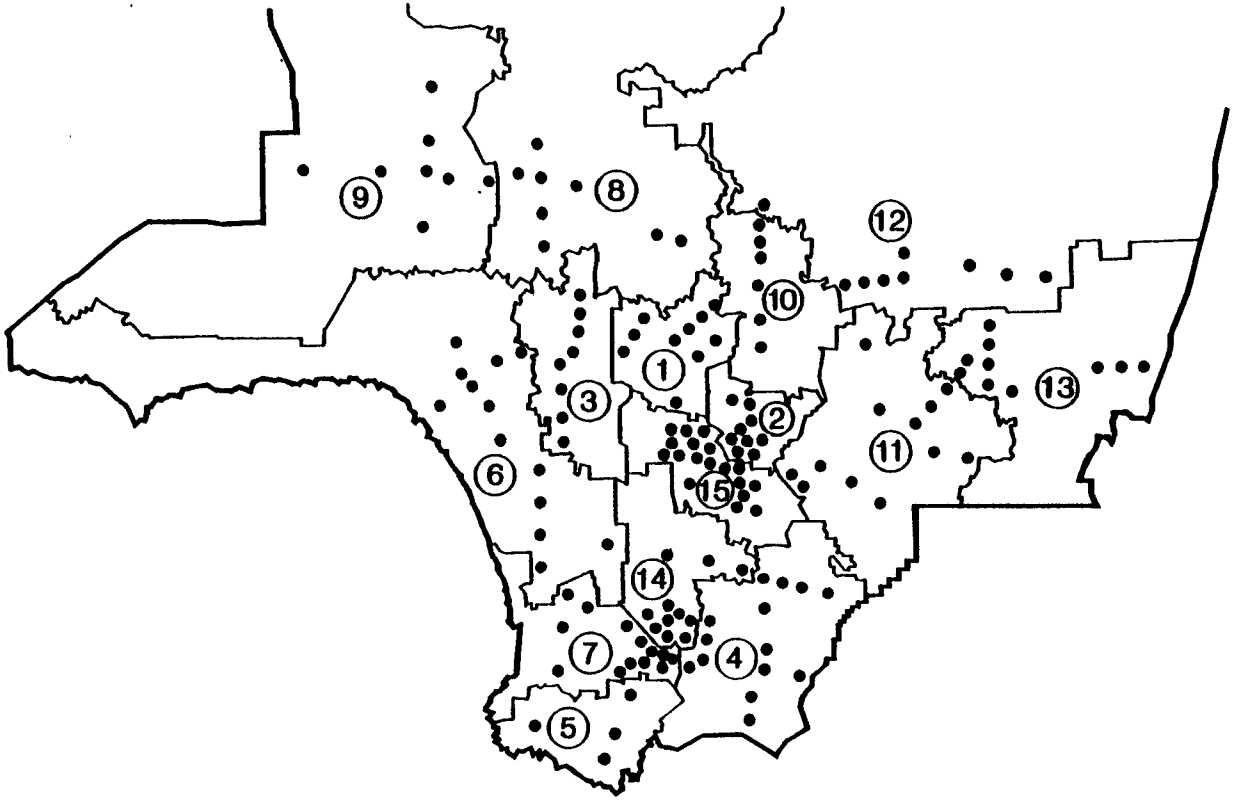
The highest DMN levels found in Los Angeles over months of sampling were a few between 0.2 and 0.5 $\mu g/m^3$. One of two highest Contra Costa samples is within this range. The other is about twice as high, and is similar to one or two samples found in Baltimore (upwind of a rocket fuel factory). Thus there is only a marginal indication of any specific point emission source, and the highest sample is at least 3.3 miles from the only known amine manufacturer.

E. Los Angeles County Census Area Survey

In connection with epidemiological studies at the USC School of Medicine, Cancer incidence data can be sorted by case residence into 26 health districts, which are groups of census tracts. For purposes of this project these districts were recombined into 15 larger areas as shown in Figure 4.8. In each area air samples were taken at spaced locations on at least two non-consecutive days. Not counting the more frequently used LAC-USC site, each area was sampled from 6 to 19 times (average 11) at different sites. In Figure 4.8 the approximate spatial distribution of the samples is shown. The summarized results are shown in Figure 4.9, while individual sample data are in the Appendix. In Figure 4.9 the first number is the average DMN concentration in the census area, the second the maximum DMN found, and the third is the fraction of positive samples. About one sample in four gave a detectable reading for DMN. The highest was 0.48 $\mu g/m^3$ in an 0700 o'clock sample on the grounds of the Los Angeles County-USC Medical Center. That location is very near the interchange of the Golden State and San Bernardino Freeways and is also close to fairly heavy local traffic.

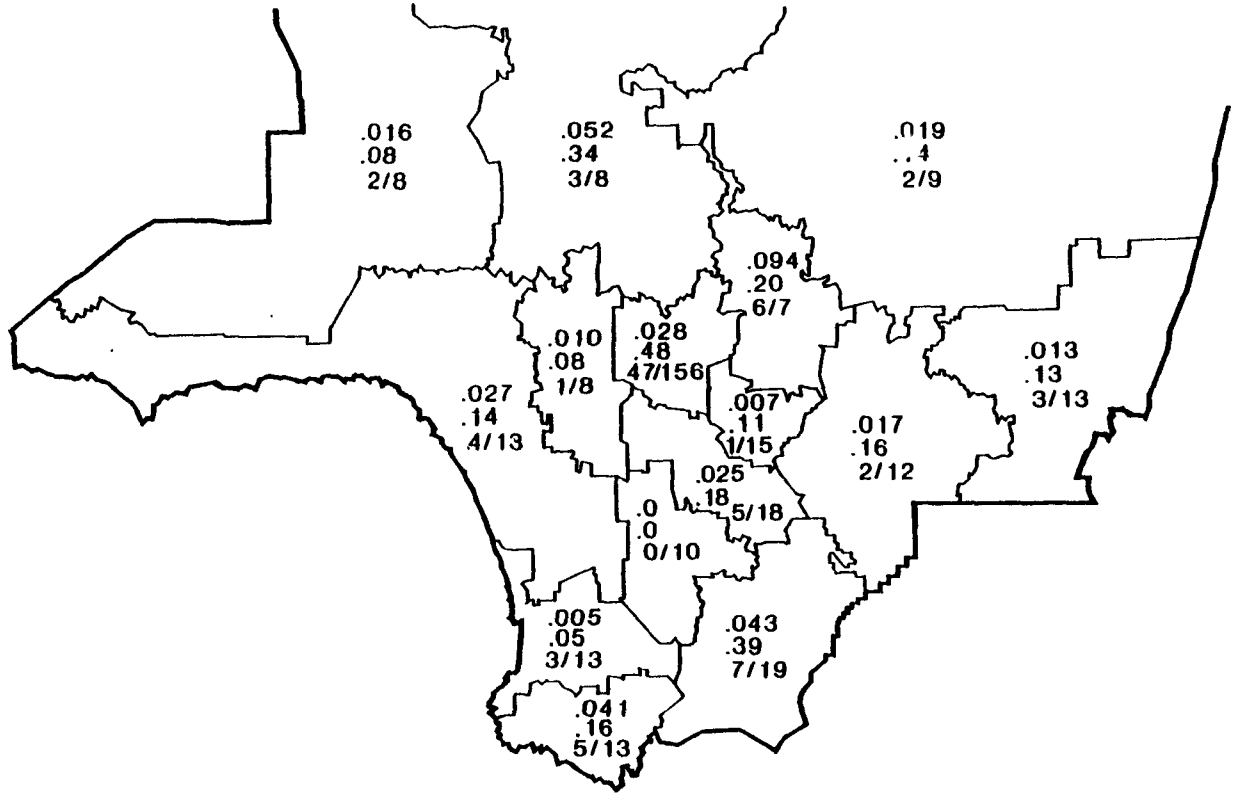
For comparison with cancer incidence data the DMN averages for each area were stratified for computer plotting as in Figure 4.10. The cancer incidence data for pharynx, liver, nose-sinus, larynx, lung, and bladder as similarly plotted in Figures 4.11 to 4.16, respectively, for white males without Spanish surname. For demographic reference average educational level and family income by area are given in Figures 4.17 and 4.18.

FIGURE 4.8



Distribution of air sampling sites in southern half of Los Angeles County

FIGURE 4.9



Summary of DMN air data in health district areas. Average and maximum levels are given, then positives as a fraction of total samples

RELATIVE LEVELS OF DIMETHYLNITROSAMINE IN AIR BY GEOGRAPHIC DISTRICT
LOS ANGELES COUNTY, 1978

FIGURE 4.10

Computer plot of relative nitrosamine concentrations by area.

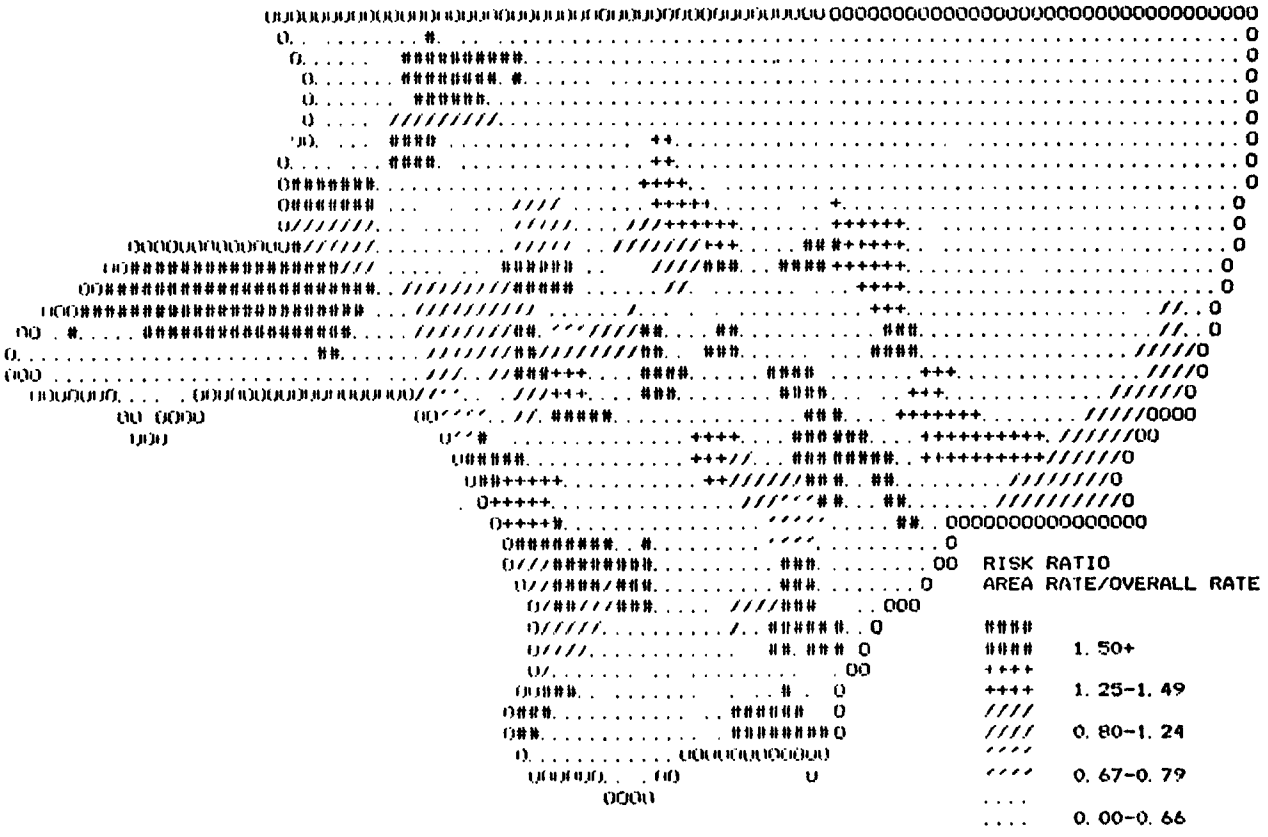
FIGURE 4.11

Computer plot of relative incidence of cancer of the pharynx for white males without Spanish surnames, by area.

RELATIVE INCIDENCE BY RESIDENCE, LOS ANGELES COUNTY, 1972-75
MALE, AGE-ADJUSTED, OTHER WHITE
LIVER CANCER, ALL HISTOLOGIES

FIGURE 4.12

Computer plot of relative incidence of cancer of the liver for white males without Spanish surnames, by area.



RELATIVE INCIDENCE BY RESIDENCE, LOS ANGELES COUNTY, 1972-75
MALE, AGE-ADJUSTED, OTHER WHITE
NOSE, SINUS CANCER, ALL HISTOLOGIES

FIGURE 4.13

Computer plot of relative incidence of cancer of the nose-sinus for white males without Spanish surnames, by area.

RELATIVE INCIDENCE BY RESIDENCE, LOS ANGELES COUNTY, 1972-75
MALE, AGE-ADJUSTED, OTHER WHITE
LARYNX CANCER, ALL HISTOLOGIES

FIGURE 4.14

Computer plot of relative incidence of cancer of the larynx for white males without Spanish surnames, by area.

RELATIVE INCIDENCE BY RESIDENCE, LOS ANGELES COUNTY, 1972-75
MALE, AGE-ADJUSTED, OTHER WHITE
LUNG CANCER, ALL HISTOLOGIES

FIGURE 4.15

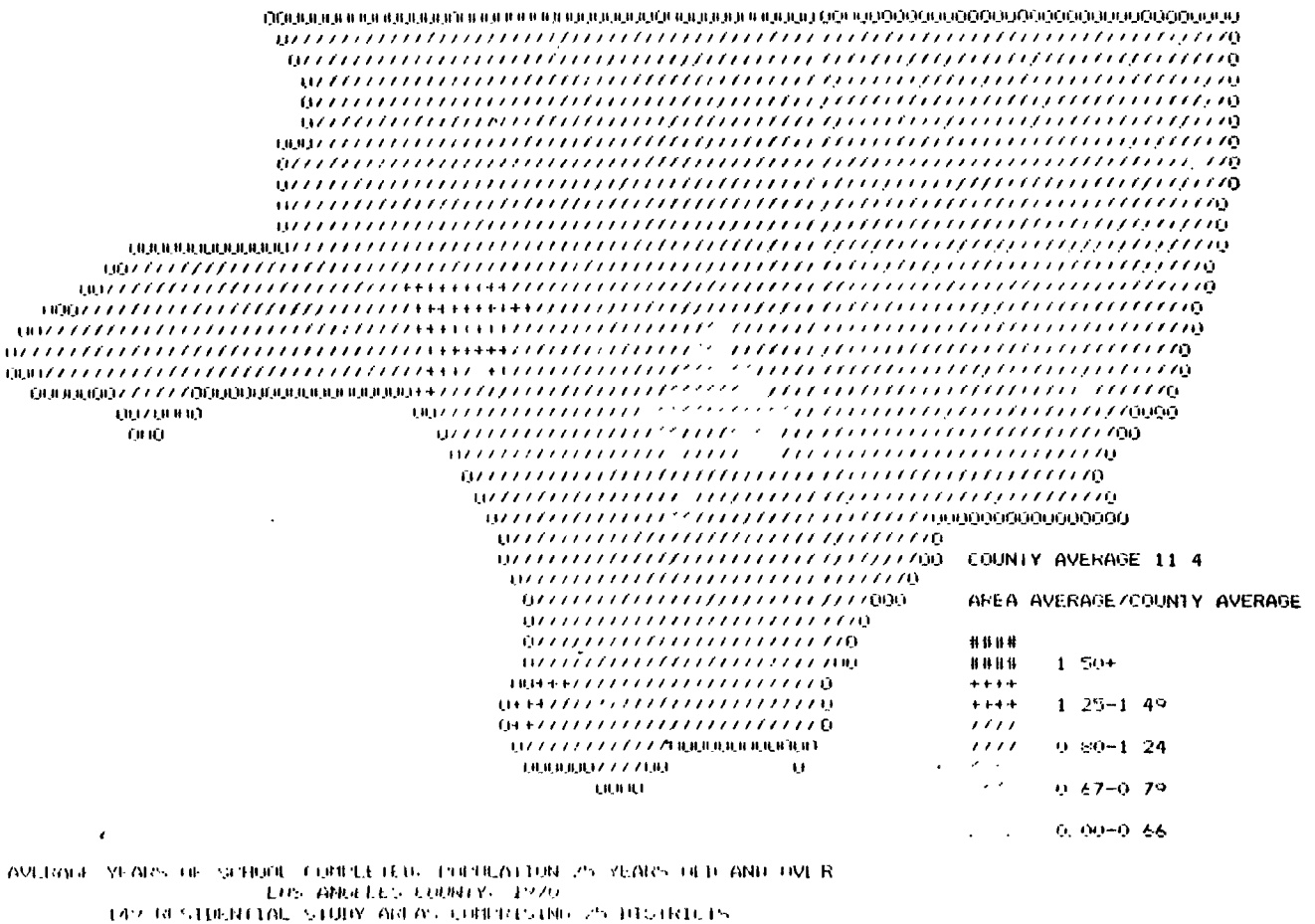
Computer plot of relative incidence of cancer of the lung for white males without spanish surnames, by area.

RELATIVE INCIDENCE BY RESIDENCE, LOS ANGELES COUNTY, 1972-75
MALE, AGE-ADJUSTED, OTHER WHITE
BLADDER CANCER, ALL HISTOLOGIES

FIGURE 4.16

Computer plot of relative incidence of cancer of the bladder for white males without Spanish surnames, by area.

35



AVERAGE YEARS OF SCHOOL COMPLETED, POPULATION 25 YEARS OLD AND OVER
LOS ANGELES COUNTY, 1970
1970 RESIDENTIAL STUDY AREAS, CONSISTING OF 25 DISTRICTS

FIGURE 4.17

Computer plot of average educational level by area.

AVERAGE FAMILY INCOME, LOS ANGELES COUNTY, 1970
149 RESIDENTIAL STUDY AREAS COMPRISING 25 DISTRICTS

FIGURE 4.18

Computer plot of average family income by area.

V. OTHER VARIABLES

A. Seasonal Effects:

Figure 5.1 shows the monthly DMN averages, without regard to sampling site, for Los Angeles daytime samples. The fractions are ratios of number of positive to total samples. The two high months were November and December, during which, except for December 28-29, all sampling days were fair. Heavy rains and cloudy weather occurred through most of January and part of February. This may have affected the DMN values for these months. Also, during January and February, more samples were collected at outlying parts of the county. It appears that higher DMN concentrations and more frequent positive samples occur in the winter.

B. Diurnal Pattern:

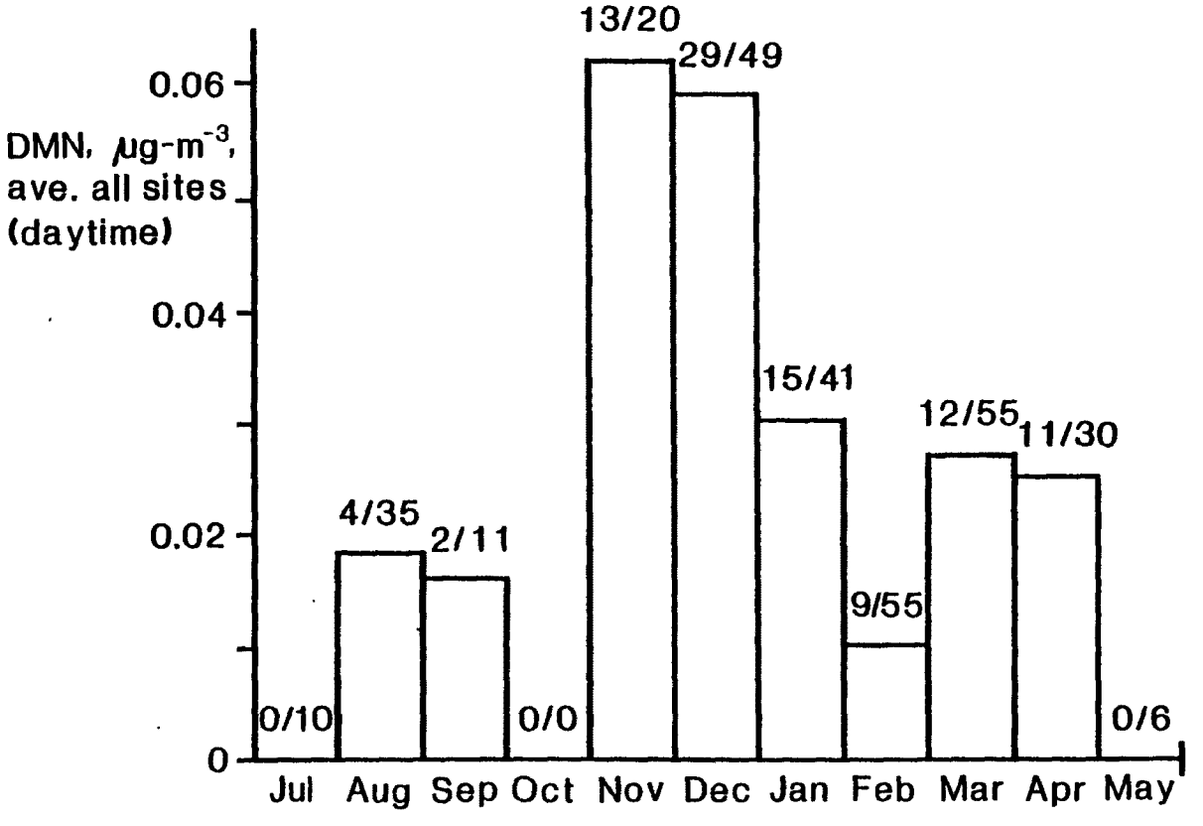
The DMN averages for each hour of the day for all samples taken during August-December at all locations were tabulated and smoothed by taking moving averages. The results are shown in Figure 5.2. The maxima at 0800 and 1800 and the minimum at 1300 are consistent with a build-up of DMN during the day (perhaps especially during traffic hours) and breakdown during the sunny hours from mid-morning on. The night-time minimum could reflect reduced traffic or other emission activity and loss through dilution processes. The maximum at 0100 is based on very few samples and may not be real.

Another series at a single location (LAC-USC Medical Center) was run in Spring of 1978. In this series six consecutive hourly samples per day were run, moving the shift around the clock. All hours of the day and night were sampled seven times in all. The averages for each hour were treated as before with the results shown in Figure 5.3. As in Figure 5.2, there are maxima at 0800 and 1800, but midday values do not drop off as much.

C. Oxides of Nitrogen

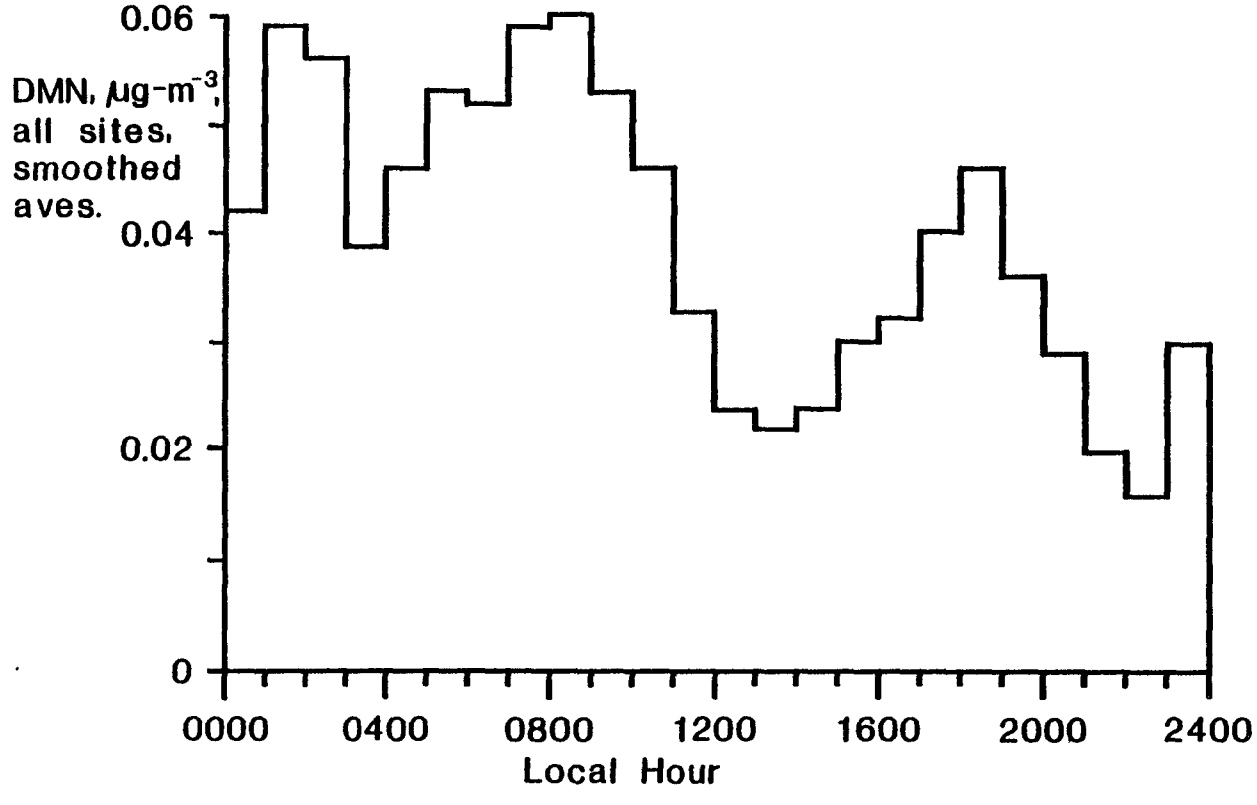
Hourly averages for nitric oxides, nitrogen dioxide, and carbon monoxide were obtained from the South Coastal Air Quality Management District for the downtown Los Angeles station between July and November. The hourly averages nearest in time to each nitrosamine sample taken during that period were plotted against DMN concentrations. No correlation was evident for any of the three pollutants. No attempt was made to introduce any time offset. The majority of the nitrosamine samples were below detection limits, while the other three pollutants almost never fell below detectability.

FIGURE 5.1



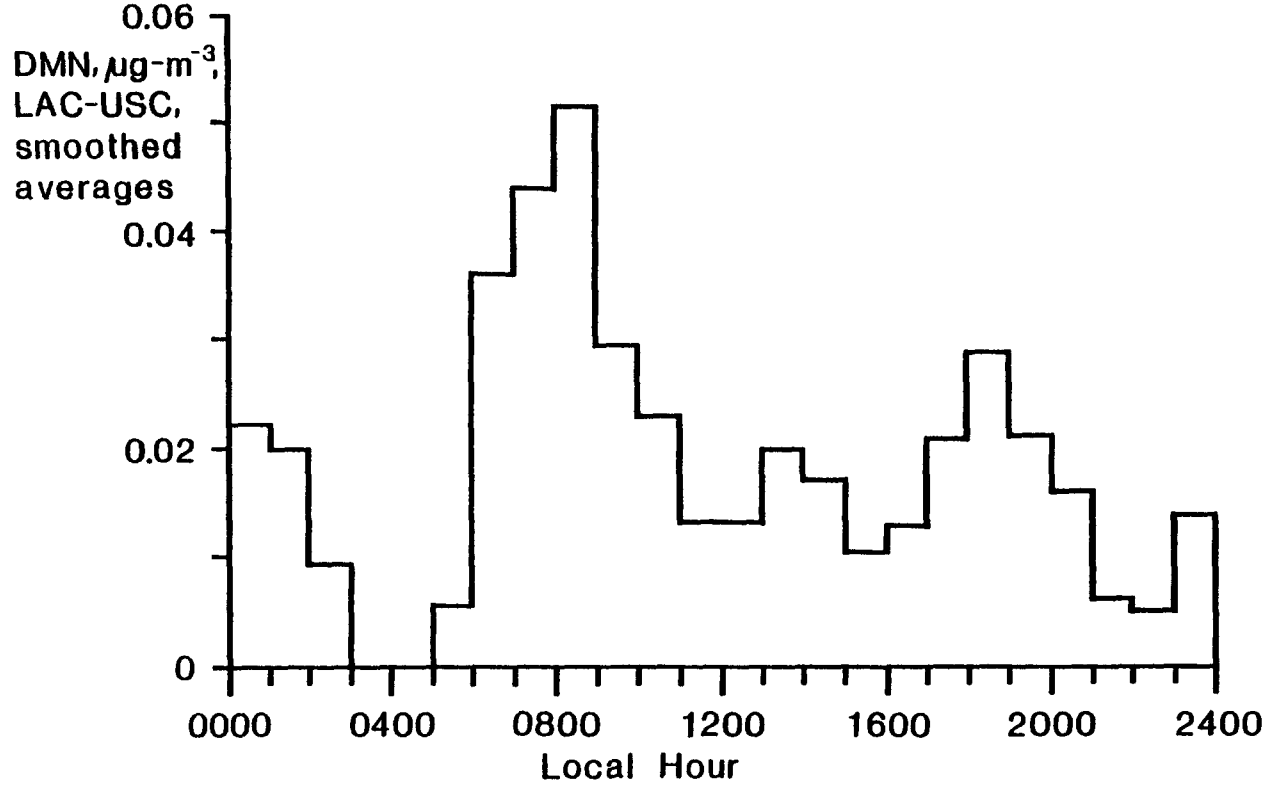
Monthly averages for DMN at all Los Angeles sites, daytime samples. Positives as fractions of total samples are given above each bar

FIGURE 5.2



Hourly averages for DMN at all Los Angeles sites during August-December, 1977. Samples begun during each designated hour are included in that hourly average. Data are smoothed by taking running averages of four, centered

FIGURE 5.3



Hourly averages for DMN at LAC-USC Medical Center during March-May, 1978. Data are smoothed by taking running averages of three

VI. DISCUSSION OF RESULTS

Out of several hundred air samples taken in many Los Angeles locations during most of the year, about one in four contained detectable DMN. The highest level was 0.48 $\mu g/m^3$ and the average of all samples was about 0.03 $\mu g/m^3$. No strong localization was observed, although there were apparently rather higher levels in the central area than in the eastern or western parts of the county. Both industry and auto traffic tend to be concentrated in the central area. More frequent sampling among the areas of highest concentration of chemical, petroleum, rubber, and meat or fish processing industry failed to indicate any unusually high concentrations. The location showing several of the highest levels observed was at the LAC-USC Medical Center, 200m east of the nearest freeway, and 400m northeast of a freeway interchange, i.e. usually downwind of the freeways. This suggested the possibility that vehicle emissions have something to do with DMN occurrence.

The temporal patterns show two effects: more frequent occurrence of DMN in winter months, and daily maxima around 0800 and 1800. The winter effect probably reflects the decreased intensity of solar ultraviolet, which is known to photolyze DMN. The diurnal decrease during midday may result from the increased sunshine during that period. The diurnal maxima approximately follow the daily vehicle traffic maxima, but perhaps also reflect some continuous emission or formation during the daytime which is diminished in strong sunlight and dies down at night.

Samples taken at Hollister and in Contra Costa County were about half positives and averaged higher than the Los Angeles samples. (They were collected in October and April, respectively) Only one sample (from Contra Costa), however, was higher than the highest from Los Angeles (1.0 versus 0.48 $\mu g/m^3$). With that one possible exception, there is no indication of point sources in the northern samples. The higher fraction of positives could be due to reduced solar photolysis of DMN at the higher latitudes, or to the time of the year when samples were taken.

Occasionally samples contained diethyl- as well as dimethylnitrosamine (DEN and DMN), in comparable amounts. A few spring samples (both Los Angeles and Contra Costa) also contained a third component with retention time matching approximately to dipropyl- or methylbutylnitrosamine, or to dimethylnitramine. The GC peaks for this material were lower than for DMN and DEN in the same samples.

In making or handling amines industrially, the dimethyl- and diethylamines would not normally be found together in one process or container, although they might occur in the same chemical plant in different operations. It is conceivable that they could be formed as trace vehicle exhaust components (analogous to ammonia) or biogenically. Subsequent nitrosation might occur atmospherically with nitrous acid or oxides of nitrogen. The possibility of an exhaust source is weakened by failure to observe other nitrosamines, particularly ethylmethyl-nitrosamine (EMN). This might be expected to have a retention time between those of DMN and DEN, and the amine should occur in any exhaust mixture that contained the other two, although not necessarily in biogenic mixtures. The lack of correlation with nitrogen oxides data at the downtown monitoring station does not support a photochemical synthesis of nitrosamines. The data are compared for samples which were usually several miles apart, however.

The geographic analysis of cancer incidence patterns within Los Angeles County for possible association with present nitrosamine levels presents some difficulty. If a relationship does exist between recently diagnosed cancer patients and nitrosamine exposure, that exposure would have had to take place some time ago. Thus any analysis using present nitrosamine levels must proceed on the assumption that present levels are indicative of past geographic patterns. Such an analysis also presumes that any effect of nitrosamines on cancer risk is strong enough relative to other etiologic factors that it would be itself discernible by geographic analysis above the effect of other factors.

The geographic distribution of nitrosamine level ratios and cancer risk ratios are illustrated in Figures 4.10 -4.16. The six cancers pictured include those of the pharynx, liver, nose-sinus, larynx, lung and bladder. Data is provided for white males without Spanish surnames. Mappings are presented rather than correlation statistics so that geographic distributions can be simply and easily visualized. Each map could accomodate up to five different categories of risk ratios.

For demographic reference purposes, mappings of average educational level and average family income per geographic area have also been included (Figures 4.17 and 4.18).

There is no apparent relationship between nitrosamine distribution and that of any of the six cancers studied. As expected, lung cancer among white males follows social class patterns as

measured by either education or income and no other relationship can be seen. No evidence is discernible within these data in support of an association between nitrosamines and cancer.

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IX. GLOSSARY

DMN - dimethylnitrosamine; N-nitrosodimethylamine

DEN - diethylnitrosamine; N-nitrosodiethylamine

GC - gas chromatograph

TEA - thermal energy analyzer; a specific detector for nitrosamines based on pyrolysis to nitric oxide and chemiluminescence detection.

EPA - United States Environmental Protection Agency

X. APPENDIX

Explanation for Appendix Column Headings:

Site: LAC-USC Medical Center, Marengo Street west of Pediatrics (Area 5).
ERB = Edmondson Research Building, 1840 North Soto Street (Area 5).
Area 1, etc = Census areas noted in Figure 4.9.

Weather: S = sunny; C = cloudy; R = rain; F = fog; H = haze.

Other: GC-TEA peaks later than DEN, unidentified. Their presence is noted by x.

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
7-11-77	LAC-USC	1700	255	5	S		n		
		1801	245	5			n		
		1902	235	4			n		
		2003	245	2			n		
7-13	ERB	1000	185	2 ½	S	26	n		
7-14	ERB	1000	225	2	S	27	n		
		1300	215	4			n		
		1445	235	3			n		
7-15	ERB	1030	165	3 ½	S	27	n		
		1300	190	4 ½			n		
		1430	235	3			n		
7-18	ERB	1000	195	1 ½	S-W	25	n		
		1300	215	3 ½	S	31	n		
		1430	235	2 ½			n		
7-20	ERB	1000	205	2 ½	S	26	n		
		1300	200	4 ½	S	26	n		
		1430	210	3 ½	S	29	n		
7-21	ERB	1000	200	3	S	26	n		
		1300	200	4	S	28	n		
		1430	205	3	S	29	n		
7-22	ERB	1000	015, 195	2 ½	S	27	n		
		1300	210	3 ½	S	31	n		
		1430	220	3	S	32	n		
7-25	LAC USC	1700	270	6			n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
7-25-77	LAC-USC	1800	250	3 1/2			n		
		1900	230	2 1/2			n		
		2000	230	2			n		
		2100	245	2			n		
		2200	245	3			n		
7-27	AREA 2	0930	175	2 1/2	S		n		
		1100	195	3			n		
		1230	235	5 1/2			n		
		1400	225	3 1/2			n		
7-28	AREA 2	0930	355, 215	3	S		n		
		1100	150	3			n		
	AREA 15	1230	175	6 1/2			n		
	AREA 2	1400	240	3 1/2			n		
7-29	AREA 15	1030	220	2 1/2	S		n		
		1200	285	3 1/2			n		
8-1	LAC-USC	0100	125, 355	1 1/2			0.13		
		0200	260	2			0.11		
		0300	150	1 1/2			0.09		
		0400	125	1			n		
		0500	125	1			n		
		0600	125, 245	1			n		
8-2	AREA 2	1030	165	3	S		n		
		1200	210	5 1/2			n		
	AREA 15	1400	240	4 1/2			n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
8-3 77	AREA 2	0935	145, 165	3 ½	S		n		
		1120	215	3 ½			n		
	AREA 15	1240	250	3 ½			n		
		1400	250	3 ½			lost		
8-4	AREA 2	1000	200	1	S		n		
		1125	240	2			lost		
		1250	210	4			n		
8-5	AREA 15	0930	130	3	S		0.07		
		1050	260	3			n		
		1230	205	5			n		
		1350	265	4 ½			n		
8-8	LAC-USC	0045	115	1			0.37		
		0145	045	<1			0.08		
		0245	055	1			n		
		0345	045	1			n		
		0445	075	1			n		
		0545	075	1			n		
8-9	AREA 2	0950	175	2 ½	S		0.11		
		1115	215	4 ½			n		
	AREA 15	1250	235	3 ½			0.05		
		1405	255	4			n		
8-11	LAC USC	1645	220	5			0.06		
		1745	235	4			n		
		1845	220	5			n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
8-11-77	LAC-USC	1945	225	3½			n		
		2045	265	3			n		
		2145	235	3			n		
8-14	LAC-USC	2130	235	3			n		
		2230	195	2½			0.11		
		2330	170	2			n		
8-15	LAC-USC	0030	055, 265	2½			n		
		0130	250	1			n		
		0230	245, 050	2			n		
8-16	ERB	1100	175, 355	3	C	34	n		
		1200	340	3	C	34	n		
		1300	225	2½	C	35	n		
8-17	ERB	1335	235	3½	R	21	n		
		1437	205	3	R	20	n		
8-18	AREA 14	1115	230	5	S	26	n		
		1245	205	3½	S	31	n		
		1400	270	3½	S	31	n		
8-19	AREA 7	0945	275	6	S	27	n		
		1100	260	5	S	31	n		
		1300	290	6	S	32	n		
		1415	270	5	S	32	n		
8-23	LAC-USC	1830	225	4½		23	0.12		
		1931	225	3		22	0.17		
		2032	215	2½		22	n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
8-23-77	LAC-USC	2133	230	3		21	n		
		2234	210	3		20	n		
		2335	225	2		20	n		
8-24	AREA 7	1315	305	5	S	33	n		
	AREA 4	1430	280	7 ½	S	27	0.39		
8-25	LAC-USC	1900	185	3		24	n		
		2000	210	1		22	0.15		
		2100	255	2 ½		21	n		
		2200	180	2		21	n		
		2300	190	3		21	n		
8-26	LAC-USC	0000	205	2 ½		20	n		
8-26	AREA 4	1315	185	5	S	26	n		
	AREA 7	1430	155, 265	6	S	28	n		
8-29	AREA 7	1420	265	4	S	32	n		
8-30	LAC-USC	1830	195	3		23	n		
		1930	215, 035	3		21	n		
		2030	155, 225	2 ½		21	n		
		2130	210	2 ½		22	n		
		2230	190	3		22	n		
		2330	215	3		21	n		
8-31	AREA 7	1300	155	6 ½	S	30	n		
		1715	170	4 ½	S	28	n		
9-1	LAC USC	1830	195	4		22	n		
		1930	215	4		21	n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
9-1-77	LAC-USC	2030	235	3		20	n		
		2130	215	2 ½		20	n		
		2230	215	2		20	n		
		2330	215	1		19	n		
9-2	AREA 7	1400	265	4	S	28	n		
9-6	AREA 5	1445	135, 235	4	S	42	0.07		
9-9	AREA 7	1015	215	4	S	30	n		
	AREA 14	1135	175	4	S	30	n		
		1250	185	3 ½	S	38	n		
		1405	230	3 ½	S	33	n		
9-12	AREA 5	1055	170	3 ½	S	26	0.11		
		1225	235	3 ½	S	32	n		
	AREA 14	1410	205	4	S	28	n		
9-13	LAC-USC	1845	225	3		20	n		
		1945	205	3 ½		19	0.27		
		2045	210	2 ½		18	n		
		2145	205	1		18	n		
		2245	210	2		18	n		
		2345	205	1		18	n		
9-14	AREA 11	1345	205	2	S	32	n		
		1500	255	4	S	28	n		

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
11-14-77	ERB	0900	245	2½	S	20	n	n	
		1000	220	1	S	22	n	n	
		1100	215	3½	S	25	0.12	n	
		1200	220	3	S	27	0 03	n	
		1300	225	3½	S	30	0.04	n	
		1400	220	4	S	30	lost	n	
11-21	ERB	0845	260	3	S	22	0.19	n	
		0945	225	2	S	24	0.18	n	
		1045	215	2½	S	20	0 02	n	
		1145	215	3	S	20	0.05	n	
		1245	220	3½	S	18	0 05	n	
		1345	215	4½	S	18	<0.08	n	
11-29	AREA 15	0940	285	3½	S	24	018	n	
		1055	275	4½	S	25	n	n	
	AREA 1	1230	285	4½	S	26	n	n	
12-1	AREA 4	0920	285	1	S	29	0.10	n	
		1020	275, 045	2	S	30	0.08	n	
		1120	050	1	S	30	0.07	n	
		1240	160	1	S	24	n	n	
		1340	195	2	S	22	n	n	
12-5	AREA 5	0925	155	1	S	16	0.16	0.12	
		1025	145	2	S	16	0 15	0.13	
		1125	140	2½	S	16	n	n	
		1225	155	3	S	18	0.04	n	x

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
12-5-77	AREA 5	1325	210	3	S	20	n	n	x
12-7	LAC-USC	0530	355	1	S	8	0.04	n	
		0630	355, 245	1	S	8	n	n	
		0730	280	1	S	9	n	n	
		0830	115	1	S	10	0.05	n	
		0930	130	1	S	10	n	n	
12-9	LAC-USC	0530	045	3 1/2	S	8	0 08	n	
		0630	045	3	S	9	0.19	n	
		0730	025	5	S	10	0.16	n	
		0830	015	3	S	11	0.07	n	
		0930	100	1 1/2	S	12	0.04	n	
12-13	LAC-USC	0530	055	3	S	8	0.08	n	
		0630	030	3	S	8	0.13	n	
		0730	340	3	S	10	n	n	
		0830	020	1	S	13	0.03	n	
		0930	025	1	S	16	0.22	n	
12-15	LAC-USC	0530	030	1	S	11	0 06	0.09	
		0630	360	2 1/2	S	12	0 09	0 07	
		0730	010	2 1/2	S	12	n	0.17	
		0830	095	3	S	14	n	0.05	
		0930	085	3	S	15	n	n	
12-19	LAC-USC	0530	015	2	S	5	0 09	0.01	
		0630	005	2 1/2	S	5	0 13	0.08	
		0730	360	1	S	8	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
12-19-77	LAC USC	0830	010	3	S	10	n	0.03	
		0930	015	2 1/2	S	12	n	0.01	
12-21	LAC-USC	0530	115, 335	5	S	13	n	n	
		0630	060	7 1/2	S	13	n	0 04	
		0730	105	7	S	14	n	0 05	
		0830	105	8	S	14	n	n	
		0930	090	8 1/2	S	15	n	n	
12-28	AREA 12	0730	225	4 1/2	R	10	0.13	n	
	AREA 10	0900	320	2 1/2	R	11	0.14	n	
		1030	305	4	R	12	0 05	n	
		1200	175, 045	2	R	12	0 05	n	
		1300	175, 045	2	C	14	0.08	n	
12-29	AREA 8	0730	050	2 1/2	C	11	0 05	0.01	
		0900	045	3	R	13	0.34	0.21	
		1030	045	2 1/2	C	16	n	n	
		1200	300	3	R	15	0.03	0.04	
1-5-78	AREA 3	0730	350	4 1/2	S	10	0 08	n	
		0900	120	3 1/2	S	12	n	n	
		1030	155	3 1/2	C	18	n	n	
		1200	075	3	R	18	n	n	
1-6-78	AREA 11	0730	115	3	R	10	0.16	0 08	
		0900	325, 155	3 1/2	R	10	n	n	
		1040	110	1	R	11	n	0 03	
		1200	075	2 1/2	C	14	0.04	0 05	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
1-10 78	AREA 15	0730	145, 315	2	C	12	0.11	n	
		0900	130	4 1/2	C	13	n	n	
		1030	265	5	S	18	n	n	
		1200	215	3	C	18	0.04	n	
1-11	AREA 6	0740	285	1	S	20	n	n	
		0900	285	1	C	16	n	n	
		1030	255, 045	1	S	15	0.14	n	
		1200	235	1	S	24	n	n	
1-12	AREA 10	0730	050	1	S	8	0.20	n	
		0900	100	1	C	14	0.14	n	
		1030	075	5	S	18	lost	—	
	AREA 2	1200	070	1	C	18	n	n	
1-13	AREA 13	0730	135	5	C	11	lost	—	
		0900	135	3	S	14	n	n	
		1030	085	3	S	16	0.01	n	
		1200	215	2	S	22	n	n	
1-17	AREA 4	0730	220	1	F	9	n	n	
		0900	065, 225	1	S	21	n	n	
		1030	225	5	S	17	0.01	n	
		1200	225	2 1/2	S	18	n	n	
1-18	AREA 6	0730	045	3 1/2	C	12	0.04	n	
		0900	075	1	S	15	n	n	
		1030	090	2	S	20	0.08	n	
		1200	055, 225	2	C	20	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
1-19-78	AREA 4	0730	045	3½	R	10	n	n	
		0900	345	4	C	11	n	n	
		1030	350	3	C	12	n	n	
		1200	345, 245	7	S	18	0.06	n	
1-20	AREA 13	0730	065	3	S	11	n	n	
		0900	165	2	S	14	0.03	n	
		1030	145	1	S	12	n	n	
		1200	245	1	S	16	n	n	
1-31	AREA 9	0730	325	2	C	10	n	n	
		0900	225	2	C	12	0.08	n	
		1030	045	2½	C	14	n	n	
		1200	005	2	C	16	n	n	
2-1	AREA 12	0730	245	1	S	8	n	n	
		0900	355	2	S	10	0.04	n	
		1045	185	1	S	20	n	n	
		1215	160	2	S	24	n	n	
2-2	AREA 7	0730	025	1	F	8	0.01	n	
		0900	205, 055	1	F	11	0.01	n	
		1045	185, 325	2	S	22	0.05	n	
	AREA 5	1200	055, 225	1	S	22	n	n	
2-3	AREA 13	0730	165	2	S	6	n	n	
		0900	185	1	S	22	n	n	
	AREA 11	1030	125	1	S	18	n	n	
		1200	205, 085	4½	S	26	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
2-8-78	AREA 9	0730	235	1	C	8	0.05	0.10	
		0900	225	3	C	12	"	"	
		1030	180	2	C	22	"	"	
		1200	345	2	C	16	"	"	
2-9	AREA 12	0730	040	1	R	10	"	"	
		0900	165	4 ½	R	10	"	"	
		1030	185	8 ½	R	10	"	"	
		1200	225	5 ½	R	11	"	0.15	
2-10	AREA 1	0730	345	6 ½	C	8	"	"	
		0900	235	8	S	15	"	"	
		1230	245	12	S	16	0.07	"	
2-14	AREA 5	0730	045	3	S	6	"	"	
		0900	055	1	S	11	"	"	
		1030	175	1	S	23	"	"	
		1200	340	2	S	18	"	"	
2-15	AREA 8	0730	045, 205	1	S	6	"	"	
		0900	045	1	S	10	"	"	
		1045	165	1	S	20	"	"	
		1200	190	4	S	19	"	"	
2-16	AREA 6	0730	345	8	S	7	"	"	
		0900	235	10	S	10	"	"	
		1030	355	9	S	17	"	"	
		1200	310	6	S	20	0.09	"	
2-17	AREA 4	0730	265	3	S	6	0.13	"	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
2-17-78	AREA 4	0900	065	1	S	10	n	n	
		1030	265, 065	2	S	19	n	n	
		1200	215	7	S	18	n	n	
2-22	AREA 3	0730	155	1	S	18	n	n	
		0900	060	2	S	17	n	n	
		1030	305, 055	1	S	24	n	n	
		1200	015	1	S	34	n	n	
2-23	AREA 6	0745	065, 165	2	F	12	n	n	
	AREA 14	0900	225	2	S	14	n	n	
		1030	155	6	S	24	n	n	
		1200	225	5	S	27	n	n	
2-24	AREA 1	0730	100	1	F	8	n	n	
		0900	125, 305	1	F	10	0.08	n	
		1030	105	1	S	14	n	n	
		1200	205	1	S	19	n	n	
2-28	AREA 11	0730	165	1	R	10	n	n	
		0900	165	3 ½	R	12	n	n	
		1030	235	2 ½	R	14	n	n	
		1200	215, 045	2 ½	R	12	n	n	
3-3	AREA 10	1030	235	3	S	16	n	n	
3-7	AREA 13	0730	125	4	S	10	0.13	n	
		0900	175	4	S	16	n	n	
		1030	065, 245	1 ½	S	22	n	n	
		1200	245	3	S	26	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
3-8-78	AREA 2	1125	235	5	S	22	"	"	
	AREA 15	1400	240	4	S	18	"	"	
3-9	LAC-USC	0600	105	1	S	8	"	"	
		0702	105	1	S	10	0.48	"	
		0803	150	3	C	10	"	"	
		0903	145	4	C	11	"	"	
		1003	145	3 ½	S	13	"	"	
		1103	160	3 ½	S	14	"	"	
3-10	LAC-USC	0600	325	2 ½	C	6	"	"	
		0700	135	2	S	8	"	0.25	
		0800	150	3 ½	S	10	"	"	
		0900	135	2 ½	C	12	"	"	
		1000	135	3	C	12	0.07	"	
		1100	135	2	C	15	"	"	
3-14	LAC-USC	1200	220	3	S	18	"	"	
		1300	190	5	S	21	"	"	
		1400	240	6	S	22	"	"	
		1500	230	3 ½	S	22	"	"	
		1600	240	3 ½	S	24	"	"	
		1700	220	3	S	16	0.12	0.26	
3-15	LAC USC	1200	215	2 ½	S	22	"	"	
		1300	230	2 ½	S	30	"	"	
		1400	355, 185	1	S	30	0.18	"	
		1500	245	1	S	30	"	0.06	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
3-15-78	LAC-USC	1600	215	3	S	30	n	n	
		1700	205	3	S	22	0.07	n	
3-16	LAC-USC	1800	345	3		20	n	n	
		1900	345, 155	1		18	0.14	n	
		2000	330	2		16	n	n	
		2100	325	4		15	n	n	
		2200	335	2		14	n	n	
		2300	335	4		14	n	n	
3-17	LAC-USC	1800	285	2		22	0.09	0.13	x
		1900	360	1		19	n	0.36	x
		2000	305	1		18	n	n	x
		2100	340	2		17	n	n	
		2200	325	3		16	n	0.06	x
		2300	355	1		17	n	0.02	x
3-21	LAC-USC	0000	210	2 1/2	C	12	0.12	n	
		0100	210	2	R	10	n	n	
		0200	195	5	R	10	n	n	
		0300	240	2	R	10	n	n	
		0400	235	2	R	9	n	n	
		0500	245	2	C	10	n	n	
3 22	LAC USC	0000	155	3	C	10	n	n	
		0100	145	3	C	10	n	n	
		0200	145	3 1/2	C	10	n	n	
		0300	190	4	C	10	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
3-22-78	LAC-USC	0400	225, 115	2 ½	C	10	n	n	
		0500	150	2	C	10	n	n	
3-23	LAC-USC	0600	125, 245	1	C	10	n	0.08	
		0700	205	2 ½	C	10	n	0 63	
		0800	200	2	S	12	n	0 04	
		0900	265, 085	5	S	14	n	0.07	
		1000	195	4	C	16	n	0 26	x
		1100	225	1	C	15	n	n	
3-24	LAC-USC	0600	325	4		8	0.08	0 14	
		0700	315	2 ½	S	8	0.05	0.10	
		0800	145	2	S	11	0.03	0 07	
		0900	135	1	S	14	0.20	0.45	
		1000	245	1	S	14	0.04	n	
		1100	260	2	S	16	0.04	n	
3-28	LAC-USC	1200	205	2	S	20	n	n	
		1300	255	4	S	22	n	n	
		1400	225	4	S	23	n	n	
		1500	225	4 ½	S	23	n	n	
		1600	215	5 ½	S	21	n	n	
		1700	185	4	S	14	n	n	
3-29	LAC-USC	1200	135	5 ½	C	14	n	n	
		1300	150	4	C	14	n	n	
		1400	155, 305	4	C	14	n	n	
		1500	155	4 ½	C	13	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
3-29-78	LAC-USC	1600	175	4 1/2	C	12	n	n	
		1700	170	4	C	12	n	n	
3-30	LAC USC	1800	205	2	R	12	n	n	
		1900	245	2 1/2	R	10	n	n	
		2000	265	2	R	10	n	n	
		2100	125, 265	3	R	10	n	n	
		2200	265	1	R	10	n	0.05	
		2300	105	2 1/2	R	10	0.04	0.13	
3-31	LAC-USC	1800	140	3 1/2	C	12	0.04	0.05	
		1900	095, 265	2	R	11	0.04	0.06	
		2000	265, 115	2 1/2	R	9	n	0 05	
		2100	115, 275	3	R	8	0.02	0 04	
		2200	280	2	R	8	n	n	
		2300	330	3 1/2	R	7	n	n	
4-4	LAC USC	0000	165	3 1/2	C	8	n	n	
		0100	185	3 1/2	C	8	n	n	
		0200	185	4	C	8	n	n	
		0300	185	4 1/2	C	8	n	n	
		0400	210	3	C	7	n	n	
		0500	235	2		7	n	n	
4-5	LAC-USC	0000	315	4		6	n	n	
		0100	270	2		5	0 02	n	
		0200	345	4 1/2		4	n	n	
		0300	320	3 1/2		4	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
4-5-78	LAC-USC	0400	335	3 1/2		5	n	n	
		0500	360	3 1/2		4	n	n	
4-6	LAC-USC	0600	355, 105	2	C	8	n	n	
		0700	105	2 1/2	C	10	n	n	
		0800	125	3 1/2	S	12	n	n	
		0900	160	3 1/2	S	14	n	n	
		1000	135	4	S	15	n	n	
		1100	105	4 1/2	C	14	n	n	
4-20	LAC-USC	0600	125	2 1/2	C	10	0.04	0.06	
		0700	135	1	C	10	0.11	0.29	x
		0800	150	4	C	11	0.14	0.16	
		0900	135	2 1/2	C	12	0.07	0.39	x
		1000	155	3 1/2	C	14	0.07	0.04	
		1100	175	4		16	n	n	
4-21	LAC-USC	0600	335	3 1/2	S	8	n	n	
		0700	315	3	C	10	n	n	
		0800	315	2 1/2	S	12	n	n	
		0900	285	3	S	13	n	n	
		1000	150	3	S	15	n	n	
		1100	145	2	S	18	n	n	
4-25	LAC-USC	1200	155	3	R	14	0.03	n	
		1300	155	4	C	15	0.07	n	
		1400	155	5	C	15	n	n	
		1500	170	5	R	17	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
4-25-75	LAC-USC	1600	160	5	R	12	n	n	
		1700	175	5	C	16	n	n	
4-26	LAC-USC	1200	215	6 ½	S	17	0.03	n	
		1300	245	9	S	20	0.11	0.09	
		1400	240	5 ½	S	17	n	n	
		1500	225	6	S	15	n	n	
		1600	220	5 ½	C	14	0.04	n	
		1700	205	5 ½	S	14	0.04	0.04	
4-27	LAC-USC	1800	170	2 ½		13	n	n	
		1900	135	4		12	0.01	0.01	
		2000	200	2 ½		11	0.01	n	
		2100	185	2		11	n	n	
		2200	195, 335	2		10	n	n	
		2300	335, 225	2 ½		10	n	n	
4-28	LAC-USC	1800	185	4		14	0.04	n	
		1900	195	3 ½		12	0.01	0.01	
		2000	185	3 ½		13	0.06	0.01	
		2100	195	3		12	0.04	n	
		2200	140	4 ½		11	n	n	
		2300	155	4		11	0.01	n	
5-9	LAC-USC	0000	305	2		15	0.12	n	
		0100	345	2		14	0.16	n	
		0200	355	≤ 1		14	n	n	
		0300	355	1		12	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, mi-hr^{-1}	Weather	Temperature °C	DMN, µg-m^{-3}	DEN, µg-m^{-3}	Other
5-9-78	LAC-USC	0400	355	1		12	n	n	
		0500	355	2 1/2		11	n	n	
5-10-78	LAC-USC	0000	195	3		10	n	n	
		0100	195, 335	2 1/2			n	n	
		0200	195	2			n	n	
		0300	325	2			n	n	
		0400	335	3			n	n	
		0500	345	2			n	n	
5-11	LAC-USC	1200	155, 275	4	5	20	n	n	
		1300	230	4	5	22	n	n	
		1400	210	5 1/2	5	22	n	n	
		1500	215	6 1/2	5	24	n	n	
		1600	180	5	5	23	n	n	
		1700	200	5	5	22	n	n	
5-16	LAC-USC	0000	120	≤1		12	n	n	
		0100	345	≤1		11	n	n	
		0200	130	≤1		10	n	n	
		0300	275	≤1		10	n	n	
		0400	310	3 1/2		10	n	n	
		0500	335	5		10	n	n	
5-17	LAC-USC	1600	245	2 1/2	5	20	n	n	
		1900	255	2	5	22	n	n	
		2000	215	1 1/2		18	n	n	
		2100	250	2 1/2		13	n	n	

LOS ANGELES NITROSAMINE DATA

Date	Site	Hour (start)	Wind Direction, °True	Wind Velocity, $mi\text{-}hr^{-1}$	Weather	Temperature °C	DMN, $\mu g\text{-}m^{-3}$	DEN, $\mu g\text{-}m^{-3}$	Other
5-17-78	LAC-USC	2200	340	2 1/2		16	n	n	
		2300	345	2 1/2		16	n	n	

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/1-79-040		October 1979

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A survey for airborne volatile nitrosamines was carried out in Los Angeles and Contra Costa Counties and at a rocket fuel plant near Hollister, California. A mobile sampling unit with ambient aqueous KOH bubblers was used, followed by extraction, concentration, and analysis by gas chromatography with thermal energy analysis detection. The detection is based on decomposition of nitrosamines to NO which gives chemiluminescence upon reacting with ozone. Low levels of dimethyl and diethylnitrosamine were observed sporadically at numerous locations but gave no clear indication of significant point sources. Most samples were below 0.03 $\mu g/m^3$ while the highest reached 1.0 $\mu g/m^3$. Temporal patterns showed morning and evening maxima and suggested photolysis in midday sun. No relationship between airborne nitrosamine levels by area and incidence of several human cancers is apparent.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Nitrosamines Air pollution Carcinogens	Airborne Nitrosamines	06C,F

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