

ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF ENFORCEMENT

EPA-330/1-77-001

*Reconnaissance  
of  
Environmental Levels of Nitrosamines  
in the Central United States*

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER  
DENVER, COLORADO

JANUARY 1977



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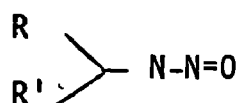
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## INTRODUCTION

The toxic and carcinogenic properties of nitrosamine compounds have been recognized for many years. Of more than 100 of these compounds synthesized, over 70 percent have been shown to be carcinogenic to some animal species. In laboratory tests, this class of compounds has produced cancer in all animal species tested. To date, however, these compounds have not been demonstrated to cause similar effects in humans due in part to the low exposure levels, the small number of people exposed, and the impact of other environmental and physiological unknowns. It is likely that continued interest in this class of compounds will stimulate the research needed to demonstrate an effect in humans. A number of comprehensive reports have been written recently assessing the technical and scientific information currently available on nitrosamines (1-5).

Nitrosamines are a class of organic compounds containing the N-N=O linkage and having the general structure



Since R and R' can represent alkyl, aryl or cyclic groups, the nitrosamine compounds have widely varying chemical, physical and toxicological properties.

Early studies of nitrosamines were directed toward the evaluation of these compounds in foods and biological specimens, since the compound has

been found in a number of products including wheat grain, unprocessed milk and cheese, tobacco and smoked meats. In particular, attention was directed to the possibility of *in vivo* or secondary formation of nitrosamines due to the ubiquitous nature of their precursors.

Only two N-nitroso compounds have been produced in significant quantities for industrial or manufacturing purposes. Diphenylnitrosamine (N-nitrosodiphenylamine) is produced by the rubber industry for use as a retardant in various curing processes. This chemical has not proved carcinogenic to test animals. The other compound, dimethylnitrosamine (N-nitroso dimethylamine) is an intermediate in the production of the rocket fuel unsymmetrical dimethylhydrazine (UDMH) and has shown carcinogenicity.

Until recently, little interest was shown in environmental nitrosamine levels. However, with the development of highly sensitive and relatively specific analytical techniques, the presence of these compounds was measured at a number of locations where amines and/or N-nitroso compounds might be expected. These results, along with an assessment of the environmental and health impact of nitroso compounds, have been reported elsewhere (1-4).

Following an EPA-funded study (6, 7) of the only known primary source of a carcinogenic nitrosamine (the FMC Corporation in Baltimore, Maryland) attention was turned to precursor sources; i.e., mainly sources of secondary amines. These included sources that might manufacture, use or discharge these compounds. Sources of primary and tertiary amines are of less interest if nitrosation is considered to occur via reaction with nitrous acid in the environment. Unlike the secondary amines which can form

nitrosamines, the primary aliphatic and aromatic amines yield other products and only a few tertiary amines form nitrosamines. If other reaction mechanisms are hypothesized to yield nitrosamines, e.g., with metallic compounds, the number of possible precursors would be expanded. However, there is no indication of measurable levels of these nitroso compounds in environmental samples to date. In fact, only dimethylnitrosamine (DMN) and diethylnitrosamine (DEN) and possibly several others observed but not identified have been reported. These results are discussed elsewhere (1, 2).

The health effects of the ambient levels reported to date are still unknown. However, the presence of the compounds in the environment required that the Agency evaluate the sources and circumstances contributing to the levels observed, concurrent with a determination of their possible public health implications. To begin this task the Office of Air Quality Planning and Standards (OAQPS), and later the Pesticide and Toxic Substances Enforcement Division (PTSED) requested that the NEIC collect and analyze a variety of environmental samples. The sampling program was established to aid in determining the necessity for the development of a control strategy for this class of compounds.

Objectives of the program were as follows:

1. To locate possible sources of direct emission of nitrosamines into the environment.
2. To assess secondary formation processes by measuring levels of nitrosamines in the vicinity of plants producing, processing, or releasing amines to the environment.

3. To measure ambient levels of nitrosamines in urban and rural areas.
4. To measure nitrosamine levels on, and transverse to, selected highways subject to diesel engine exhaust.



## FIELD STUDY - PHASE I

The first phase of the study was conducted during August 1976 near Houston, Texas, in the vicinity of three chemical plants known to be amine producers or users. These were Dow Chemical USA at Freeport, E. I. DuPont DeNemours and Company at LaPorte, and Union Carbide Corporation at Texas City. The study arose through a coordinated effort by officials of State, County and City governments, representatives of the three industries and of EPA's Office of Air Quality Planning and Standards (OAQPS) and Environmental Sciences Research Laboratory (ESRL).

An NEIC mobile laboratory was set up first at Dow Chemical and then at DuPont to provide analytical support for the determination of nitrosamine,  $\text{NO}_x$  and wind direction information. The laboratory was outfitted with special lighting to reduce ultraviolet radiation and contained a Thermo Electron Corporation thermal energy analyzer for nitrosamine analysis. The analyzer was on loan to EPA through the courtesy of the DHEW National Cancer Institute.

Air samples were collected in aluminum foil-covered impingers containing 60 ml of 1N KOH. Flow through the impingers was regulated to about 2 l/min with a critical orifice. Air samples were collected for about 90 minutes to obtain the necessary analyzer sensitivity. Water samples were collected in amber glass bottles having teflon-lined caps. Immediately following collection, samples were taken to the mobile laboratory for analysis. Analytical procedures are presented in Appendix A. Using these procedures, the detection limits for DMN were about  $20 \text{ ng/m}^3$  in air and 20 ng/l in water. The detection limits

for other N-nitroso compounds reported here increase almost in direct proportion to molecular weight.

#### Dow Chemical USA

Dow Chemical USA at Freeport, Texas, was producing ethylenediamine (EDA), diethylenetriamine (DETA), piperazine, aminoethylpiperazine (AEP), tetraethylenetriamine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), hexaethylenehexamine (HEHA) and higher amines at the time of the survey (August 10-11, 1976). Temperatures ranged between 31-33°C (87-92°F) during the sampling periods, and winds were southeasterly as usual for that time of the year.

Each day a set of air samples was collected around the amine producing block and another set downwind of the Dow Plant "A" and transverse to the wind. Each set included one upwind and three downwind samples. The location of sampling stations around the amine production block (A-38) is shown in Figure 1 and the location of the off-plant stations are shown in Figure 2. No nitrosamine compounds were detected in any of these samples.

In addition to the above, a water sample was collected at the main amine plant ditch and at the scrubber stream from the thermal oxidizer. These streams joined before flowing from the east side of the amine area. No nitrosamines were detected in either of these samples.

#### Union Carbide Corporation

Sampling at the Union Carbide Corporation at Texas City (August 16, 17, 19) was conducted while the mobile laboratory was set up at the DuPont plant. Impingers were prepared in the laboratory at LaPorte, taken to Texas City to collect the necessary samples, and then returned to



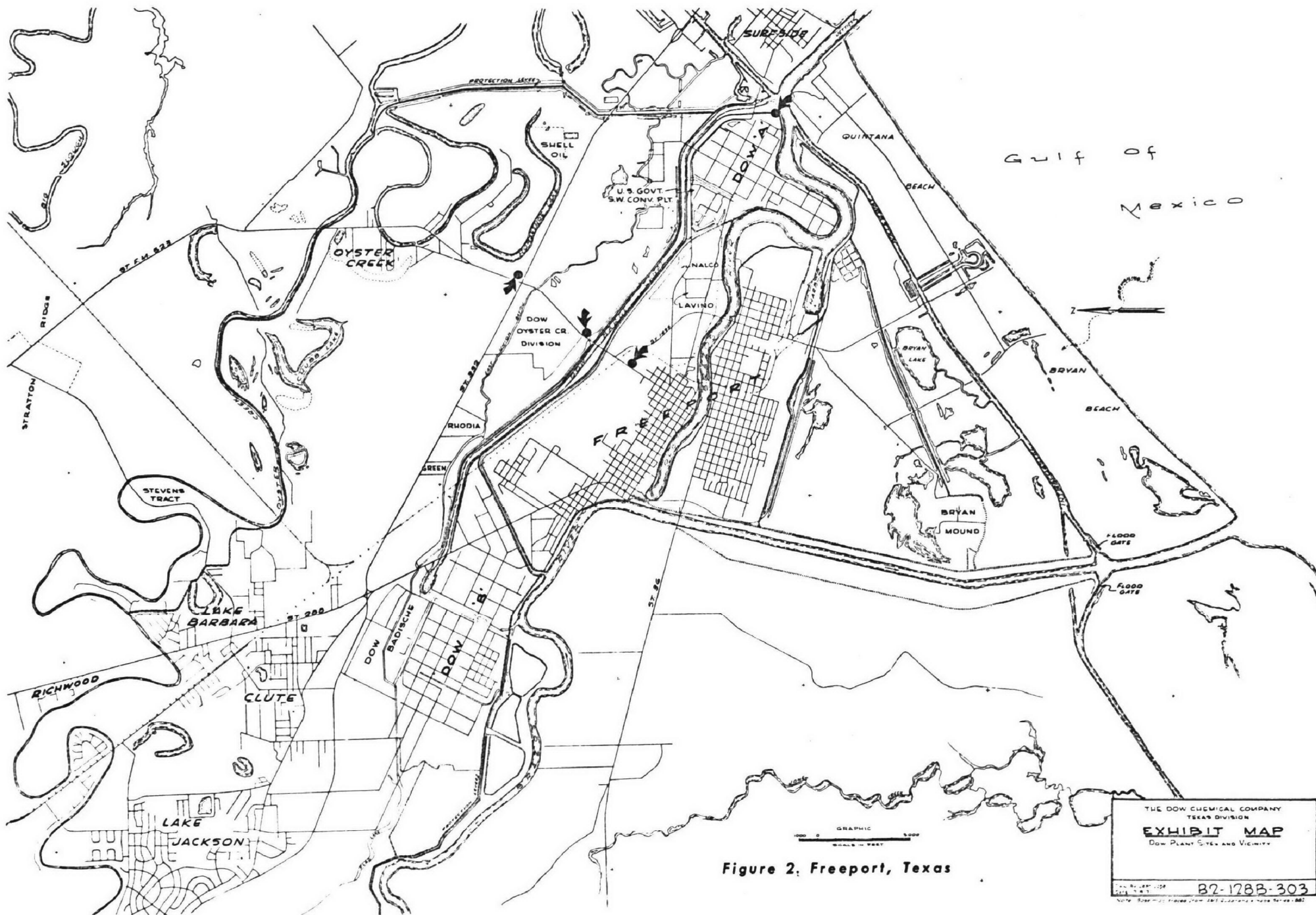


Figure 2, Freeport, Texas

the laboratory for analysis. This avoided the necessity for moving the laboratory a third time at a considerable savings in time and effort.

At the time of the survey the Union Carbide Corporation was producing EDA, TEA and triethylenetetramine and polyamines.

Four air sampling sets were collected at Union Carbide Corporation. Two sets, one morning and one afternoon, were collected around the amine production facility (Building 51). Sampling locations are shown in Figure 3. During the morning set (August 19) winds were variable so the impingers were spaced SE, SW, N and NW of the plant to obtain uniform coverage. At the time of the afternoon series (August 16), winds were southeasterly so one sample was located upwind (SE) and the others downwind (NE, NW and NNW) of the facility. The third set of samples (August 16) was collected on the plant perimeter, again with one sample upwind and three downwind [Figure 4]. This set was started about 8 p.m. and therefore would represent nighttime conditions when ultraviolet radiation would not be a factor. The last series of air samples (August 19) was collected around the Off-Plant Disposal Area (OPDA) lagoons [Figure 4]. Residence time in this system was estimated by the company at 120 days. The wastes then flowed to lagoons operated by the Gulf Coast Waste Disposal Authority (GCWDA) for additional treatment.

Two wastewater samples were collected from the OPDA lagoons during the survey, one each of the influent and of the effluent. While nitrosamines were not found in any of the air samples, both wastewater samples showed the presence of DMN. The influent sample contained 1.2  $\mu\text{g/l}$

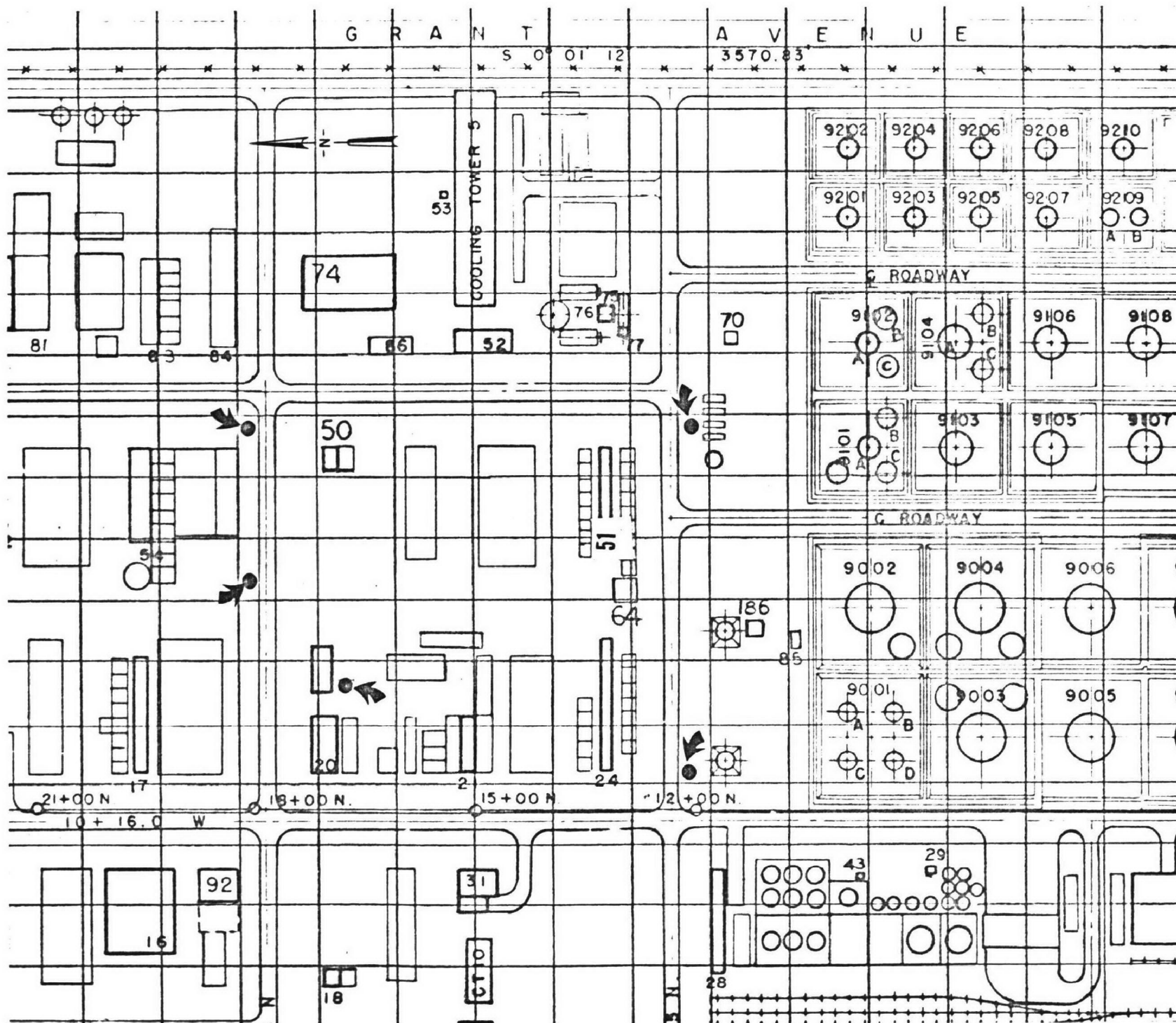
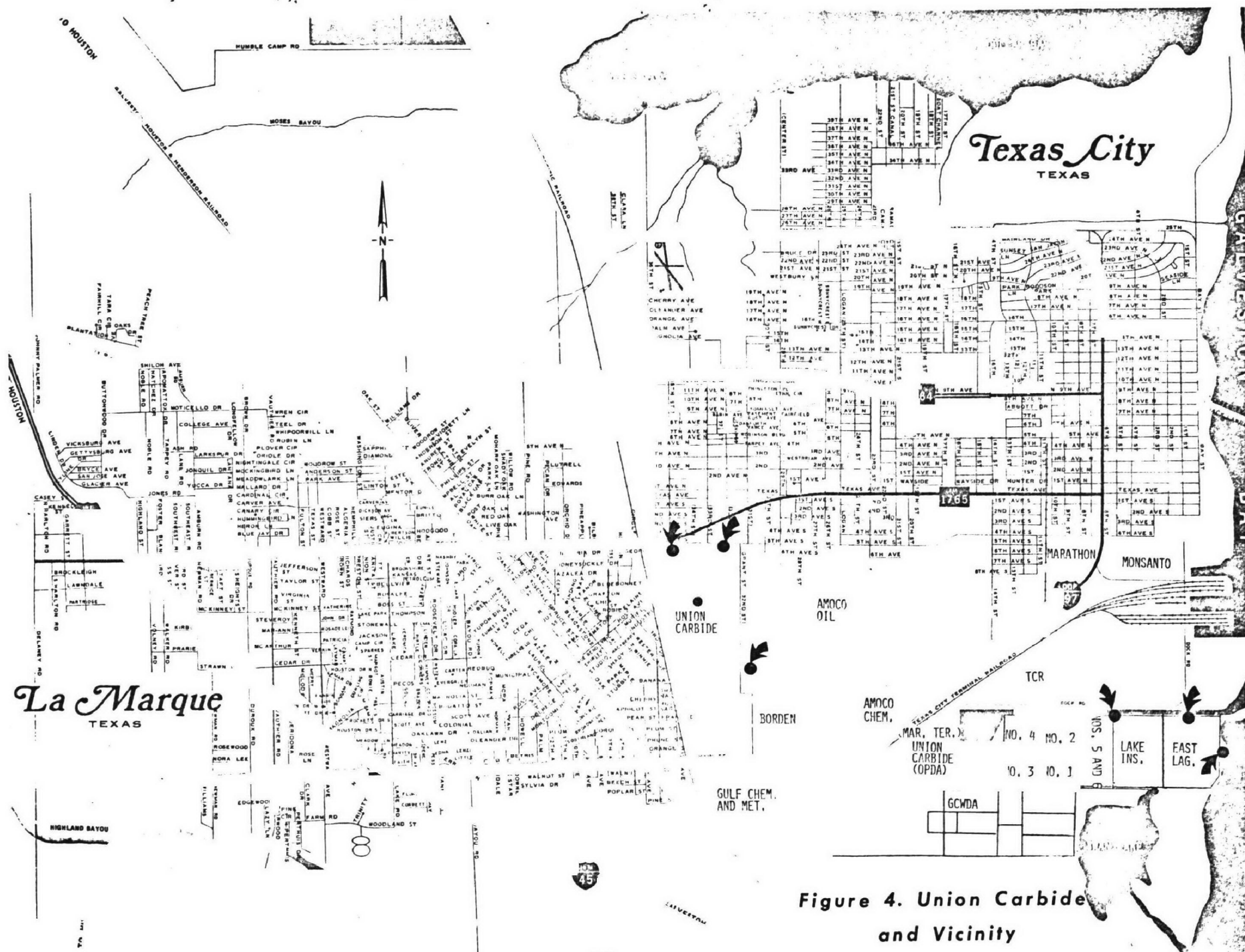


Figure 3. Vicinity of Union Carbide Amine Plant





and the effluent sample 0.4  $\mu\text{g/l}$ . These reported values do not reflect the extraction and concentration efficiencies of the analysis which is estimated at about 32 percent. The OPDA lagoons have now been drained as Union Carbide is reclaiming this land. The wastes now go directly to the GCWDA for processing.

#### E. I. DuPont DeNemours and Company

Sampling in the vicinity of this plant was much more extensive than at the other two. Since DuPont was bordered on the south and east by Highways 225 and 146 and was known to produce and use amines in their processing, this proved an excellent opportunity to determine whether amines reacted in the atmosphere with oxides of nitrogen ( $\text{NO}_x$ ) to produce measurable amounts of N-nitroso compounds. With winds generally southeasterly it was anticipated that automobile generated  $\text{NO}_x$  would be transported over the plant providing an opportunity to react with atmospheric amines.

During the sampling period (August 13-18) the company was producing dimethylamine (DMA) and monomethylamine, filling cylinders of trimethylamine, and using DMA to produce a urea herbicide (Diuron), a uracyl herbicide (Velpar) and a carbamate fungicide (Thiram). On August 16, the amine production unit began to leak, terminating production for about three weeks. The company indicated that opening the unit for repairs might increase amine levels in air and water so sampling continued.

To determine an average  $\text{NO}_x$  level during the sampling period, NEIC constructed teflon-lined containers to sample concurrently with the impingers. The vacuum pump pulling samples through the impinger was



also evacuating the container surrounding the teflon liner. This expanded the liner, drawing in the air sample. Since the system exposed to the atmosphere was completely teflon, it was felt that the  $\text{NO}_x$  collected would be representative of average ambient levels. Measurement of these samples was unsuccessful when neither of the two  $\text{NO}_x$  analyzers in the mobile laboratory would operate. However, independent of this effort, personnel from the Harris County Pollution Control Department collected  $\text{NO}_2$  samples using impingers and the Texas Air Control Board "Modified Christie Technique" for analysis. Results of analyses of samples collected at E. I. DuPont during the period of interest was made available to NEIC.

Concurrent with the NEIC nitrosamine sampling, personnel from E. I. DuPont collected a similar sample, as well as a sample for dimethylamine analysis. The latter was analyzed gas chromatographically in the company laboratories and results were provided to the survey team when requested. This analytical support, as well as electrical power and services for the mobile laboratory, proved invaluable.

With a southerly wind it was necessary to sample in Upper San Jacinto Bay and the Houston Ship Channel. This was accomplished with support from the Houston Office of the Texas Air Control Board which provided a boat and two engineers for assistance.

Six sampling runs were made in and around the DuPont facility. Two were made around the amine production unit, two were downwind and transverse to the plant in Upper San Jacinto Bay and the Houston Ship Channel, and two were on downwind trajectories from the plant. Because of northerly winds, the downwind trajectories were south of the plant. Off-plant sampling points are shown in Figure 5 and results presented in Table 1.

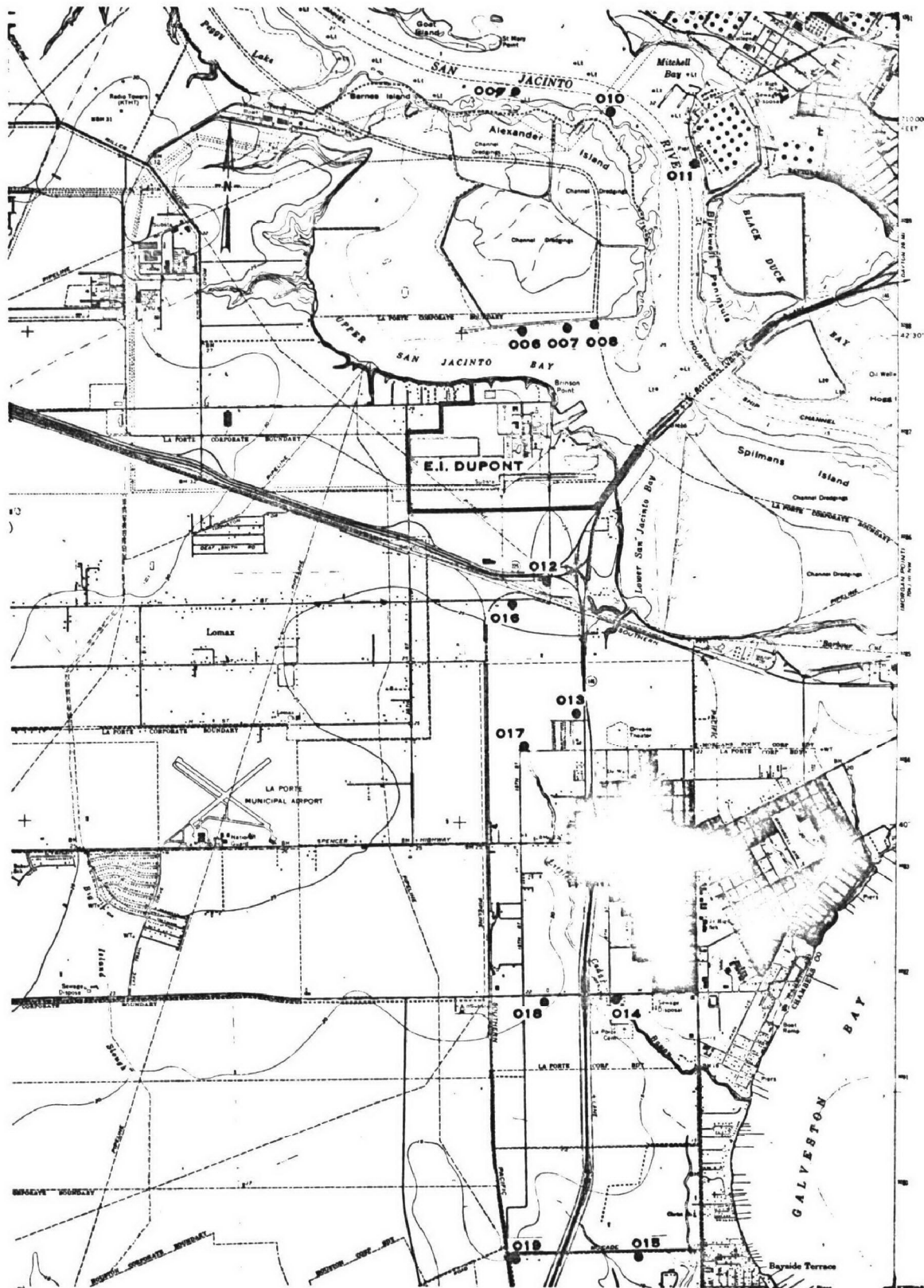


Figure 5. E. I. DuPont and Vicinity

TABLE 1

## Results of Amine (DMA) and Nitrosamine (DMN) Analyses at E. I. DuPont

<u>Run</u>	<u>Date</u>	<u>Sample Location</u>	<u>DMA μg/m<sup>3</sup></u>	<u>DMN<sup>c</sup> ng/m<sup>3</sup></u>	<u>Sampling Time</u>	<u>Wind Direction</u>
1	8/13	SE corner of amine plant block	5.9	-	--	SW
		NE corner of amine plant block	3.0	23.0 <sup>b</sup>	0926-	
		NW of amine plant	12.0	N.D. <sup>a</sup>	0914-1052	
		W of amine plant	9.1	N.D.	0917-1100	
2	8/13	At mobile lab SW of plant	N.D.	N.D.	1630-1800	SSW
		Map location 006	N.D.	N.D.	1650-1803	
		Map location 007	5.9	N.D.	1700-1816	
		Map location 008	16.5	N.D.	1705-1825	
3	8/14	At mobile lab SW of plant	N.D.	N.D.	1130-1300	SW-SE
		Map location 009	4.8	N.D.	1147-1324	
		Map location 010	N.D.	N.D.	1141-1312	
		Map location 011	N.D.	N.D.	1135-1305	
4	8/15	SE corner of amine plant block	21.9	N.D.	0813-1002	S
		NE corner of amine plant block	9.8	7.3	0819-1004	
		NW of amine plant	-	N.D.	0805-0950	
		W of amine plant	N.D.	N.D.	0810-0957	
5	8/18	Map location 12	N.D.	N.D.	0813-0950	N
		Map location 13	100.0	N.D.	0758-0944	
		Map location 14	N.D.	N.D.	0751-0937	
		Map location 15	64.5	N.D.	0746-0929	
6	8/18	Map location 016	N.D.	N.D.	1605-1738	E
		Map location 017	9.7	N.D.	1556-1730	
		Map location 018	18.7	N.D.	1549-1718	
		Map location 019	N.D.	N.D.	1541-1712	

<sup>a</sup> N.D. - not detectable (DMN detection limit - 7 ng/m<sup>3</sup>)

<sup>b</sup> A blown fuse caused vacuum pump to stop sampling. In addition, this substance is unconfirmed since peak was slightly later than normal retention time for DMN.

<sup>c</sup> Uncorrected for collection and extraction efficiency (78 percent).

The data indicate only two occasions when DMN was observed, although DMA was detected in 13 samples. Both positive samples were found at the same location, in the immediate vicinity of the amine production facility. Positive values of DMA tended to indicate that samplers were being set downwind of the plant. The absence of DMA at the mobile laboratory when it was upwind of the plant tended to confirm this situation. However, on August 18, 1976, when the impingers were being set out for Run 6, the wind was from due north, indicating that the trajectory should be sampled as indicated by location 016-019 [Figure 5]. After the samplers were in place the winds shifted 90°, blowing toward the west and maintained that direction throughout the 90-minute sampling period. The data [Table 1] however show measurable concentrations of DMA at two stations. This would indicate other sources of DMA in the vicinity. In an area as heavily industrialized as the Houston Ship Channel, this is to be expected.

Data provided by Harris County indicate on August 13 that the  $\text{NO}_2$  level during Run No. 1 was  $<6\mu\text{g}/\text{m}^3$ . An hour before Run No. 2 they report  $31\mu\text{g}/\text{m}^3$   $\text{NO}_2$  and the same value at the time Run No. 2 began. On August 18 two hours before Run No. 6 began, while the wind was still northerly, they report  $19\mu\text{g}/\text{m}^3$   $\text{NO}_2$  and an hour later report  $27\mu\text{g}/\text{m}^3$ .

Two wastewater samples were taken at the plant, one of the treatment plant influent and one of the effluent to San Jacinto Bay. The plant includes activated sludge ponds followed by clarifiers. The effluent is diluted 3 to 4 times with non-contact cooling water before being discharged to the Bay. The diluted effluent was sampled. Both samples were found to contain DMN and diethylnitrosamine (DEN). The influent contained

5.4  $\mu\text{g/l}$  DEN and 10  $\mu\text{g/l}$  DMN. The treated and diluted effluent contained 0.3  $\mu\text{g/l}$  DEN and 0.7  $\mu\text{g/l}$  DMN. Assuming that these grab samples are representative, the treatment facility is removing about 75 percent of the N-nitroso compounds, at least for this single sample. Reduction could be attributable to microbial activity, photolysis and/or evaporation.

### Houston, Texas

At the request of the Harris County Pollution Control Department and the City of Houston Health Department, a single traverse was sampled across Houston. Impingers were set at four locations. At two of these locations  $\text{NO}_2$  samples were also collected by Harris County personnel. Results are shown in Table 2. While  $\text{NO}_2$  was found at both locations sampled, nitrosamines were not present in measurable concentrations.

TABLE 2

Results of Nitrosamine and  $\text{NO}_2$  Analysis  
in Harris County - August 19, 1976

<u>Location</u>	<u>DMN</u>	<u><math>\text{NO}_2</math> <math>\mu\text{g}/\text{m}^3</math></u>
Harris County Building, Pasadena	N.D. <sup>b</sup>	
C.H.A.M.P.S. Trailer, 9525 Clinton Dr.	N.D.	39
Polk and Crawford Street	N.D.	
City Health Department, MacGregor Dr.	N.D.	66 <sup>a</sup>

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<sup>a</sup> Average of two samples

<sup>b</sup> Not detectable

## FIELD STUDY - PHASE II

The second phase of the study was designed to sample a wide variety of possible amine and/or nitrosamine sources and to measure ambient levels in urban and rural areas. Samples were collected at petroleum refineries, coke batteries, sewage treatment plants, rendering plants and chemical and pesticide producing facilities among others. Because of the mobility required for the task, the thermal energy analyzer remained in Denver and a van was outfitted to contain all the sampling equipment necessary to permit air sampling while moving along the highway or at locations where power was not available. Air and water samples were collected as before; however, these were cooled in an ice chest before being returned to Denver.

Scheduling requirements made it necessary for this phase of the study to be completed in two parts. The first part included a sampling program beginning at NEIC Denver and following Interstate 70 (with several side trips) through Kansas, Missouri, Illinois, and Indiana. After the last samples were obtained in Terre Haute, Indiana, the van was stored in Indianapolis for several weeks while the air and water samples were returned to Denver for analysis.

Several weeks later the second part of the program was begun with sampling at Lafayette, Indiana, north to Chicago and then back to Denver along Interstate 80 through Iowa and Nebraska. As before, the samples were cooled in ice chests until ready for analysis at NEIC. Each part of Phase II sampling required slightly over a week.

In addition to the air and water samples collected for analysis in the NEIC laboratories, occasional air samples were collected on prefiltered Tenax resin columns for subsequent analysis by gas chromatography and mass spectroscopy (GC/MS) at the Research Triangle Institute in North Carolina. The GC/MS analyses were funded through an EPA Office of Research and Development contract. These samples were collected simultaneously with the impinger samples to provide quality assurance for laboratory analysis.

Analytical results of both parts of Phase II sampling follow. Tables 3 and 4 present the results of air and water analyses for the first half of the program, and Tables 5 and 6 the results of the second part. These data are presented in chronological order and are not corrected for extraction or concentration efficiencies which were indicated earlier to be about 32 percent for DMN and higher for heavier compounds [see Appendix A]. Analysis of these data and possible anomalies that may exist are included in the Discussion.

TABLE 3  
Results of Phase II Air Sampling<sup>a</sup>- First Part - 1976

Date	Sample Location	DMN		Sampling Time	Temp. °C	Weather	
		ng/sample	ng/m <sup>3</sup>			Wind	Speed - mph
Nov. 11	Along I-70 Colby, KS - Ogallah, KS	10	46	1107-1232	0	Variable	6 - 8
	0.25 mi SW of I-70 on State 232 at Wilson, KS	13	57	1425-1555	1		
	Centerline of I-70 on State 232 overpass at Wilson, KS	13	55	1427-1604			
	0.15 mi NE of I-70 on State 232 at Wilson, KS	10	44	1429-1606			
Nov. 12	Missouri Chemical Corporation, St. Joseph, MO					N	5 - 10
	pesticide packaging plant						
	SE corner downwind of plant	9	42	1218-1353	1		
	S side of plant	11	57	1231-1403			
	N side of plant, upwind	10	55	1242-1411		N	5 - 10
	Amchem Corporation, St. Joseph, MO						
	pesticide packaging plant						
	N side of plant, upwind	9	48	1519-1647	1		
	SE side of plant, downwind	14	71	1527-1700			
	S side of plant	18	95	1537-1705			
Nov. 13	Phillips Petroleum, Kansas City Refinery, KS					Calm	
	petroleum refinery						
	*SE corner of plant on levee	9	51	0847-1009	-7.5		
	SW of plant on Fairfax Road	10	57	0901-1020			
	NW of plant at Fairfax Road and Quindaro Boulevard	11	69	0906-1025		Calm	
	Chemagro, Kansas City, MO						
	chemical plant						
	SE corner on levee	6	31	1124-1256	0		
	*SSW of plant on levee	-	-				
	W of plant at Guard House	7	35	1142-1315		Calm	
	Big Blue River STP, Kansas City, MO						
	E of plant at grit chamber	8	46	1326-1450	0		
	S of plant at effluent structure	17	92	1330-1457			
	NW corner of plant	N.D. <sup>b</sup>	N.D.	1336-1509			



TABLE 3 (Continued)

Date	Sample Location	DMN		Sampling Time	Temp. °C	Wind	Weather	Speed - m
		ng/sample	ng/m <sup>3</sup>					
Nov. 13	Along I-70 from MO 291 to MO 41 & 135	9	48	1548-1714	2	Calm		
Nov. 14	0.2 mi S of I-70 on US 54, MO	11	55	0834-1000	2	Calm		
	Centerline of I-70 on US 54 overpass, MO	9	45	0837-1005				
	0.2 mi N of I-70 on US 54, MO	8	42	0847-1012				
	Lemay STP, Lemay, MO							
Nov. 15	SW corner of primary clarifiers	6	32	1301-1425	8	Calm		
	E side of grit chamber building	9	52	1318-1434				
	N side of plant	N.D.	N.D.	1325-1441				
	Monsanto Chemical Corporation - St. Louis, MO							
	N side of plant	12	70	0839-0953	6			
	SE corner of plant	5	31	0848-1004				
	*SW side of plant	6	30	0903-1033				
	National By Products, Inc., St. Louis, MO							
	rendering plant							
	NW corner of plant	N.D.	N.D.	1128-1253				
	SW corner of plant	N.D.	N.D.	1135-1258				
	SE corner of plant	N.D.	N.D.	1142-1302				
	Great Lakes Carbon Corporation, St. Louis, MO							
	Missouri Coke and Chemical Division							
	coke producers							
	N side of plant at main gate	8	45	1353-1511	9.5			
	SW corner of plant	14	81	1401-1517				
	*SE corner of plant	9	52	1413-1530				
	Granite City Steel Corporation, Granite City, Ill.							
	steel mill							
	WSW of coke ovens on Illinois 162	20	102	1707-1832	6	Variable		0 - 3
	NW of coke ovens and by-product area on Illinois 162	N.D.	N.D.	1715-1842				
	SE of coke ovens in coal preparation area	9	49	1727-1851				

TABLE 3 (Continued)

Date	Sample Location	DMN		Sampling Time	Temp. °C	Weather	
		ng/sample	ng/m <sup>3</sup>			Wind	Speed -
Nov. 16	Shell Oil Company, Wood River, Illinois						
	petroleum refinery						
	SE of production area at S. gate	6	25	0854-1031	10	NW	5 - 1
	W side of plant, N. of main entrance on Illinois 111	14	58	0902-1048			
	NE of plant on Illinois 143	4	19	0922-1102			
	Along I-70 from Illinois 4 to Illinois 49	5	21	1150-1339			
	Indiana Gas and Chemical Corporation, Terre Haute, Ind.						
	coke producer						
	N side of plant on Hulman Street	12	52	1551-1730	10	Calm	
	*E side of plant near switching yard	11	52	1605-1739			
	W side of plant on 13th Street	7	28	1615-1756			
Nov. 17	IMC Corporation, Terre Haute, Indiana						
	chemical plant, amine producer						
	SW corner of plant on Wabash River	15	72	1032-1207	12		
	*NW corner of plant	22	100	1042-1220			
	SE corner of plant at Research Center	18	96	1049-1214			
	SW corner of plant on First Street	9	44	1101-1230			

\* Samples collected concurrently for analysis by Research Triangle Institute

<sup>a</sup> Uncorrected for collection and extraction efficiency (65 percent).

<sup>b</sup> N.D. - Not detectable. (DMN detection limit - 20 ng/m<sup>3</sup>)

TABLE 4

## Results of Phase II Wastewater Sampling - First Part - 1976

<u>Date</u>	<u>Sample Location</u>	<u>DMN</u> <u>μg/l</u>	<u>DEN</u> <u>μg/l</u>	<u>DPN</u> <u>μg/l</u>	<u>PBN</u> <u>μg/l</u>	<u>DBN</u> <u>μg/l</u>
November 12	Phillips Petroleum, Kansas City Refinery, KS Outfall 001 to Missouri River	N.D.	N.D.	N.D.		
	Chemagro, Kansas City, MO Outfall 001 to Blue River	0.32		1.5		
	Amchem Corporation, St. Joseph, MO Ag line wastewater to city sewer	3.3				
November 13	Phillips Petroleum, Kansas City Refinery, KS Resample of Outfall 001	0.07				
	Big Blue River STP, Kansas City, MO Effluent	0.08	0.07			
November 14	Lemay STP, Lemay, MO Primary effluent to Mississippi River	N.D.				
November 15	Monsanto Chemical Corporation - St. Louis, MO Clean acid sewer to Missouri River	N.D.				
	Great Lakes Carbon Corporation, St. Louis, MO Outfall 001 to Mississippi River	N.D.				
	Granite City Steel Corporation, Granite City, Ill. Outfall 001 to Horseshoe Lake	N.D.				
November 16	Shell Oil Company, Wood River, Ill. Composite effluent to Mississippi River	N.D.				
	Indiana Gas and Chemical Corp., Terre Haute, Ind. Effluent to city sewer	1.7	0.24	0.24	0.48	0.82
November 17	IMC Corp., Terre Haute, Ind. Outfall 003, non- contact cooling water, DMA	0.11			0.29	

TABLE 5  
Results of Phase II Air Sampling<sup>d</sup> - Second Part - 1976

Date	Sample Location	DMN		Misc. Compounds		Sampling Time	Temp. °C	Weather	
		ng/sample	ng/m <sup>3</sup>	ng/sample	ng/m <sup>3</sup>			Wind	Speed-mph
Nov. 29	Eli Lilly Corporation, Lafayette, Ind.								
	-pharmaceutical and pesticide manufacturing								
	NW corner of pesticide production area, upwind	5	16			1240-1458	-10		
	SW corner of pesticide production area	9	31	4	14 <sup>a</sup>	1249-1505			
	*SE corner of pesticide production area, downwind	4	15	16	58 <sup>a</sup>	1309-1510			
				6	22 <sup>b</sup>				
	NE corner of pesticide production area	7	27	18	69 <sup>a</sup>	1316-1516			
Nov. 29	Lafayette STP, Lafayette, Ind.								
	E of plant at plant office building	5	25			1730-1900	-10	ENE	7
	W of plant at trickling filters	8	41			1741-1912			
	Middle of plant near digesters	4	21			1752-1916			
Nov. 30	Junction Halsted Avenue (Rt. 1) and Dixie Highway								
	Chicago Heights, Illinois Industrial Area								
Nov. 30	Daylight Sample (0849)	5	23			0849-1035			
Dec. 1	Night Sample (1805)	19	94	16	79 <sup>a</sup>	1805-1933	-9		
Nov. 30	SW corner 103rd and Cottage Grove								
	Chicago (South Side), Illinois Industrial Area								
	Daylight Sample (1113)	4	13			1113-1328			
Dec. 1	Night Sample (1732)	13	64			1732-1900	-9		
Nov. 30	Rooftop 1817 W. Pershing Road (EPA Lab)								
	Chicago (Mid-town), Illinois Industrial Area								
	Daylight Sample (1226)	N.D.	N.D.			1226-1435			
Nov. 30	General Motors, McCook, Illinois								
	Electromotive Division								
	West side of plant, upwind	5	24	18	87 <sup>a</sup>	1324-1654			
				24	120 <sup>b</sup>				
				23	110 <sup>c</sup>				
	North Side of plant, downwind	N.D.	N.D.			1554-1726			
	South Side of plant	4	22			1616-1738			

TABLE 5 (Continued)

Date	Sample Location	DMN		Misc. Compounds		Sampling Time	Temp °C	Weather	
		ng/sample	ng/m <sup>3</sup>	ng/sample	ng/m <sup>3</sup>			Wind	Speed-mph
Nov. 30	Business Rt. 20, Elgin, Illinois NW Chicago Light Industry Area Night Sample (1938)	15	80			1938-2108			
Dec. 1	Black Leaf Products, Elgin, Illinois Pesticide packaging plant SW corner downwind of plant	19	90	19 12 13	90 <sup>a</sup> 57 <sup>b</sup> 62 <sup>c</sup>	0829-1000	-9	Variable	0 - 10
	NW corner of plant	24	180			0903-1032			
	SE corner of plant	17	82			0909-1040			
Dec. 1	Union Oil Chicago Refinery, Lemont, Illinois petroleum refinery West plant boundary at water influent, upwind NE corner of plant at North gate *SE corner of plant, downwind	16 16 20	58 61 130			1241-1440 1256-1450 1315-1500	-9	WSW	5 - 10
Dec. 2	Mobil Oil Refinery, Joliet, Illinois petroleum refinery SW corner of plant *South side of plant, downwind North side of plant, upwind	24 17 15	110 80 65	18	85 <sup>a</sup>	0935-1105 0953-1124 1003-1142	-9	N	8 - 10
Dec. 2	Monsanto Chemical, Muscatine, IA chemical plant East side of plant *SW corner of plant, downwind West side of plant	12 N.D. 4	58 N.D. 21			1637-1807 1655-1820 1700-1825	-16	NNW	2 - 5
Dec. 3	National By-products, Des Moines, IA rendering plant NW corner of plant *NE corner of plant, downwind South of plant downwind of cooling towers	4 N.D. N.D.	16 N.D. N.D.			1119-1318 1133-1326 1141-1338	-6	S	0 - 5

TABLE 5 (Continued)

Date	Sample Location	DMN		Misc. Compounds		Sampling Time	Temp. °C	Weather	
		ng/sample	ng/m <sup>3</sup>	ng/sample	ng/m <sup>3</sup>			Wind	Speed-mp
Dec. 4	Des Moines STP, Des Moines, IA								
	NW corner of plant at administration building	20	98			0841-1018	-6	Calm	
	Middle of plant at pumphouse	21	100			0858-1029			
	East end of plant at intermediate clarifiers	19	91			0909-1039			
Dec. 4	Along I-80 Des Moines, IA to Avoca, IA	16	78			1122-1259			
Dec. 6	Imperial Chemical, Shenandoah, IA								
	pesticide formulation plant								
	*SE corner of plant, downwind	16	74			0905-1044	-7	NNE	10
	North side of plant, upwind	15	63			0911-1058			
Dec. 6	Along I-80 York, Neb. to Kearney, Neb.	13	66			1455-1630	-12		
Dec. 7	Along I-76 Colorado State Line to Brush, Colo.	7	31			0800-0945	4	NNE	12 -

N.D. Not detectable. (DMN detection limit - 20 ng/m<sup>3</sup>)

\* Concurrent samples collected for analysis by Research Triangle Institute.

a Dipropylnitrosamine

b Dibutylnitrosamine

c Nitrosomorpholine

d Uncorrected for collection and extraction efficiency (65 percent)

TABLE 6

## Results of Phase II Wastewater Sampling - Second Part - 1976

<u>Date</u>	<u>Sample Location</u>	<u>DMN</u> <u>μg/l</u>	<u>DPN</u> <u>μg/l</u>	<u>EBN</u> <u>μg/l</u>	<u>NPD*</u> <u>μg/l</u>
Nov. 29	Eli Lilly Corporation, Lafayette, Ind. 001 Outfall to Wabash River 002 Outfall to Wabash River	0.03 0.11	0.12 2.8	0.04 2.3	N.D. N.D.
Nov. 29	Lafayette STP, Lafayette, Ind. Outfall to Wabash River	N.D.	N.D.	N.D.	N.D.
Dec. 1	Union Oil Chicago Refinery, Lemont, Ill. Outfall 001 to Chicago Sanitary and Ship Canal	N.D.	N.D.	N.D.	N.D.
Dec. 2	Monsanto Chemical, Muscatine, IA 001 Effluent to Mississippi River Taken from 24-hour composite sampler	N.D.	N.D.	N.D.	N.D.
Dec. 3	National By Products, Des Moines, IA Effluent to Des Moines STP	0.02	N.D.	N.D.	0.20
Dec. 4	Des Moines STP, Des Moines, IA Outfall to Des Moines River	N.D.	N.D.	N.D.	N.D.

\*NPD - nitrosopyrrolidine

## DISCUSSION

### Phase I

The air sampling results obtained in the Houston area indicated that either nitrosamines were not emitted from the plants, or that once in the atmosphere these compounds decomposed rapidly. In the case of the air and water samples collected at Dow Chemical USA, the absence of positive results in either medium provided no information of the validity of either possibility.

At Union Carbide where results from air samples were negative, both wastewater samples were positive for DMN and of the same magnitude found elsewhere (6). On the basis of this limited data, effects of passage through the lagoon system were minimal when considering that the reduction occurred over a detention time estimated at 120 days. Even if reduction resulted from evaporation, the small amount lost at a very slow rate would not have been detected.

Results obtained at DuPont did indicate that DMN may occasionally be emitted in the immediate vicinity of the processing units, however, none was ever detected off plant property. These data also showed little evidence for amines and oxides of nitrogen combining to produce N-nitroso compounds under the conditions present in the study area. Both high temperatures ( $>29^{\circ}\text{C}$ ) and summer sunlight probably affected the results.

Losses from the DuPont wastewater treatment system, as indicated by reduction in N-nitroso levels, may have introduced both DMN and DEN into the air. However, these compounds were never detected, even though several air samples were collected at the mobile laboratory in



the immediate vicinity of the wastewater treatment facilities. While the DMN level here was in the range of those reported (6-8) at the DuPont plant in Belle, West Virginia, (2.3 - 8.6  $\mu\text{g/l}$ ), the DEN had not been detected earlier in the Belle effluent.

## Phase II

In direct contrast to the results obtained in Phase I, the Phase II air sampling produced mainly positive results. During the first part of this sampling program the only negative results were those samples collected in the vicinity of the National By Products rendering plant in St. Louis. Little difference was seen across highways, around steel mills, or at pesticide formulating facilities. The uniformity of these positive results, where little had been anticipated, required a close scrutiny of all aspects of sample collection and analytical procedures for the purpose of assuring the quality of the data.

A careful review of sample handling procedures, supported by laboratory experimentation, pointed out the possibility that DMN standards in sealed vials were able to contaminate the atmosphere of the laboratory refrigerator. With standards containing mg/l concentrations, very little loss was necessary to produce concentrations in the refrigerator measurable with instruments detecting picogram quantities. Thus, when small quantities of methylene chloride evaporated, even at refrigerator temperatures of  $-4^{\circ}\text{C}$  ( $25^{\circ}\text{F}$ ) DMN was apparently codistilled, diffusing into the refrigerator. When the first series of samples were returned to the laboratory for processing they were extracted, placed in glass bottles and sealed with a teflon-lined cap to await further

processing. It is hypothesized that as these samples cooled and the vapor condensed, reducing pressure in the containers, vapor in the refrigerator may have been drawn into each of them contaminating the sample. Reviewing the data in Table 3, it is possible that samples containing less than about 10 ng DMN were, in fact, only showing effects of this contamination and only quantities above this level should be considered as positive. Thus, the mass and concentration might be reduced proportionately, or the results as presented when corrected for correction and extraction efficiencies considered as maximum values.

Since the first set of water samples collected during Phase II were processed in a similar manner, these might be expected to show similar effects. However, since the quantity of methylene chloride used in the extraction is larger (100 ml vs 24 ml) the head space is reduced and potential contamination minimized. Thus a number of samples in Table 4 showed no detectable levels of N-nitroso compounds. However, several samples did show compounds eluting at times corresponding to DPN, PBN and DBN which have not been reported elsewhere and would not have been possible contaminants. In fact, the effluent sample from Indiana Gas and Chemical Corporation showed peaks corresponding to five different N-nitroso compounds.

Samples collected during the second part of Phase II also showed levels significantly higher than anticipated at some locations, even though precautions were taken to avoid the contamination suspected earlier. Continued checking showed that one bottle of distilled water contained 250 ng/l of a compound having the same elution time as DMN. While the reagents and distilled water originally carried from NEIC showed no

contamination, one container of distilled water was refilled at the Shell Oil laboratories in Wood River. The laboratory generates distilled water by passing steam condensate through ion exchange resin. Both ion exchange resins and steam system additives to prevent scaling may be sources of amines and/or nitrosamines. A second set of distilled water samples provided by Shell Oil also showed the presence of DMN but in lower concentrations. If the ion exchange resin is the source of N-nitroso compounds, this could have significant public health implications in some deionizers in private homes.

After each air sample was collected, the KOH was transferred to a glass bottle. The impinger was rinsed with distilled water several times, and the rinse water added to the sample. From the volume received it can be estimated that the rinse water could have contributed up to 8 ng DMN to each sample collected after the survey team departed from Wood River and began using the contaminated water. Thus, after November 16 DMN levels in each sample may have been increased by approximately 8 ng.

While only DMN was found in the first set of Phase II samples, the second set indicated N-nitroso compounds with elution times equivalent to DPN, DBN and nitrosomorpholine. These had not been reported earlier.

In the two instances where day and night samples were collected, the latter concentrations were higher in both cases, possibly due to the reduced effect of photolysis after sundown.

The General Motors plant at McCook, Illinois, was of interest because of the reported use of cutting oils at this facility. Some cutting oils have been shown to contain N-nitroso compounds. While downwind

levels were insignificant, the upwind sample showed DPN, DBN and nitrosomorpholine. These same compounds and DMN were also found downwind of Black Leaf Products at Elgin, Illinois.

Wastewater samples collected during the second part of Phase II, and unaffected by the contaminated distilled water, generally showed low concentrations of nitrosamines. The presence of a compound having an elution time equivalent to nitrosopyrrolidine (NPyr) in the effluent sample collected at National By Products, Des Moines, has not been reported earlier in aqueous samples. However, NPyr has been identified in cooked or processed meat products (4).

During Part 1, six samples on Tenax columns were collected concurrently with impinger samples as indicated in Table 3. Of these, five were available for comparison with NEIC data. Only the sample collected at Indiana Gas and Chemical Corporation showed a detectable nitrosamine level. This sample indicated  $9.4 \text{ ng/m}^3$  DMN. During Part 2, an additional six samples were collected [Table 5]. Three of these are available for comparison. The sample at Eli Lilly Corporation was analyzed for DPN, while the samples at Union Oil and Mobil Oil were analyzed for DMN. Nitrosamines were not detected in any of these samples. Even while using a more sensitive technique, in only one case did Research Triangle Institute (RTI) find nitrosamines while NEIC measured these in all comparable samples. Differences between NEIC and RTI results may have occurred for several reasons. The possible introduction of contaminants into NEIC samples, discussed earlier, would have increased these results without affecting RTI samples. On the other hand, the filter preceding the Tenax cartridge

but not in the EPA sampling train could remove particulates and condensed nitrosamines, particularly at low sampling temperatures, thereby lowering RTI collection efficiency. In addition, the effect of low temperatures on the collection efficiency of Tenax columns is unknown. Additional data collection is underway in an attempt to determine the cause of these differences.

## SUMMARY AND CONCLUSIONS

Samples in the vicinity of a number of different industries, primarily sources of amines, have been collected and analyzed for nitrosamines. This has been done under both summer and winter conditions (Phase I and Phase II). Unfortunately, contamination problems that arose during Phase II limit the ability to make definitive statements regarding much of these data. The possibility of contamination of distilled water requires further examination.

The data show that nitrosamines may be more prevalent during winter months, possibly due to reduced decomposition rates at colder temperatures and/or reduced ultraviolet radiation as the sun angle lowers.

While not substantiated by air sampling results, water samples indicate that there are primary sources of direct emissions to the environment of a number of N-nitroso compounds, several not reported earlier. The compounds probably arise during the synthesis of other compounds and are then emitted to the environment during the use or modification of these products. Thus, N-nitroso compounds were observed in chemical, pesticide and coke plant effluents and the surrounding air as well.

The Phase I sampling did not present any evidence to substantiate secondary production in the vicinity of amine sources. Only two air samples showed nitrosamines and these were in the immediate vicinity of the DuPont amine production unit. Effluent samples from DuPont, as well as the Union Carbide Corporation showed that DMN was present however, indicating that under the conditions that existed the decomposition rate may exceed the rate of formation if secondary production was occurring.

In addition to DMN compounds showing retention times equal to DPN, DBN and nitrosomorpholine were detected in Phase II samples. These have not been reported earlier in ambient air. Although nitrosamines were found at a number of sites, there are no data that would indicate formation in the atmosphere as opposed to the nitrosamine presence as a contaminant. Separation of the two possibilities would require in-plant process and waste stream sampling during periods when ambient nitrosamine levels existed.

Limited data collected along major highways showed possible contributions from diesel engine exhaust. These levels, however, were close to the instrument detection limits. Diffusion from these highways and truck traffic would introduce nitrosamines into rural areas, but these levels are low compared to values observed near urban industrialized areas.

While nitrosamines have been observed in a number of areas of the Midwest, the values in air have been below  $1 \mu\text{g}/\text{m}^3$  even when corrected for collection and extraction efficiency. Additional data are still needed to determine the cause of discrepancies between NEIC and RTI results. These data are now being collected. In the absence of data indicating the level at which health effects are observed and what these effects are, one cannot safely speculate as to the significance of these numbers or the population at risk. Where these compounds are discharged into waterways, it is possible that they may find their way into drinking water supplies. This has been routinely demonstrated with other compounds. However, where health effects data are lacking, the safest posture is to assume no threshold level exists and minimize the environmental impact of known carcinogens wherever possible.

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## APPENDIX A

### ANALYTICAL PROCEDURES AND QUALITY ASSURANCE

## NEIC ANALYTICAL PROCEDURE FOR NITROSAMINES

Air Samples

Air samples were collected in foil-covered impingers (SGA catalog #JV8550) filled with 60ml of 1N KOH. Air samples were drawn through the impinger by a vacuum pump and the flows metered by a calibrated stainless steel hypodermic needle (B&D #21). Normal collection volumes range from 180 to 200 liters of air.

All laboratory work was carried out under low UV "bug" lights to minimize the possibility of light catalyzed degradation of the nitrosamines. The KOH solutions were extracted in a 125 ml separatory funnel with three 8 ml portions of dichloromethane (Burdick and Jackson, "distilled in glass"). The combined extracts were concentrated to 0.5 ml in Kuderna-Danish evaporative concentrators, each consisting of a three ball Snyder column attached to a specially made 50 ml concentrator flask which in turn was attached to a 4-ml calibrated receiving tube. The column and receiving tube are available through Kontes Glass Company; the 50-ml flask was custom made locally. Before concentration, 0.5 ml of 2,2,4 trimethylpentane was added as a keeper. A hot water bath maintained at 58 to 60°C was used as the heat source.

Microliter aliquots of the concentrates were injected into a Varian Model 600D gas chromatograph attached to a Thermo Electron Corporation Thermal Energy Analyzer (GC/TEA). An isopropanol/liquid nitrogen cold trap was used in conjunction with the TEA.

Where possible, samples thought to contain nitrosamines were spiked with known standards to confirm retention time and to help establish concentrations. Two columns were employed in this work (i.e., 10% Carbowax 20M, 1% KOH on 60/80 mesh Chromosorb WAW, 20 foot x 1/8 inch O.D. stainless steel and a similar column with 15% FFAP), and in all cases reported, the retention time of the sample peaks matched those of the standard on both columns. Unfortunately, the two columns employed elute nitrosamines in the same sequence; different elution orders would have provided stronger support for the reported results. A column with radically different properties, however, was not available.

Quantitation of compounds reported was made by peak height comparison with authentic standards. The DMN standard was obtained through Research Triangle Institute, North Carolina, while the other standards were obtained through the Food and Drug Administration, Washington, D. C.

### Water Samples

Grab samples were collected in amber glass quart bottles with teflon liners. Two 50-ml portions of dichloromethane were used to extract each sample in a 2000-ml separatory funnel. The combined extracts were concentrated as above, only using a 250-ml concentrator flask and 1 ml of 2,2,4 trimethylpentane as a keeper. In some cases it was not necessary to concentrate to 1 ml in order to obtain measurable amounts of nitrosamines. Normally, volumes injected into the GC/TEA were kept as small as possible.

Granular anhydrous sodium sulfate (Mallinkrodt AR) was used to treat emulsions when they occurred during extractions.

The detection limit for DMN was established at 4 ng/sample or assuming 0.2 m<sup>3</sup> air samples, this would correspond to 20 ng/m<sup>3</sup> for air samples and 20 ng/l for water samples. The detection limit for the other nitrosamines reported increase in almost direct proportion to their molecular weight.

### QUALITY CONTROL

During these studies, the following quality control considerations were evaluated:

#### Solvent Blanks

Methylene chloride (dichloromethane - DCM) was concentrated from at least three different bottles from 100 ml to 1 ml using an isooctane keeper and was found to contain no peaks which specifically interfere with the analyses. Similarly, unconcentrated Burdick and Jackson methylene chloride and isooctane were analyzed with the TEA/GC system and found to be free from interferences.

#### Field Blanks

During the sampling period extending from the end of November through the beginning of December, two bottles of washwater were used. Twenty to 30 ml of this washwater per sample is used to rinse impinger solutions into sample containers.

When these one-gallon bottles were returned to Denver they were analyzed individually: one showed no contamination, while the other contained about 250 ng/l of what again appeared to be DMN. It is believed that this contaminated wash water was obtained from the Shell Oil Company, Wood River Refinery in which case contamination of samples from this source would have

occurred only after November 16 and at a level of approximately 5-8 ng/sample.

Several of the septum capped standard solutions were found to lose solvent even when stored in a refrigerator. In order to check for possible contamination of the refrigerator by nitrosamines in these standards, an open beaker of 100 ml DCM was exposed overnight. The solution was found to absorb what appeared to be DMN, but no other nitrosamines. Subsequent washing of the interior of the refrigerator has substantially reduced the concentration of this material to barely measurable levels, however, sample storage in this refrigerator has been discontinued. These results open the possibility that all sample extracts originally stored in the refrigerator may have become contaminated with DMN even though they were kept in capped bottles which had teflon liners and were wrapped with teflon tape. This possibility includes all samples in this report collected between November 11-17, 1976.

#### Extraction Efficiencies

Quart samples of water were spiked with DMN, DEN (diethyl-N-nitrosamine) and DBN (dibutyl-N-nitrosamine), extracted and concentrated in the normal manner to determine recovery from water samples. The average recoveries were as follows: DMN 32% DEN 87% and DBN 96%. The effect of addition of NaCl to increase recovery during water extractions is presently being studied.

Overall collection and extraction efficiency was determined for air samples by passing known quantities of dimethyl-N-nitrosamine, ethylmethyl-N-nitrosamine, diethyl-N-nitrosamine, dipropyl-N-nitrosamine, ethylbutyl-N-nitrosamine, nitrosopyrrolidine, and nitrosomorpholine through KOH impingers

at ambient temperatures of  $-2^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ , then extracting and concentrating as usual. For these compounds the average recovery at  $-2^{\circ}\text{C}$  was 65% and at  $20^{\circ}\text{C}$  78%. There was no apparent difference in efficiencies between the various compounds examined.