

ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF ENFORCEMENT

EPA-330/1-77-009

*Reconnaissance
Of
Environmental Levels Of Nitrosamines
In The Southeastern United States*

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
DENVER, COLORADO



AUGUST 1977

Environmental Protection Agency
Office of Enforcement
EPA-330/1-77-009

RECONNAISSANCE
OF
ENVIRONMENTAL LEVELS OF NITROSAMINES
IN THE SOUTHEASTERN UNITED STATES

August 1977

National Enforcement Investigations Center
Denver, Colorado

CONTENTS

I.	INTRODUCTION	1
II.	BACKGROUND	2
III.	FIELD STUDIES	4
	Ciba-Geigy Corp.	4
	Martin-Marietta (SODYECO)	13
	Proctor Chemical Co., Inc.	18
	Velsicol Chemical Co.	30
	Farmers Supply and Produce	32
IV.	SUMMARY AND CONCLUSIONS	35
	REFERENCES	37

TABLES

1	Monitoring Site Description - Ciba-Geigy Corp.	10
2	Monitoring Site Description - Martin-Marietta Corp.	19
3	Monitoring Site Description - Lumber Street Plant	28
4	Monitoring Site Description - Cedar Springs Plant	29
5	Monitoring Site Description - Velsicol Chemical Co.	33

FIGURES

1	Wastewater Treatment Schematic - Ciba-Geigy Corp.	7
2	General Plant Layout - Ciba-Geigy Corp. . . .	11
3	Wastewater Treatment Schematic - Martin-Marietta Corp. SODYECO Division . . .	15
4	General Plant Layout - Martin-Marietta Corp. SODYECO Division . . .	20
5	General Plant Layout - Proctor Chemical Co. Lumber St. Plant . . .	22
6	General Plant Layout - Proctor Chemical Co. Cedar Springs Plant . .	23
7	Typical Amine Reaction Sequences - Proctor Chemical Co., Inc. Salisbury, N.C. .	26

I. INTRODUCTION

In 1976, the Environmental Protection Agency (EPA), National Enforcement Investigations Center (NEIC) conducted investigations to determine environmental levels of nitrosamines in the Central United States.¹ The data from the investigations showed that there was little indication of N-nitroso compounds in the air in the vicinity of the numerous sources examined, even on those occasions when these compounds were observed in plant effluent. The water samples indicated that there were primary sources of direct emissions to the environment of a number of N-nitroso compounds. It was concluded that these compounds probably arose as impurities during the synthesis of other compounds and they were emitted to the environment during the use or modification of these products. These N-nitroso compounds were observed in chemical, pesticide and coke plant effluents, some consistently.

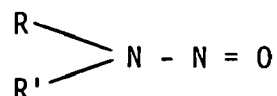
The EPA Region IV Administrator identified potential dischargers of nitrosamines in the southeastern United States, and because of the above experience, requested that NEIC conduct air and water monitoring investigations to determine if the compounds were being released to the environment.

The five industrial facilities monitored in April and May 1977 by NEIC were:

1. Ciba-Geigy Corporation, McIntosh, Alabama
2. Martin-Marietta (SODYECO), Charlotte, North Carolina
3. Proctor Chemical Company, Salisbury, North Carolina
4. Velsicol Chemical Company, Chattanooga, Tennessee
5. Farmers Supply and Produce, Monticello, Kentucky

II. BACKGROUND

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.

Nitrosamines are relatively stable, resisting reduction, moderate temperature oxidation (less than 300°C) and pyrolysis at even higher temperatures. They are very photoreactive in water or in the atmosphere.

Nitrosamines are formed naturally in moist air and in soil and water in which secondary and/or tertiary amines and nitrites exist or are being formed. Only two N-nitroso compounds have been produced in significant quantities for industrial or manufacturing purposes.

Diphenylnitrosamine (DPN or N-nitrosodiphenylamine) is produced by the rubber industry but has not proved carcinogenic to test animals. Dimethylnitrosamine (DMN or N-nitrosodimethylamine) has been identified as an air pollutant in Baltimore, Maryland and Belle, West Virginia. Because DMN has been shown to be carcinogenic to laboratory animals, its presence as an air pollutant is cause for concern.

Following the studies of the only known primary source of the carcinogenic nitrosamine (the FMC Corporation in Baltimore, Maryland), investigations have turned to precursor sources, i.e. mainly sources of secondary amines. 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 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.

The health effects of the ambient levels reported to date are still unknown. Of more than 100 of these N-nitroso compounds synthesized, over 70% 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.

III. FIELD STUDIES

Samples were collected from four^{*} of the five industrial facilities to determine nitrosamine levels in both the ambient air and the water. Air samples were collected over a 2-hr period using foil-covered^{**} impingers filled with 60 ml of 1N KOH. The air samples were drawn through the impingers by a vacuum pump and the flows controlled by a calibrated stainless steel hypodermic needle. Water and wastewater samples were collected on a grab basis in amber glass quart bottles with Teflon^{***} liners. The NEIC analytical procedure for nitrosamines is included in Appendix A.

Because the monitoring for nitrosamines was conducted on a "screening" type basis to determine if the compounds were present, detailed process evaluations were not made. In addition, due to the proprietary nature of the processes, Company personnel were reluctant to discuss processes or the types and amounts of materials used. In several plants, N-nitroso compounds were found in wastewater samples; in-plant sampling would be required to locate the sources of these compounds. With the exception of one sample at Ciba-Geigy Corporation, N-nitroso compounds were not detected in the air samples.

CIBA-GEIGY CORPORATION

The Ciba-Geigy Corporation is an international organization which

* Samples were not collected from Farmers Supply and Produce.

** Impingers covered with foil to prevent photoreaction.

*** Teflon is a trade name.

originates, manufactures and markets organic chemical specialties. The McIntosh plant began operating in 1952 and produced only DDT. In the early 60's, DDT production ceased after newer and more effective insecticides were developed.

The McIntosh plant, one of the larger Ciba-Geigy facilities, produces more than 75 different products including agricultural chemicals, dyestuffs, plastics and additives, and sequestrene products. Herbicides include Triazine and Fluometuron; the basic insecticides manufactured are Diazinon,* Spectracide,* and Chlorobenzilate. Fluorescent whitening agents are manufactured for detergents, and other optical brighteners are produced for use in the textile and paper industries. The plant operates 24 hr/day, 7 days/week.

Water Supply and Wastewater Treatment

Water used for cooling purposes is pumped to a large reservoir from the Tombigbee River, and then pumped to the plant and used on a once-through basis. The spent cooling water is returned to the river via National Pollutant Discharge Elimination System (NPDES) Outfall 001; the flow is variable, but averages $7.6 \times 10^4 \text{ m}^3/\text{day}$ (20 mgd).

Approximately $2.3 \times 10^4 \text{ m}^3/\text{day}$ (6 mgd) of water is withdrawn from the reservoir, clarified, filtered, and demineralized, and used for boiler make-up. An additional $2.3 \times 10^4 \text{ m}^3/\text{day}$ is pumped from five wells. The pH is adjusted with soda ash, the water is degassified and chlorinated, and then is used in the processes and also as the potable supply.

* Trade name.

All process wastewater is collected in segregated sewers and discharged to one of three treatment systems [Figure 1]. Some process wastewaters are collected in a common sewer and flow to an equalization pond. An auxiliary pond, located upstream of the equalization pond, receives process wastewaters high in ammonia; this wastewater is released into the equalization pond under controlled conditions because the treatment system does not reduce the ammonia. This method is used to bring the effluent into compliance with the NPDES limitations for ammonia.

After equalization, the wastewater is neutralized, aerated for 10 days, and then polished an additional 5 days in another aerated lagoon. Finally, the wastewater is clarified, neutralized, and discharged through Outfall 001.

Wastewater from the Diazinon process and wastewaters containing cyanide are discharged to the detoxification system. The acidic wastewaters flow to the destruct basin for mixing purposes. After 20 days, the flow is sent to the alkaline chlorination system^{*} for CN destruction. After detoxification, the wastewater is sent to the equalization pond.

Dilute process wastewaters, designated by the Company as slightly contaminated, along with stormwater runoff and water from the cascade coolers, flow to a large holding pond. Since the dilute wastewater is slightly acidic, spills are routed to the holding pond and mixed with dilute wastewater. The spilled materials are less stable in an acid environment.

* *This system installed for plant upsets and is not required under normal operating conditions. Acidic wastewaters are not mixed with wastewaters containing cyanide.*

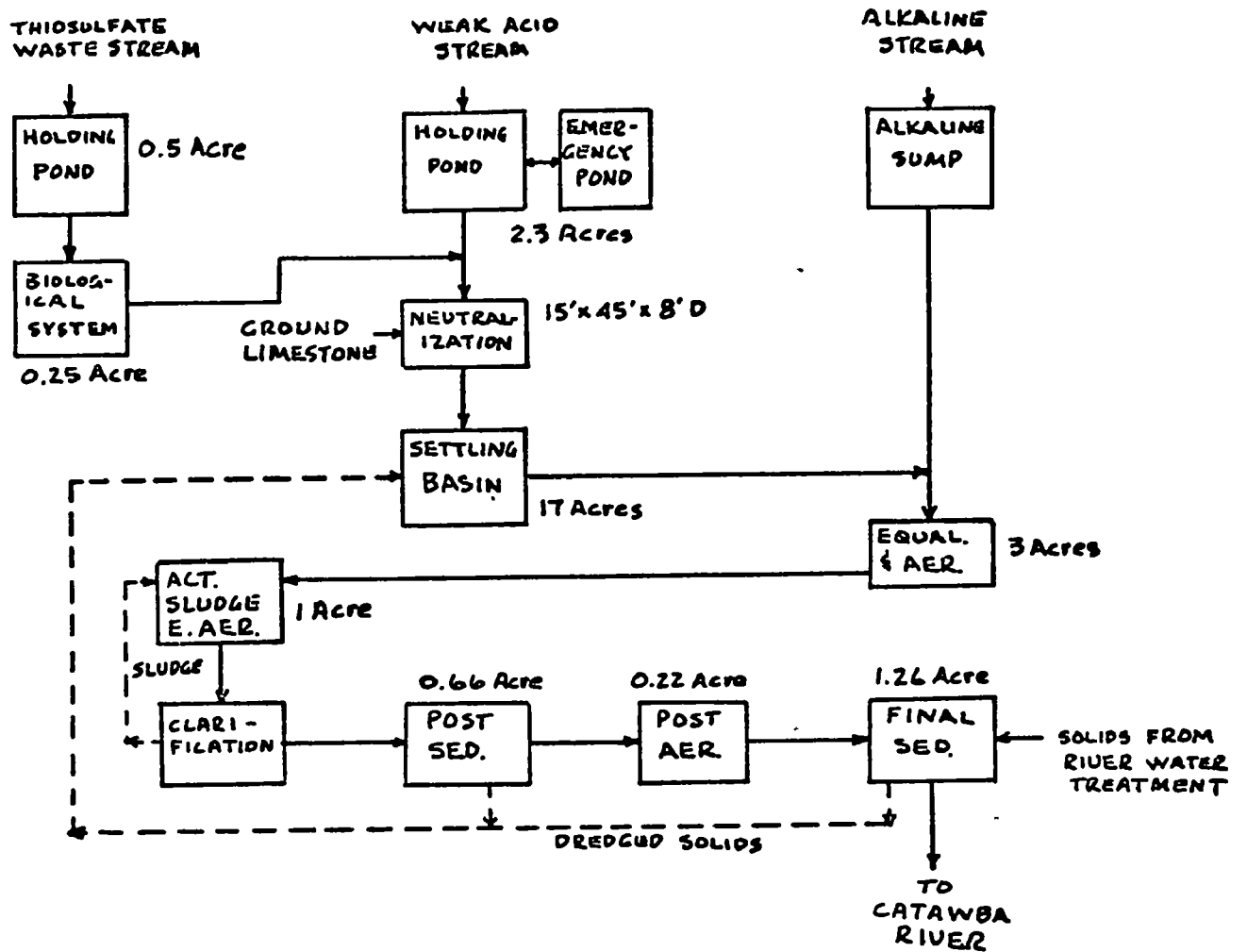


FIGURE 1
CIBA-GEIGY CORPORATION
McINTOSH, ALABAMA
WASTEWATER TREATMENT SCHEMATIC.

All wastewaters combine with the spent, once-through cooling water, and flow to the river, about 1.2 km (0.75 mi) from the treatment area.

Sanitary wastewaters are treated in 9 extended aeration package plants which discharge to the equalization pond. The package plants are designed to treat a total of 187 m³/day (49,500 gpd).

Solid Waste Disposal

The Company's policy is that solid wastes are not to be removed from the property for disposal or treatment. All flammable material, toxic and nontoxic, is burned in a multipurpose, gas-fired incinerator equipped with primary and secondary burners. Emission control equipment consists of a water quench tank followed by a high-energy venturi water scrubber and a packed tower using a caustic scrubbing solution. Nonburnables are buried in a landfill located on the northeast section of the property. The site has been classified by the State as acceptable for hazardous and toxic wastes.

Processes

There are more than 25 processes, all batch operated. Products from this facility include Diazinon, herbicides, thioherbicides, atrazine, sequesterines and whitening agents. Raw or intermediate materials containing amines used in their processes include:

- Monoethylamine
- Isopropylamine
- Secondary butylamine
- n-methylethanolamine
- Cyclopropylmethyl-n-propylamine
- Propylamine
- Ethylene diamine
- Aniline

Morpholine
 Dimethylamine
 Triethanolamine
 Diethanolamine
 Meta amino benzo trifluoride
 Diaminostilbene disulfonic acid
 Diethylenetriamine
 Aminoethylethanolamine
 Pyrrolidine
 Other amines considered proprietary

These compounds are all active ingredients, but are not used all the days the plant is operating. However, during the NEIC monitoring period, processes using amines were operating. According to plant personnel, the only nitrating agent used by the facility is sodium nitrite for one of their brightener reactions. This agent is used periodically. Insignificant quantities of nitric acid are used throughout the plant; ammonia is used on-site for refrigeration and other processes.

Monitoring Results

Monitoring was conducted on May 25, 1977; a description of the air and water monitoring sites is given in Table 1 and shown in Figure 2. The air speed varied between 4.8 and 16 km (3 and 10 mi)/hr, and the wind was mainly from the southwest. The temperature during the monitoring period was between 85° and 90°F; the sky was cloudy.

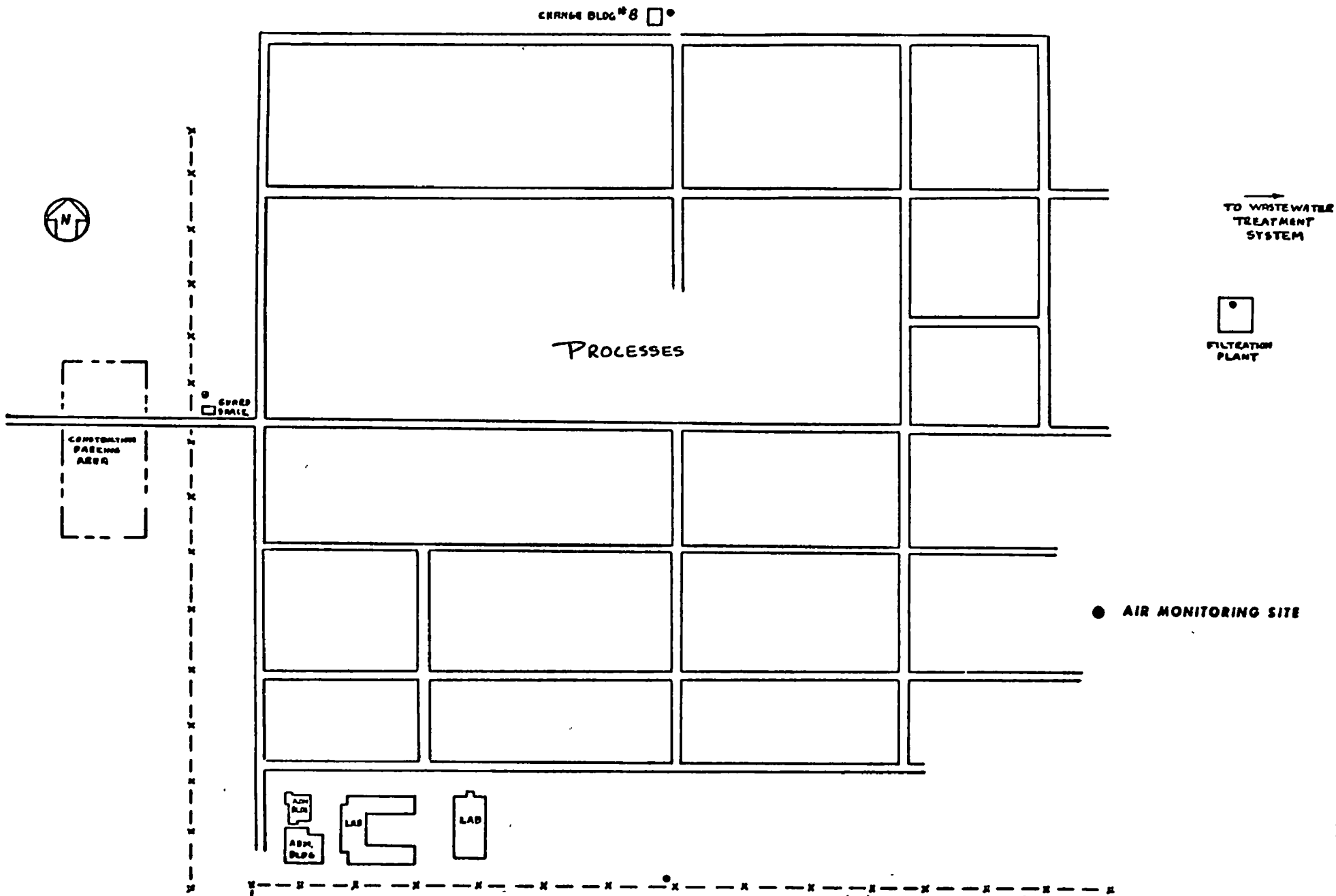
Nitrosamines were not detected in the untreated or treated well and river water samples nor in the ambient air samples collected at the east, north, and west monitoring sites. In the grab sample collected from the treated wastewater effluent, 0.05 µg/l^{*} dimethylnitrosamine (DMN) and 0.63 µg/l^{**} nitrosopyrrolidine (NPyr) were detected. A mass

^{*} Detection limit - 0.05 µg/l.

^{**} Detection limit - 0.1 µg/l.

Table 1
MONITORING SITE DESCRIPTION
CIBA-GEIGY CORPORATION
McIntosh, Alabama

Sample Description	Site Location
Untreated well water	Well water sump, next to degassifier, prior to degassification
Treated well water	Primary pump station
Untreated river water	Pump house at reservoir
Treated river water	Clear well, east of filtration plant
Treated wastewater effluent	Effluent ditch, about 1/4 mile from river, at bridge
Air - south of processes	Ditch on south side of plant at fence line (ground level)
Air - east of processes	Roof of filtration building
Air - north of processes	North side of change room #8 (ground level)
Air - west of processes	North side of Brown and Root guard shack (ground level)



CIBA-GEIGY CORPORATION GENERAL PLANT LAYOUT
McINTOSH, ALABAMA

of $0.02 \mu\text{g}^*$ DMN was detected in the air sample collected at the south monitoring site. However, these levels were too low to be confirmed by mass spectrometry. An unidentifiable nitrosamine was also detected in the wastewater effluent, but in a lesser concentration than NPyr.

Since the intake waters did not contain nitrosamines, the source of the N-nitroso compounds in the effluent must have originated in the processes. The process wastewater comprises about 12% of the total effluent flow of $93,000 \text{ m}^3/\text{day}$ (24.5 mgd). If the N-nitroso compound concentrations are assumed to be constant in the effluent, then the concentrations of DMN and NPyr in the process wastewater would be as high as 0.42 and $5.3 \mu\text{g/l}$, respectively.

The wind direction during monitoring was variable, but mainly from the southwest. The DMN was detected in the air sample upwind of the processes. Olin Chemical is located about 0.8 km (0.5 mi) south of the Ciba-Geigy facility; however, whether the nitrosamine originated from Olin, or Ciba-Geigy, is not known. Approximately 472 liters of air was drawn through the impingers [Appendix B - sample volumes], therefore, the concentration of DMN was 42 ng/m^3 which is in the range of 40 to 300 ng/m^3 found at Baltimore, Maryland and Belle, West Virginia.^{2,3} Based on the one positive sample, it cannot be concluded that nitrosamines are present at low levels or are ubiquitous in the plant's environment. It is equally incorrect to infer that nitrosamines are not present based on the three negative samples. The negative results at the other three sites indicate that: 1) nitrosamines are not emitted, 2) nitrosamines were not emitted during sampling, 3) once in the atmosphere these compounds decomposed rapidly, or 4) the compounds were present, but not collected by the impingers due to environmental conditions. However, DMN is a known carcinogen to laboratory animals, therefore its

* Detection limit (in air sample) - $0.02 \mu\text{g}$.

presence indicates some degree of risk and Ciba-Geigy should take action to eliminate the emission of nitrosamines. Since only a screening type of monitoring was conducted, the maximum levels or sources, of N-nitroso compounds emitted, cannot be determined. Ciba-Geigy personnel collected air samples concurrently with NEIC; therefore, they have the monitoring and analytical capability to determine sources and atmospheric levels of nitrosamines.

MARTIN-MARIETTA (SODYECO)

The SODYECO Division of Martin-Marietta Corporation began manufacturing liquid sulfur dyes for the textile industry in 1936; the Company was known as Southern Dyestuff Company. SODYECO now produces over 200 organic chemical compounds and textile dyes. There are between 30 and 40 organic chemicals produced, including pesticides. The pesticides are prepared under contract to other companies while the dyestuffs are prepared for general sales.

The plant is located on 182 ha (450 acres) on the east side of the Catawba River and south of highway 27 in Mt. Holly (NW of Charlotte). Approximately 12 to 14 ha (30 to 35 acres) of the site is dedicated to manufacturing processes and supportive facilities. An additional 12 to 14 ha consists of lagoons for process wastewater treatment.

The plant operates 3 shifts, 7 days/week. There are approximately 190 processes used at the plant, all of which are batch operated. The average production capacity is rated at 333,000 kg (734,000 lb)/day of finished product.

Water Supply and Wastewater Treatment

All water used in the plant for domestic purposes is obtained from

wells; the water is not treated. Process water and cooling water is withdrawn from the Catawba River, coagulated and filtered.

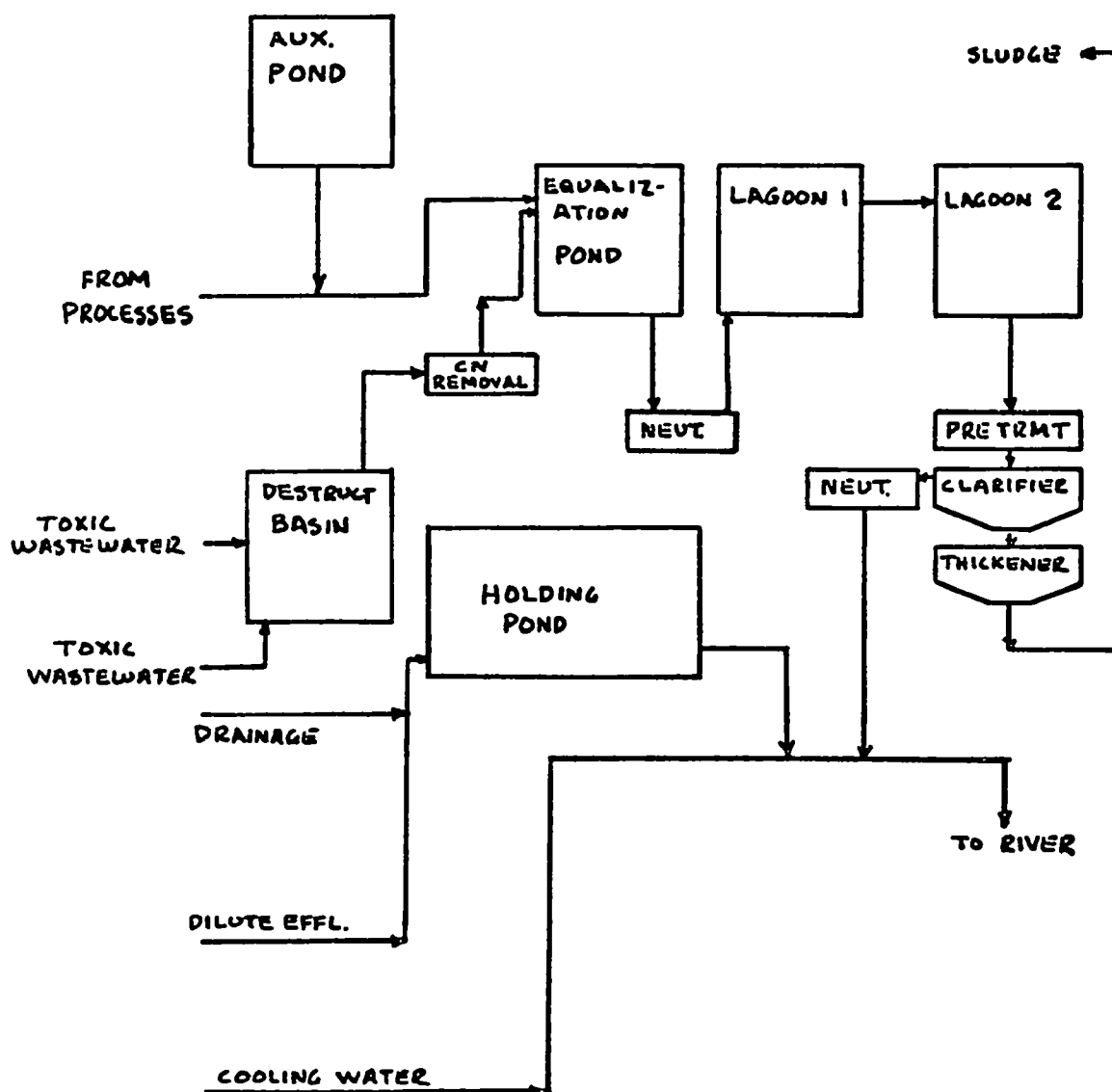
Sanitary wastes are discharged to various septic tanks throughout the plant; septic tank effluent is discharged to the process alkaline wastewater sewers.

All process wastewaters are treated prior to discharge to the Catawba River. The single outfall is authorized by a Federal NPDES permit; currently the effluent complies with all of the limitations except BOD. BOD limitations are generally met during the warmer months.

There are three process wastewater streams: the thiosulfate waste stream, the weak acid stream, and the alkaline waste stream [Figure 3]. The thiosulfate waste stream is collected in a holding pond and then sent to a aerated lagoon where the wastewater is biologically converted to 1% H_2SO_4 and sodium thiosulfate at pH 1 to 2. The weak acid stream is collected in two lagoons; the biologically converted effluent is combined with the effluent from weak acid lagoons and neutralized with ground limestone in a concrete basin. The neutralized effluent is sent to a 6.9 ha (17 acre) lagoon and the gypsum settled. The supernatant from the 6.9 ha lagoon is combined with the alkaline waste stream and sent to a flow equalization and aeration basin. The flow is then routed to an extended aeration-activated sludge lagoon; sludge is settled in a steel Permutit Company clarifier. Post settling and post aeration lagoons follow the clarification process. After final settling, the effluent is discharged to the Catawba River, about 0.54 km (0.33 mi) downstream from the final settling lagoon. The flow averages 7,570 m^3/day (2 mgd). The EPA has provided a grant to the Company to help fund this treatment system.

All herbicide wastewaters are incinerated. The incinerator is operated only when the holding tank for the wastewaters becomes full.

FIGURE 3
MARTIN MARIETTA CORPORATION
SODYECO DIVISION
CHARLOTTE, N. CAROLINA
WASTEWATER TREATMENT SCHEMATIC



The incinerator is fired with No. 2 fuel oil; it is equipped with once-through, dilute caustic spray scrubber with two packed sections. The spent caustic is sent to the wastewater treatment system.

Processes

Of the more than 190 processes, secondary amines are used in only 5 major process reactions; the end products are either sent out of the plant as finished product or used in other plant processes. There are also at least 25 other processes which use tertiary amines in the reactions. Company personnel stated that all of the reactions are proprietary, therefore only a general description was provided with the emphasis on the possibilities of amines being emitted to the air or discharged in the wastewater.

There is a possibility of nitration of secondary amines released to the environment because one of SODYECY's specialties is nitration. According to Company personnel, the adjacent industries do not use nitric acid, nitrogen compounds, or secondary amines.

The 5 reactions using secondary amines are discussed briefly:

1. Di-n-propylamine. This amine is very volatile and the reaction is conducted in a closed system. Safety valves and pop valves are vented directly to the atmosphere. The amine attaches to the benzene ring and becomes part of the product, Oryzalin, a powdered herbicide.

During the process, the product is filtered. The liquid filtrate is sent to the incinerator. Other wastewaters generated in the process before the herbicide becomes active are sent to the treatment ponds. The flow, about $115 \text{ m}^3/\text{day}$ (30,000 gpd), could contain amines.

The process(s) using this amine was operating during the monitoring period.

2. n-cyanoethylorthochloroaniline. This amine is used as a coupler in the production of a dispersed dye. Between 5 and 10% of the final product consists of this amine. Since the emission sources from the reaction train are not equipped with control devices, the possibility exists that the amine may be emitted.

During the reaction, wastewater is discharged to the treatment system; the majority of the flow originates from the plate and frame filter press. The total flow is unknown, but is highly variable.

The process was operating up to the day of NEIC's monitoring, but was down on the monitoring day.

3. Diphenylamine. The amine is used in the production of sulfur dyes. The off-gases from the reaction are vented to the atmosphere. Filtrate, approximately 11 m³/day (3,000 gpd) from the plate and frame filters, is sent to the treatment system. Since the process reaction occurs at 0°C and the amine has a low vapor pressure, emissions to the air are not probable.

The process was operating during NEIC's monitoring.

4. Parahydroxyphenylamine. The amine is added in a rotary thionator (closed system) in the production of dyes. The reaction occurs in a high temperature ball mill; the off-gases are vented to caustic absorbers. The spent absorbent is used in other process reactions and not discharged. There are no wastewater streams from this process.

This process was operating during NEIC's inspection.

5. Carbazole. This low vapor pressure amine is used as a raw material in several reactions, including the production of sulfur dyes and organic chemicals. Company personnel stated that this amine could possibly be emitted and also discharged in the wastewater stream.

The material was being used during NEIC's monitoring.

Monitoring Results

Monitoring was conducted on May 5, 1977; a description of the air and water monitoring sites is given in Table 2 and shown in Figure 4. The air speed varied between 8 and 24 km (5 and 15 mi)/hr and the wind was mainly from the southwest. The temperature was 75°F. Sky conditions were clear; however, it had rained 0.11 inches overnight.

Nitrosamines were not detected in any of the ambient air samples nor in the untreated well and river water samples. In the grab sample collected from the treated wastewater effluent, 13 $\mu\text{g/l}$ * dipropylnitrosamine (DPN) was detected, and confirmed by mass spectral analysis. This amine probably originated in the process making Oryzalin. At this low level concentration, DPN would not be detected in the Catawba River.

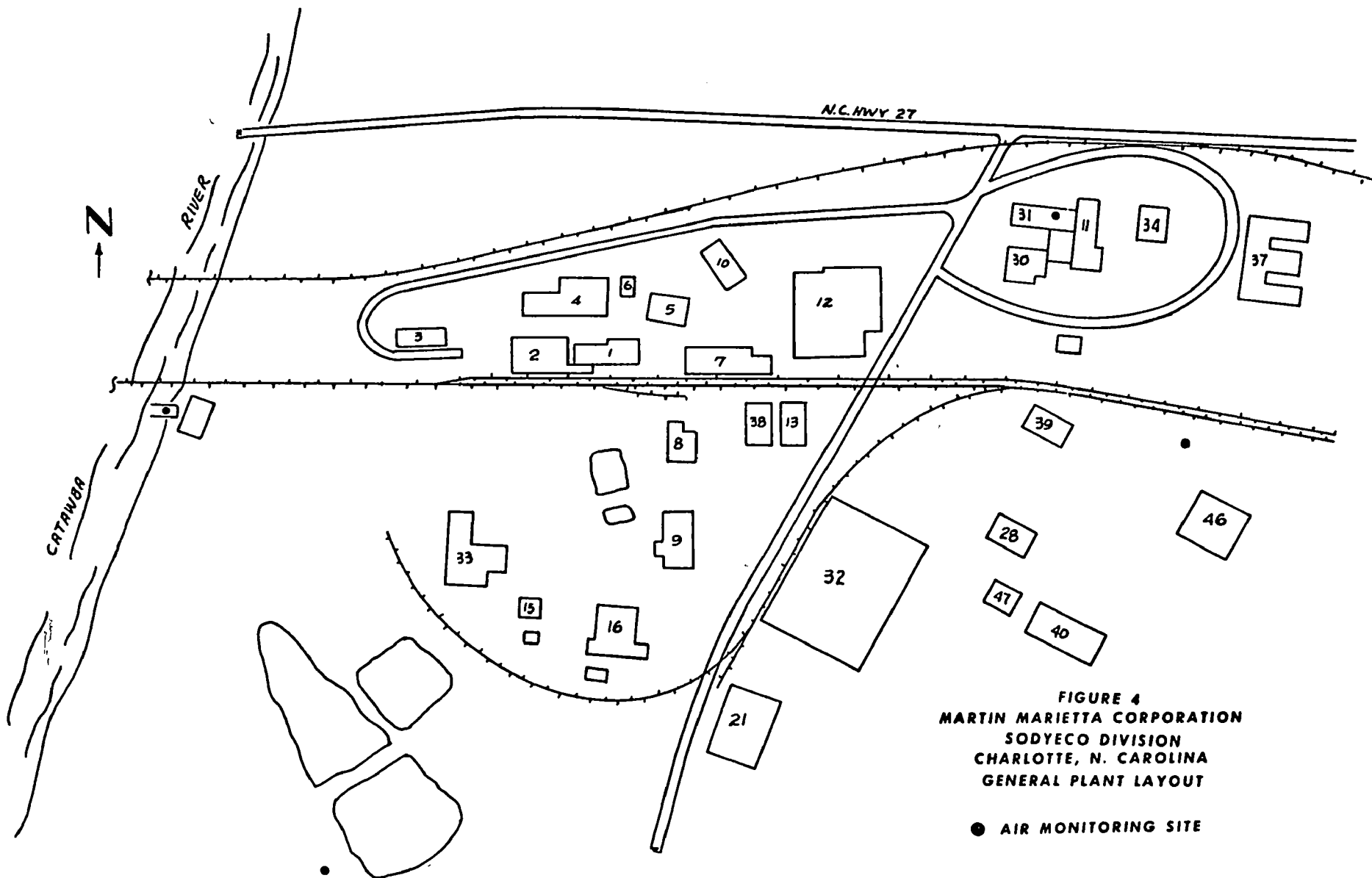
PROCTOR CHEMICAL COMPANY, INC.

In 1938, the Proctor Chemical Company was founded by Edward C. Proctor. The Company became the wholly owned subsidiary of National Starch and Chemical Corporation, Inc. in 1969. The Company manufactures almost every chemical compound used in the textile industry, except for

* Detection limit - 0.2 $\mu\text{g/l}$.

Table 2
MONITORING SITE DESCRIPTION
MARTIN-MARIETTA CORP.
Charlotte, North Carolina

Sample Description	Site Location
Untreated river water	Intake pump house, from the fish bioassay feed line
Untreated well water	Water fountain in Sales Service Building
Treated wastewater effluent	Canal, approximately 0.54 km (0.33 mile) downstream from the final settling lagoon, about 9 m (30 ft) upstream from confluence with river
Air - north site	Roof of building 11, analytical laboratory. About 45 to 60 m (150 to 200 ft) from highway 27 (downwind site)
Air - west site	Intake pump house, about 91 m (100 yd) downstream from highway 27 bridge; on intake pipe superstructure dock, about 3 m (10 ft) west of stairs on dock (ground or dock level)
Air - south site	West side of preaeration pond on SW side of pond. Upwind site (ground level)
Air - northeast site	About 30 m (100 ft) south of spur railroad tracks, behind bldg. 39 (ground level)



dye stuffs, and produces over 500 products in varied lot sizes from 55-gallon drums to tank truck and railroad car bulk quantities. Proctor Chemical has the capability to produce almost any chemical formulation to a customer's specification. The plant also produces custom chemicals for larger chemical companies which do not want to invest capital for new processes. About 40% of their products are manufactured for other companies.

Proctor Chemical Company consists of two plants, situated approximately 8 km (5 mi) apart. The Lumber Street Plant [Figure 5] consists of 4,600 m² (49,000 ft²) of manufacturing, warehousing, shipping and main offices while the new (1971) Cedar Springs Plant [Figure 6] consists of 5,000 m² (53,600 ft²) of manufacturing and warehousing. The Cedar Springs Plant is located on 16 ha (40 acres) in the rural area of Salisbury while the Lumber Street facility is within the City limits and bounded on all sides by other businesses. Both facilities operate 5 days/week, 24 hr/day.

Water Supply and Wastewater Treatment

All water used at both plants is purchased from the City. Fresh water used for condensers and reactors is recycled through cooling towers; there are three towers at the Lumber Street Plant and one tower at Cedar Springs.

Sanitary wastewater from the Lumber Street facility is discharged directly to the municipal wastewater treatment plant. Sanitary wastewater is discharged to a septic tank and leach field at the Cedar Springs Plant.

Process wastewater is not discharged from either plant to receiving waters. At the Lumber Street Plant, all wastewaters, clean-up waters,

● AIR MONITORING SITE.

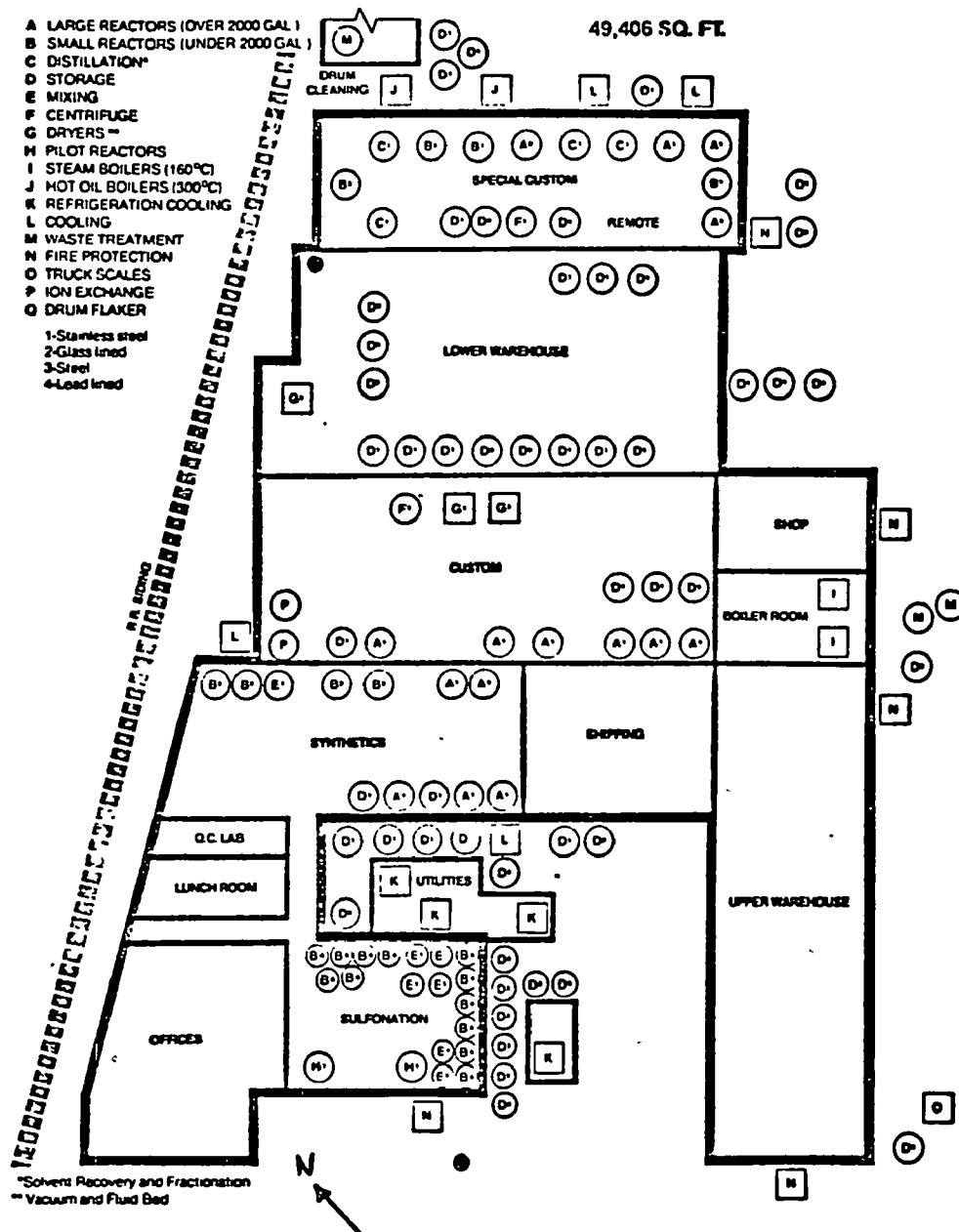
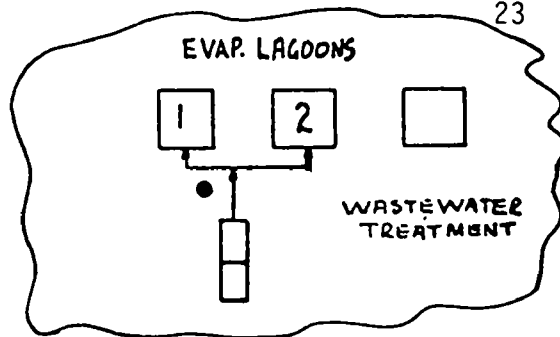
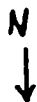


FIGURE 5
PROCTOR CHEMICAL COMPANY, INC.
SALISBURY, N. CAROLINA
LUMBER STREET PLANT
GENERAL PLANT LAYOUT

AIR MONITORING SITE



53,590 SQ. FT.

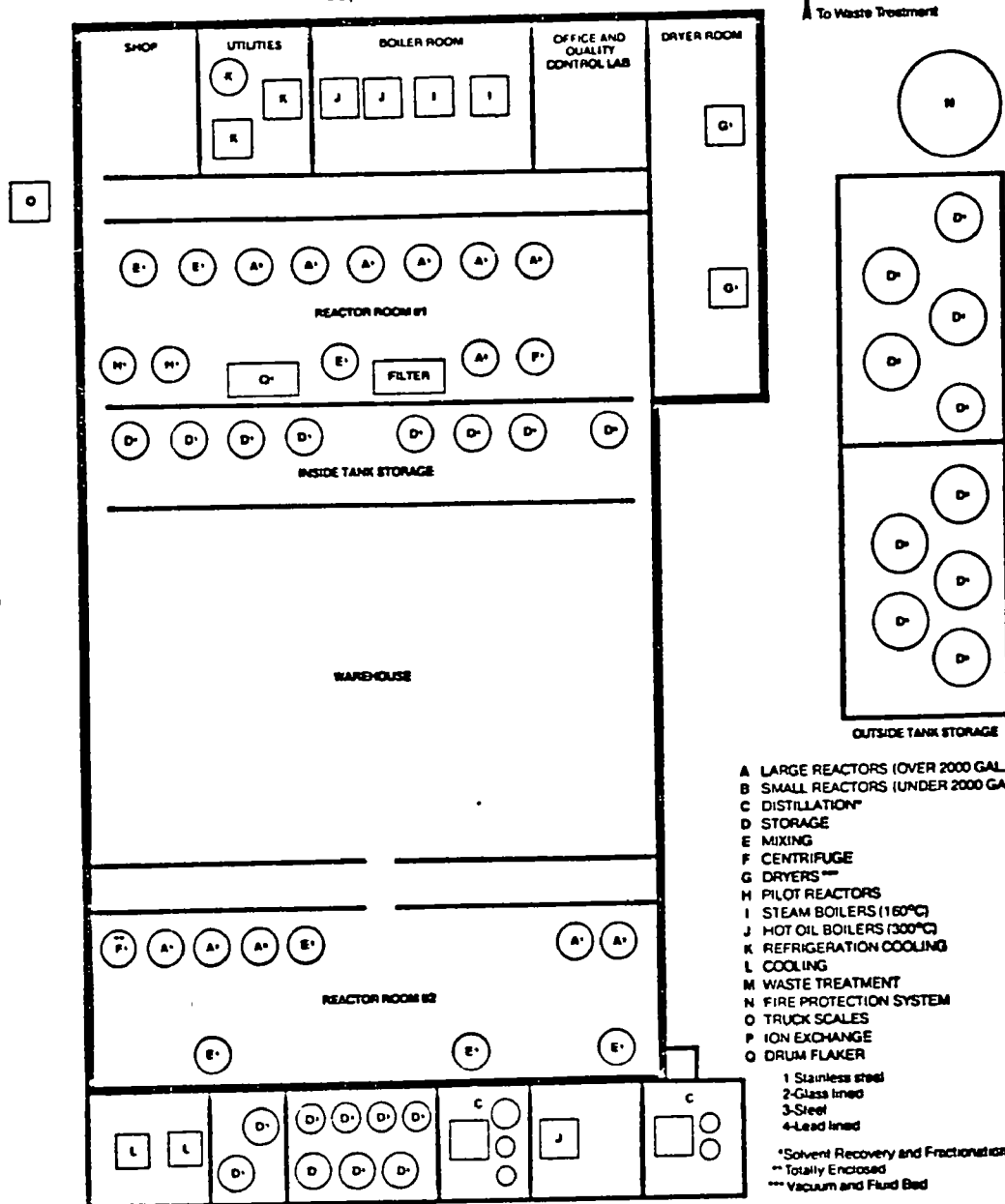


FIGURE 6
PROCTOR CHEMICAL COMPANY, INC.
SALISBURY, N. CAROLINA
CEDAR SPRINGS PLANT
GENERAL PLANT LAYOUT

rainwater, cooling tower and boiler bleedoff are discharged to the municipal wastewater treatment facility. Prior to discharge to the municipal sewer, the wastewaters flow to two 530 m³ (140,000 gal) capacity tanks, operated in parallel; the wastewaters are aerated with surface aerators. The flow averages 380 liters/min (100 gpm). The two aeration tanks are located above ground and are open to the atmosphere. A portion of the wastewater flows through a 76 m³ (20,000 gal) underground holding tank located in the drum cleaning area, before discharge to the two surface tanks.

Process wastewaters are not discharged from the Cedar Springs facility. All wastewaters drain to two settling and separation pits, each about 3 m square x 0.9 m deep (10 ft square x 3 ft deep), operated in series. Material is either recovered from the pits or pumped to one of two unlined lagoons, operated in parallel. There are actually three lagoons; however, one does not receive plant wastewater, and contains storm water runoff. The wastewaters in the two lagoons are continually recycled through spray nozzles into the air to assist in evaporation. There is no known discharge from either lagoon.

Six wells, ranging in depth from 6 to 12 m (20 to 40 ft) deep, are used for monitoring on the Cedar Springs property to determine if the wastewater from the lagoons is seeping into the ground water. The wells are monitored weekly for pH, manganese, chloride, COD, total hardness, total solids, and total volatile solids; to date the data has not indicated that the wastewater is entering the ground water.

Processes

The total production capacity of both plants is 27 million kg (60 million lb)/yr. Originally, the Company sulfonated animal oils and fats for the textile industry; however, the chemical formulations for textiles

have grown to include dye auxiliaries, thermosetting resins, wetting agents, etc. Formulations include concentrates, fluids, flakes, small chunks, and waxy materials. All processes are operated on a batch basis using stainless steel, glass-lined steel, or lead-lined reactors. In addition, specialized systems such as distillation columns and enclosed centrifuge and solids handling equipment are available for formulations with specialized requirements. Units processes include:

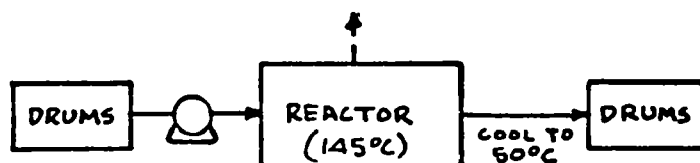
Alcoholysis	Propoxylation
Alkylation	Reduction
Amidation	Sulfonation (0°-230°C)
Crystallization	Vacuum Drying
Distillation	Chlorination
Esterification	Quaternization
Flaking	Organometallic Condensation
Hydrolysis	Etherification
Oxidation	Sulfation
Phosphation	

Product categories include:

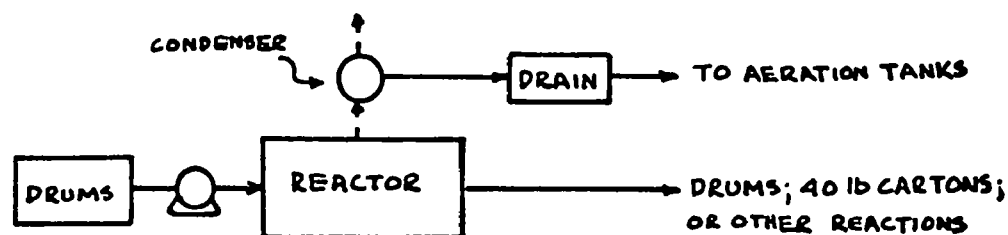
Antistatic Agents	Reactants
Antistick Agents	Resins
Catalyst	Sanforizing Agents
Detergents	Scouring Agents
Dye Assistants	Softeners
Dye Fixatives	Sulfonated Fats and Oils
Emulsifiers	Weighers
Flame Retardants	Wetting Agents
Lubricants for Yarn	

Due to the large number of batch processes available at Proctor Chemical, detailed process evaluations were not conducted. However, typical process descriptions for reactions using amines fall into three categories.

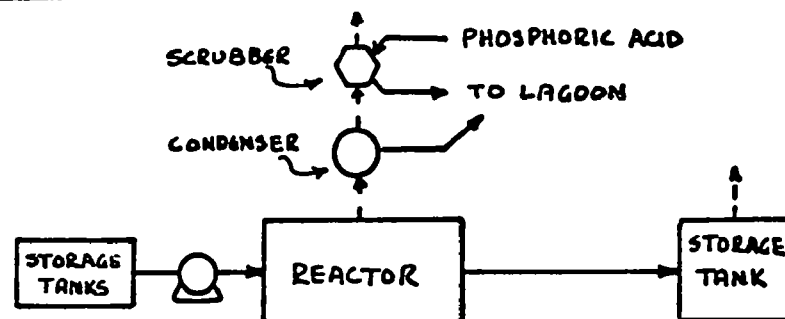
1. Diethanol Amine Reaction [Figure 7-A] - This process is located at the Lumber Street facility only, in the synthetic area. The only source of amines would be to the atmosphere as there is no wastewater discharge. The air emissions are not controlled.



A. DIETHANOLAMINE REACTION



B. AMIDE PRODUCTION



C. TRIMETHYLAMINE REACTION

FIGURE 7
PROCTOR CHEMICAL COMPANY, INC.
SALISBURY, N. CAROLINA
TYPICAL AMINE REACTION SEQUENCES

2. Amide Production [Figure 7-B] - This process is conducted at both plants. Air emissions are vented through a shell and tube condenser; condensables are discharged to the wastewater system while non-condensables are vented to the atmosphere.

3. Trimethylamine Reaction [Figure 7-C] - Air emissions from the reactor are vented to a shell and tube condenser and then to a counter-current fume scrubber, packed with berl saddles. Phosphoric acid solution cascades through the scrubber from the top. About 180 kg (400 lb) of acid, mixed with 1,500 liters (400 gal) of water, is used each day. The spent scrubbing solution is discharged to the lagoon system. This process is used only at the Cedar Springs Plant.

The raw and intermediate materials used in the processes were provided to NEIC, however, Company personnel consider these materials proprietary and requested that they not be identified in the report.

Monitoring Results

Monitoring was conducted on May 3, 1977; a description of the air and water monitoring sites for both plants is given in Tables 3 and 4, and shown in Figures 5 and 6. The air speed varied between 6 and 15 km (4 and 9 mi)/hr and was out of the southwest. The temperature during the monitoring period was between 75° and 80°F; sky conditions were partly cloudy.

Nitrosamines were not detected in the ambient air samples at either process facility nor in any water/wastewater sample from the Lumber Street Plant. A concentration of 0.1 µg/l of dimethylnitrosamine* (DMN) was detected in the municipal water supply sample at the Cedar Springs

* Detection limit = 0.1 µg/l.

Table 3
MONITORING SITE DESCRIPTION
PROCTOR CHEMICAL COMPANY
LUMBER STREET PLANT
Salisbury, North Carolina

<u>Sample Description</u>	<u>Site Location</u>
Municipal water supply	Main office building, sink in men's room
Process wastewater effluent after 24 hr of aeration	Valve from aeration tank closest to the research building, farthest from plant (filled 5-2-77)
Process wastewater effluent before aeration	Valve from aeration tank to the plant (being filled on 5-3-77)
Air - south of processes, upwind of site	Inside of fence line, approximately 0.6 m (2 ft) off of Lumber Street, about 6 m (20 ft) west of alley entrance (unit on top of 55 gal. drum)
Air - west of processes	38 to 46 m (125 to 150 ft) downwind of the two aerated storage tanks, about 3 m (10 ft) inside of fence line (unit elevated about 2 m (7 ft) off of ground)
Air - northeast of processes, downwind of site	Northeasternmost section of plant, adjacent to drum cleaning facility (unit elevated about 6 m (20 ft) above ground)
Air - east of processes	On NW corner roof of Lower Warehouse

Table 4
 MONITORING SITE DESCRIPTION
 PROCTOR CHEMICAL COMPANY, INC.
 CEDAR SPRINGS PLANT
 Salisbury, North Carolina

Sample Description	Site Location
Municipal water supply	Fresh water intake at burner shed spigot, adjacent to lagoons
Process wastewater, untreated	From second settling and separation pit (closest to lagoons)
Process wastewater from east lagoon	About 7.6 m (25 ft) east of pump house on west side of lagoon #1
Process wastewater from middle lagoon	From middle of lagoon #2 (lagoon almost dry)
Grant's Creek	Creek as it leaves north side of property, about 30 m (100 ft) off property at bridge
Air - south of processes, upwind site	Midway between settling and separation pits and lagoons near east end of lagoon #1 (unit on 55 gal. drum)
Air - east of processes	Approximately 15 m (50 ft) north of scale house, about 4.6 m (15 ft) east of road (unit at ground level)
Air - north of processes	Between ammonia burner and plant building, about 12 m (40 ft) north of building across road (unit at ground level)
Air - west of processes	On tank truck ramp (unit at ground level)

Plant, but was not detected in any of the process wastewater samples, nor in the Grant's Creek sample. Also, DMN was not detected in the municipal water supply at the Lumber Street Plant, and both fresh water supplies are from the Salisbury utility. Therefore, DMN was most probably not present in the sample, but was detected due to the solvents used in extraction.*

Nitrosamines were not detected in the Grant's Creek sample nor in the sample collected from the middle lagoon (lagoon #2); this lagoon was almost dry. However, 8.2 µg/l propylbutylnitrosamine** (PBN) and 3.2 µg/l PBN were detected in the wastewater effluent from the settling and separation pit (influent to lagoon #1) and in the sample collected from lagoon #1), respectively. The PBN could not be confirmed by GC/MS at the levels detected due to a masking effect by a large number of components at higher concentrations. Although a number of occurrences of prominent PBN masses were found, the spectra of those peaks were not PBN. Of the amines used at the plant, the precursor of PBN was not in the inventory.

VELSICOL CHEMICAL COMPANY

Velsicol Chemical Company operates two plants at Chattanooga. These are designated as the Semi-works and Main Plant, located across the street from each other.

Water Supply and Wastewater Treatment

Fresh water for both plants is supplied by the City of Chattanooga. The amount of water was not provided during the NEIC inspection.

* The solvents used in NEIC's extraction method produces peaks that appear similar to DMN and nitrosomorpholine in the presence of residual chlorine.

** Detection limit = 0.2 µg/l.

Sanitary wastewaters from both plants are discharged to the municipal sewer system.

Process wastewater, water used to clean reaction vessels, mix tanks, etc., from the Semi-works are discharged into a holding tank. After neutralization, the wastewaters are discharged to the municipal sewer system. Sediments from the holding tank are landfilled. If the process wastewater contains materials such as toluene, the wastewater is discharged into drums and hauled away for incineration by a private contractor. Process wastewater and wastewaters from air scrubber systems at the Main Plant are discharged to the City sewer. The wastewaters are pretreated; however, the Company considers the treatment to be confidential. At the time of the survey, the sewer was being replaced because the wastewater had apparently dissolved the pipe.

Stormwater and seepage from the north side of the Main Plant are discharged to the Tennessee River via a drainage ditch.

Processes

The Semi-works develops new products through research and also manufactures some specialty products. These products include esters of benzoic acid, dicyclopentadiene, methendic alcohol, dimethylchlorpentacine, dimethylchlorendate, and sucrose benzoate. One product, designated as MAADMA^{*} contains amine compounds. The majority of the processes are conducted on a batch basis in 1.9 m³ (500 gal) vessels. Other equipment use consists of stills, autoclaves, neutralization tanks, and mix tanks.

The Main Plant produces benzoic acid, benzoic acid esters, benzo nitrile, benzo guanamine, benzo alcohol, benzo trichloride, benzoyl

^{*} Chemical name is considered confidential.

chloride, benzoyl alcohol, and similar chemicals. Production figures are considered confidential.

Process vapors in the Semi-works plant are normally returned to the reaction vessel. However, some vapors, including fugitive, are vented to the atmosphere. Air pollution control at the Main plant is by means of scrubbers. The Company indicated however, nitrogen is emitted to the atmosphere from the benzoic acid process. They indicated that stack tests have been conducted at the Main Plant to determine if manufactured compounds were being emitted. The results were not available at the time of the NEIC survey.

Monitoring Results

A description of the air and water monitoring sites for both plants is given in Table 5. The air speed ranged between 4.8 and 11 km (3 and 7 mi)/hr and varied in direction. The temperature was about 80°F.

N-nitroso compounds were not detected in the ambient air, water or wastewater samples.

FARMERS SUPPLY AND PRODUCE

Farmers Supply and Produce, a retail store, supplies hardware, feed, seed, fertilizer, pesticides and herbicides to the general public. The pesticides and herbicides are purchased pre-packaged and are either sold as-received or mixed with liquid nitrogen or dry fertilizer. On an average basis, the store sells about 2,700 kg (6,000 lb)/yr of pesticides and herbicides with only 900 kg (2,000 lb) being pre-mixed at the store with fertilizers. The amount of these compounds sold in 1976 are as follows:

Table 5
 MONITORING SITE DESCRIPTION
 VELSICOL CHEMICAL COMPANY
 Chattanooga, Tennessee

Sample Description	Site Location
Semi-Works	
Air - south of processes	At fence line
Air - west of processes	At fence line
Air - north of processes	At fence line
Air - east of processes	Roof of office building
Main Plant	
City water supply	Main office building
Process wastewater after pretreatment	Discharge to the municipal sewer
Runoff	North side of plant
Air - south of processes	South side of plant
Air - west of processes	At fence line next to office building
Air - north of processes	At fence line adjacent to Coke Plant
Air - east of processes	East side of plant near wastewater discharge to sewer

Liquid atrazine	300 l (80 gal)
Atrex 80 W	900 kg (2,000 lb)
Paraquat	380 l (100 gal)
Lorax	90 kg (200 lb)
Balan	450 l (120 gal)
Princep 80 W	110 kg (250 gal)

At the time of NEIC's inspection, atrazine powder (Atrex 80W) was being mixed in water and added to ammonia. Mixing is conducted outside; only a very small amount of dust was lost during mixing due to the care taken by employees. The total mixing time takes less than 5 minutes; the number of batches varies daily, depending on customer orders.

Water is only used for mixing of the compounds; the operation does not have any process discharge. Empty chemical containers are placed in trash containers and removed by a contractor.

Due to the limited amount of materials being used and the nature of the operation, ambient air and water samples were not collected.

IV. SUMMARY AND CONCLUSIONS

Ambient air and water samples were collected at four industrial facilities and analyzed for N-nitroso compounds. Farmers Supply and Produce, a retail store, was not sampled.

Except for one sample collected at the Ciba-Geigy Corporation plant at McIntosh, Alabama, N-nitroso compounds were not detected in the ambient air samples. The wind direction during monitoring at Ciba-Geigy was variable, but mainly from the southwest. About 40 ng/m^3 of dimethylnitrosamine (DMN) was detected in the upwind monitoring site sample. This concentration is in the range found at Baltimore, Md., and Belle, W. Va. Olin Chemical is located south (upwind) of Ciba-Geigy's property and has nitrating facilities. However, whether the DMN originated from Olin Chemical, or Ciba-Geigy, is unknown. Based on one positive sample, it cannot be concluded that nitrosamines are present at low levels or are ubiquitous in the plant's environment. The negative results indicate that 1) nitrosamines are not emitted, 2) nitrosamines were not emitted during sampling, 3) once in the atmosphere the N-nitroso compounds decomposed rapidly, or 4) the compounds were not collected by the sample train due to environmental conditions. DMN's presence indicates some degree of risk and Ciba-Geigy should eliminate the emission. The Company has the capability to monitor and analyze nitrosamines.

Water samples collected from Ciba-Geigy Corporation, Martin-Marietta (SODYECO), and Proctor Chemical Company indicate that there are primary sources of direct emissions to the environment of a number of N-nitroso compounds. The compounds probably arise as impurities during the synthesis of other compounds and are emitted to the environment during the use or modification of these products. The source and types of nitrosamines detected are as follows:

<u>Facility</u>	<u>Sample Description</u>	<u>Conc. µg/l</u>	<u>N-Nitroso Compound</u>
Ciba-Geigy	Treated wastewater effluent	0.05	Dimethylnitrosamine
		0.63	Nitrosopyrrolidine
Martin-Marietta	Treated wastewater effluent	13.0	Dipropylnitrosamine
Proctor Chemical's Cedar Springs Plant	City water	0.1	Dimethylnitrosamine
	Process wastewater influent to evaporation lagoon	8.2	Propylbutylnitrosamine*
	Wastewater in evaporation lagoon	3.2	Propylbutylnitrosamine*

* PBN could not be confirmed by GC/MS due to masking by the large number of components at higher concentrations and because a PBN standard was not available at a high enough concentration to measure the exact retention time and detection limits by GC/MS.

In-plant sampling would be required to locate the sources of these compounds; however, at the levels observed, it is doubtful that this effort would be useful expenditure of EPA's resources.

There is a lack 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 the 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. Where health effects data are lacking, the safest posture is to assume no threshold level exists, and to minimize the environmental impact of known carcinogens wherever possible.¹

REFERENCES

1. "Reconnaissance of Environmental Levels of Nitrosamines in the Central United States," EPA Office of Enforcement, National Enforcement Investigations Center, Denver, Colorado, January 1977, EPA-330/1-77-001.
2. Fine, D. H., Rounbehler, D. P., Belcher, N. M., Epstein, S. S., "International Conference on Environmental Sensing and Assessment," Catalogue #75-CH 1004-1 ILESA, pp. 30-7, IEEE, New York, New York, 1976.
3. Fine, D. H., Rounbehler, D. P., Belcher, N. M., Epstein, S. S., SCIENCE, 192, 1328 (1976).

APPENDIX A

NEIC ANALYTICAL PROCEDURE FOR NITROSAMINES

NEIC ANALYTICAL PROCEDURE FOR NITROSAMINES

Air Samples

Air samples were collected in foil-covered impingers (SGA catalog #JV8550) filled with 60 ml of 1N KOH. Air samples were drawn through the impinger by a vacuum pump and the flows controlled by a calibrated stainless steel hypodermic needle (B&D #21). Normal collection volumes ranged from 200 to 250 liters of air per needle. Dual impingers were used to collect samples at each monitoring locations. The two samples were combined in the NEIC Laboratory prior to analysis.

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 250 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 59 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 modified Thermal Energy Analyzer (GC/TEA). An n-propanol/liquid nitrogen cold trap was used in conjunction with the modified TEA.

Where possible, samples thought to contain nitrosamines were spiked with known standards to confirm retention time and to help establish concentrations. A 10% Carbowax 20M, 1% KOH on 60/80 mesh Chromosorb WAW, column was employed for analysis. The retention time of the sample peaks matched those of the standard solutions of nitrosamines.

Quantitation of compounds reported was made by peak height comparison with authentic standards, obtained through the Food and Drug Administration, Washington, D.C.

Water Samples

Grab samples were collected in amber glass 0.946 liter (quart) bottles with Teflon liners. Two 50-ml portions of dichloromethane were used to extract each sample in a 2,000-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. 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.

QUALITY CONTROL

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

Solvent Blanks

Methylene chloride (dichloromethane) 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 GC/TEA system and found to be free from interferences.

Nitrosamines Free Water

Nitrosamine free water was taken to the field and used to prepare the 1 N KOH solution for the impingers. Twenty to fifty ml of the nitrosamine free water was used to wash each impinger sample into sample containers. The sample bottles were capped (caps had Teflon liners) and were sealed with electrician's tape.

The nitrosamine free water was analyzed in the NEIC laboratory to confirm the absence of N-nitroso compounds.

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 addition of NaCl to increase recovery during water extractions was studied but found ineffective.

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°C and 20°C, then extracting and concentrating as usual. For these compounds, the average recovery at -2°C was 65% and at 20°C, 78%. There were no apparent differences in efficiencies between the various compounds examined.

APPENDIX B
SAMPLE VOLUMES

APPENDIX B

SAMPLE VOLUMES April-May, 1977

Location	Station Description and Sample Type	Date	Sample Volume (liters)
Ciba-Geigy	Untreated well water	5/25	0.946
	Treated well water	5/25	0.946
	Untreated river water	5/25	0.946
	Treated river water	5/25	0.946
	Treated wastewater	5/25	0.946
	South site--air	5/25	471.6
	East site--air	5/25	471.6
	North site--air	5/25	478.8
	West site--air	5/25	484.8
Martin Marietta	Untreated river water	5/5	0.946
	Well water	5/5	0.946
	Treated wastewater	5/5	0.946
	North site--air	5/5	462.6
	West site--air	5/5	477.0
	South site--air	5/5	467.4
	Northeast site--air	5/5	505.8
Proctor Chemical Lumber Street	Municipal water	5/3	0.946
	Wastewater after aeration	5/3	0.946
	Wastewater before aeration	5/3	0.946
	South site--air	5/3	462.6
	West site--air	5/3	477.0
	Northeast site--air	5/3	467.4
	East site--air	5/3	505.8
Cedar Springs	Municipal water	5/3	0.946
	Untreated wastewater	5/3	0.946
	Wastewater--east lagoon	5/3	0.946
	Wastewater--middle lagoon	5/3	0.946
	Grant's Creek water	5/3	0.946
	South site--air	5/3	462.6
	East site--air	5/3	477.0
	North site--air	5/3	467.4
	West site--air	5/3	505.8
Velsicol Semi-works	South site--air	4/19	434.1
	West site--air	4/19	565.8
	North site--air	4/19	572.5
	East site--air	4/19	494.1
Main Plant	Runoff water--north	4/19	2.0
	Wastewater	4/19	2.0
	City water	4/20	2.0
	South site--air	4/20	465.6
	North site--air	4/20	491.5
	West site--air	4/20	524.4
	East site--air	4/20	471.1