

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
CENTER FOR DISEASE CONTROL  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION  
REPORT NO. 77-126-646

SHELL CHEMICAL COMPANY  
ROCKY MOUNTAIN ARSENAL  
DENVER, COLORADO

DECEMBER 1979

I. TOXICITY DETERMINATION

The following determinations have been made by the National Institute for Occupational Safety and Health based on environmental, medical and epidemiological information, literature reviews and professional judgement.

A hazard to the health of Shell Chemical employees existed for those who were exposed to DBCP during its production dates based on review of Shell Chemical medical records. It was found that those employees who were exposed to DBCP have suffered a definite adverse effect on testicular function. Of the 172 potentially exposed employees (as determined by Shell Chemical), Shell Chemical examined 83 (48%). Of these 7.8% were azoospermic and 14.1% oligospermic ( $<20 \times 10^6$  sperm cells/ml semen).

Environmentally it was found that a hazard to the health of employees exposed to the organic vapors of acetone, chloroform, isopropyl alcohol, hexane, methyl isobutyl ketone and toluene did not exist on the dates surveyed. Employee exposures to Atrazine and Bladex® were also found not to be a health hazard. It was also determined that at the present there are no adequate sampling and analytical methods for determining employee exposures to low levels of multiple airborne pesticides or their by-products as produced or formulated at this facility. The pesticides include: Azodrin®, Bidrin®, Ciodrin®, Pydrin®, Nudrin®, DDVP and Vapona®. The other compounds without analytical methods include diketene, dimethyl amine, trimethyl phosphite, monomethyl chloroacetoacetamide, and di and tri methyl phosphates and phosphonates.

The evaluation of the facility is described in the text of this report and recommendations to help employee health and safety are included.

## II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio, 45226. After 90 days, the report will be available through the National Technical Information Service, (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

- a) Shell Chemical Company, P.O. Box 2171 Denver, Colorado
- b) Authorized Representative of Employees, Oil, Chemical and Atomic Workers (OCAW) Local 2-477 Denver, Colorado
- c) Authorized Representative of Employees, International Brotherhood of Electric Workers (IBEW) Local, Denver, Colorado
- d) Authorized Representative of Employees, International Union of Operating Engineers (IUOE) Local, Denver, Colorado
- e) Authorized Representative of Employees, Laborers International Union (LIU) Local, Denver, Colorado
- f) OCAW International Union, Denver, Colorado
- g) IBEW International Union, Washington, D.C.
- h) IUOE International Union, Washington, D.C.
- i) LIU International Union, Washington, D.C.
- j) U.S. Department of Labor, Region VIII
- k) NIOSH, Region VIII

For the purpose of informing the approximately 180 "affected employees" the employer shall promptly "post" for a period of thirty calendar days, this Determination Report in a prominent place(s) near where exposed employees work.

## III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees regarding employee exposures to several pesticides. The request specifically

requested a medical evaluation of employees who had been associated with the manufacture and handling of dibromochloropropane (DBCP), to ascertain if the employees had experienced any adverse health effects. The request also wanted an evaluation of employee exposures to numerous pesticides manufactured or formulated at the facility which included: Atrazine, Azodrin®, Bidrin®, Bladex®, Ciodrin®, DDVP, N-Monomethyl Chloro Acetoacetamide, Nudrin®, Pydrin®, Vapona®, Shell Nitrogen Solution 8-0-0-1S, and a determination on the mutagenicity/carcinogenicity potential from chronic exposures to the substances.

NIOSH industrial hygienists conducted on-site environmental evaluations on January 26-27, and May 15-23, 1978. The NIOSH medical contractor conducted an on-site evaluation on April 3-5, 1979. Interim results of the evaluations were reported to management and labor on February 8, July 28, and November 15, 1978.

#### IV. HEALTH HAZARD EVALUATION

##### A. Facility Description

The Shell Chemical Company is located at the Rocky Mountain Arsenal in Denver, Colorado. The company leases several buildings, on a 60 acre plot, for pesticide manufacture, formulation and storage. There are about 318 full-time employees at the facility, about 140 of whom are administrative. The facility operates 7 days per week with employees working an 8-10 hour day, forty-hour week with rotating shift schedules.

##### B. Process Description

The various insecticide and herbicide pesticides that are manufactured and/or formulated at the facility are processed in closed reaction systems and drummed under local exhaust ventilation and enclosed engineering control systems. A brief description of each process will be presented below by building number but specifics of the operations are not detailed, due to trade secrets.

###### 1. Building 471

This building has had the most notoriety because dibromochloropropane (DBCP) was previously manufactured here from about 1955-1976. The Shell trade name for DBCP is Nemagon®. The building has had all DBCP equipment removed and it has been chemically and steam cleaned several times to decontaminate the area. There are 3 floor levels to the building with an open central bay.

The units now produce Vapona®, DDVP and formulated Pydrin®. Raw materials are distilled in closed column systems and then reacted in

closed looped reactor systems. The products can then be drummed at central drumming (Building 451), or at a small drumming station within Dept. 471 or can be pumped directly into tank cars. All processes contain local exhaust ventilation. The process sampling ports are also under engineering controls. There are one to two operators for each shift in this building.

## 2. Building 451 - Central Drumming

This building is solely used to drum the various products, label and prepare shipments. The drumming stations are enclosed and locally exhausted. Two lines fill 30 or 55 gallon drums and a third line fills 5-gallon cans. During the NIOSH survey, primarily formulated Azodrin<sup>®</sup> was being drummed. The drummers are contracted from a local labor pool and are not Shell employees per se. The number of contract employees varies daily depending on demand. The employees rotate jobs every fifteen minutes from filling cans, wiping, labeling and stacking.

## 3. Building 422

This building was recently converted to can Pydrin<sup>®</sup> which is formulated in Building 471 and pumped to 422. The process fills 1-gallon cans which are then weighed, solvent wiped, labeled and packed. Pydrin<sup>®</sup> is a new developmental insecticide. Contract employees are used in the canning process. All are under a Shell employee's supervision.

## 4. Buildings 515 West and 532

Solid Atrazine and Bladex<sup>®</sup> (herbicides), are ground and formulated in Building 515 West. The dumping station is enclosed and locally exhausted. The process control room is under positive pressure. Upon completion of the process the formulated product is pumped to Building 532 where it is bottled. The bottles are wiped, labeled and packed for shipment. Contract laborers are used to dump barrels, fill, wipe, label and pack bottles.

## 5. Buildings 525 and 515 East

Nudrin<sup>®</sup>, a carbamate insecticide is produced in Buildings 525 and 515 East. Each building contains three floor levels with the operator's control room/lunchroom on the second floor. The control rooms are air conditioned and under positive pressure.

Building 525 contains closed reactors for reaction steps 1, 2 and the extraction process. The material proceeds outside to a dehydration process and then to Building 515 for reaction step 3 (toxification), recrystallization, centrifugation/drying and drumming. The process is basically a batch operation producing about 25 to 30 drums/batch.

#### 6. Buildings 514/516

Azodrin<sup>®</sup>, Bidrin<sup>®</sup>, and Ciodrin<sup>®</sup> are produced in these buildings, however only one of the pesticides can be produced at one time. Building 516 contains closed reactors for reactions 1 through 3, neutralization, and extraction. The material is then pumped to building 514 for reaction 4 (toxification) and purification. At this point the Technical Azodrin<sup>®</sup> can be drummed into 5-gallon quads in an enclosed exhaust ventilated drumming station or it can be blended with solvent to form formulated Azodrin<sup>®</sup> which is drummed in Building 451. Each building has four floor levels for process equipment. Building 514 contains the operator's lunch area which is air conditioned and under positive pressure.

#### 7. D.E.T.

All wastes from the processes are cycled through the on-site waste treatment facility called Denver Effluent Treatment (D.E.T.). As wastes are received at the facility, the pH is adjusted with caustic and the solids precipitate out in a setting chamber. The solids are then land-filled. The effluent proceeds through an organic column stripper. The organics are neutralized with HCl and burned with natural gas. The non-organic aqueous portion from the stripper is pumped to large oil-fired incinerators containing electrostatic precipitators. The quenched salt from here is cooled, conveyed to rotating drying drums where salt "balls" form which are loaded into dump trucks for land-filling. The entire process is automated and requires only four operators. Each stage of the process contains engineering controls to prevent toxic emission, electrical lockout procedures, safety alarms, and local exhaust ventilation on the drumming station.

All of the buildings described contain eye wash fountains, emergency showers, gas mask cannisters, supplied air respirator hose connections, gas alarms, and fire extinguishers on each floor in several easily accessible strategic locations. Where it is possible, the processes contain solvent recovery systems for recycling of the solvents to the processes. The various tank farms also have emergency equipment and gas alarms. Maintenance at the facility is divided into assigned zones. Most of the support personnel are based from a central maintenance shop which also has showers and lunch areas. The contract laborers have a lunchroom/shower area separate from the Shell employees.

The facility contains its own powerhouse operated by Shell employees. The supply air for respiratory protection is generated here and is monitored and controlled continuously. The operators have a lunch-room and shower area. There is emergency equipment and alarms located throughout the powerhouse.

### C. Chronology of Events

Results of a health hazard evaluation (HE 77-103) of OCAW members exposed to DBCP at one facility indicated that they suffered from an adverse testicular effect resulting in oligospermia or azoospermia. OCAW subsequently requested that NIOSH conduct health hazard evaluations at two Shell Chemical company locations where DBCP had been manufactured. Prior to acting on the requests, however, NIOSH sponsored an informational exchange meeting with labor and management representatives from the various companies that produced or had produced DBCP.

The health hazard evaluation was then initiated at Shell Chemical Company located in Denver, Colorado and was visited by NIOSH scientists on January 26, 1978. Following the first environmental site visit, the NIOSH contract medical investigator visited the plant on April 3, 1978 to review/verify medical and employment data. During this period NIOSH began the development of a DBCP Registry to attempt to compile data on all exposed industrial workers. In that Shell Chemical utilized contract laborers to drum and package DBCP, letters were sent to 127 former contract laborers on May 1, 1978 to offer them medical evaluations.

In the interim NIOSH decided that Shell Chemical medical data was scientifically valid; thus, NIOSH did not repeat the medical tests. The returns from the letters to contract laborers yielded only 24 positive responses, 1 deceased and 102 unknown addresses.

A second environment evaluation was conducted during May 15-23, 1978 to attempt to measure employee exposures to currently produced pesticides. (DBCP had not been produced at the Denver facility since June, 1976, although trace contamination ( $\approx 0.1 \text{ mg/M}^3$ ) had been found by Shell environmental samples taken during the first NIOSH site visit).

After considerable elapse in time, the NIOSH laboratories reported that the environmental samples could not be analyzed for lack of accurate analytical techniques for low concentrations of the multiple pesticides and by-products potentially on the samples. Also, the medical contractor reported that only 3 of the 24 laborers responded to his follow-up for examination and only 1 of those reported for his medical tests; thus, no additional information appeared to be obtainable then that what Shell Chemical already had. The evaluation was subsequently terminated.

During the course of the evaluation DBCP that was stored at the Denver site was shipped elsewhere.

#### D. Environmental Evaluation

An opening conference was held with representatives of management and labor and information was requested regarding employee demography, raw materials used, products manufactured/formulated, DBCP production dates, industrial hygiene, medical, and safety programs, process flowcharts and descriptions, drumming schedules, facility blueprints, technical bulletins and toxicological data for the products manufactured.

Environmental aerometric, bulk and swipe samples were obtained, local exhaust ventilation, temperature and relative humidity measurements made and thirty-four (34) employees were interviewed via non-directive medical questionnaires. During the follow-up environmental evaluation, additional environmental samples were taken, local exhaust ventilation systems and work practices evaluated, photographs of processes obtained, and sixty-eight (68) employees interviewed. A walk-through of the D.E.T. was also performed.

##### 1. Environmental Sampling

###### a. Bulk and Swipe Samples

Bulk samples of the various technical and formulated grades of pesticide manufactured at the facility were obtained in glass scintillation vials with Teflon<sup>®</sup> lined caps. The vials were sealed and DOT labeled for shipment to the NIOSH laboratory. Swipe samples for pesticide contamination were obtained utilizing Whatman\* filter swipes. The samples were obtained from tables in all lunchroom areas, a forklift truck's steering wheel in central drumming, employees' hands after removal of their protective gloves, pesticide containers after being wiped off for shipment, handrails, and process equipment likely to be touched by hands. Some swipes were obtained dry and others were pre-moistened in the same solvent that the particular pesticide was formulated with. All swipe samples were placed in glass scintillation vials and sealed prior to shipment.

###### b. Direct Reading Measurements

Direct reading measurements were obtained throughout the facility with a portable Organic Vapor Analyzer. Direct readings were also obtained for methanol utilizing Draeger\* indicator tubes.

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\* Mention of manufacturer's name does not constitute a NIOSH endorsement.

### c. General Area and Personal Aerometric Samples

General area and personal samples for potential airborne contaminants were obtained utilizing calibrated battery-operated personal sampling pumps operated at airflows of 2.0, 1.5, 1.0, 0.2 and 0.05 liters per minute.<sup>1,2</sup> For personal samples the pumps were hung on belts around the employees' waists and were connected to the sampling media trains via Tygon<sup>®</sup> tubing. General area samples were placed near reactors, drumming apparatus, or operator control panels. The personal sampling media was clipped to the employee's shirt via his breathing zone. Due to the variety of potential airborne contaminants, multiple media sampling trains were utilized and included; fiberglass filters, solid adsorbents containing 150 milligrams of activated charcoal, silica gel, porous aromatic polymer, or florisol, and liquid absorbents in midge impingers containing nitro reagent or ethylene glycol. The various medias were used both singly and in combinations by attaching the media in series with Tygon<sup>®</sup> tubing of the shortest length possible.

Relative humidity and temperature measurements were obtained daily utilizing a battery-operated psychrometer. All drumming stations in operation were photographed and their face velocities evaluated using a hot wire anemometer.

## 2. Environmental Sample Analysis

Due to the multiple contaminants possible on any single media, the samples were divided into groups that could have chromatographically compatible compounds. Solid adsorbents were desorbed in 1 milliliter (ml) of an appropriate solvent (generally carbon disulphide, CS<sub>2</sub>) and analyzed via gas chromatography.<sup>3-6</sup> Filter and liquid absorbent samples were extracted and analyzed chromatographically. Due to the potential presence of multiple pesticides and/or their derivatives, the majority of the samples from the second evaluation were not analyzed for lack of adequate analytical techniques. It became clear that a major developmental effort would be required to analyze the sample and due to several factors it was not possible for NIOSH to undertake the method development at this time.

The samples in the interim despite being kept frozen, began to decompose and thus overtime became invalid due to short shelf-lives.

## E. Medical Evaluation

The medical evaluation was performed under contract and the contractor's report is attached as Appendix A.

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\* Mention of manufacturer's name does not constitute a NIOSH endorsement.



## F. Evaluation Criteria

## 1. Environmental

The following occupational exposure criteria were used in evaluating the environmental contaminants found at the time of the survey:

(1) National Institute for Occupational Safety and Health (NIOSH), Recommended Criteria for Occupational Exposures, (2) American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Substances and Physical Agents in the Workroom Environment and Supporting Documentation, and (3) U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Standards (29 CFR 1910.1000). As the table indicates, there are several substances with no existing occupational exposure criteria or standard.

Substance	(1) NIOSH (mg/M <sup>3</sup> )*	(2) ACGIH (mg/M <sup>3</sup> )*	OSHA (mg/M <sup>3</sup> )*
Acetone	590	1800	2400
Atrazine <sup>1</sup> ***	---	10	---
Azodrin <sup>2</sup> ***	---	0.25	---
Bladex <sup>3</sup>	---	---	---
Bidin <sup>4</sup> ***	---	0.25	---
Chloroform	9.78	50	240***
n-Hexane	---	90	1800
Isopropyl Alcohol***	984	980	980
Methyl Isobutyl Ketone***	200	205	410
Methanol***	262	260	260
Nudrin <sup>5</sup> ***	---	2.5	---
Toluene***	375	375	750
Vapona <sup>6</sup>	---	1.0	1.0

\* Approximate milligrams of substance per cubic meter air, as an 8-hour time-weighted average (TWA) daily exposure

\*\* Ceiling value, for a 15-minute exposure, not be exceeded

\*\*\* Notation indicates that substance is known to be absorbed through intact skin

1. herbicide: 6-Chloro-n-ethyl-N<sup>1</sup>-(1-methylethyl)-1,3,5,-triazine-2,4-diamine
  2. organophosphate insecticide (monocrotopos): (E)-Phosphoric acid dimethyl [1-methyl-3 (methylamino)-3-oxo-1-propenyl] ester
  3. herbicide: 2-((4-chloro-6-(ethylamino)-s-triazan-2-ylamino)-2-methyl) propionitrile
  4. organophosphate insecticide (dicrotophos): (E)-Phosphoric acid 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl ester
  5. carbonate insecticide (methomyl): N-[[ (Methylamino) carbonyl] oxy] ethanimidothioic acid methyl ester
  6. organophosphate insecticide (dichlorvos or DDVP): phosphoric acid 2,2-dichloroethenyl dimethyl ester
- R Shell registered trademark - U.S. Patent Office

These criteria are designed to protect most workers for an eight to ten-hour day, forty-hour week, during a normal working lifetime. However, there are numerous factors that may influence an individual's response to a particular substance, such as age, sex, health status, smoking, and alcohol habits, etc. Also, these criteria are based on single substance exposures; thus, effects from exposures to combinations of substances may be additive or synergistic when the substances elicit similar physiological responses.

#### G. Medical Criteria

Appendix A contains the contract medical report which describes the criteria used in evaluating the DBCP results. Because of the voluminous amount of information on pesticides and the lack of clear elucidated data on chronic human effects from low levels of pesticide exposure, it is recommended that the NIOSH Criteria Document on manufacture and formulation of pesticides be consulted. Listed in the reference section of this report are other sources that can provide some information on this vast, somewhat unknown area. The acute effects of organophosphate poisoning are, however, well documented and these references listed describe the affects in detail.

#### H. Results and Discussion

##### 1. Environmental

The results of the environmental evaluation are contained in Tables I-X. These results should be considered as the minimum concentrations present due to possible competitive binding and differential desorption rates of the multiple compounds potentially present. Also, the samples do not cover as long a time period as the employees work; thus, their exposure time may be greater than indicated.

The environmental results contained in Tables I-V were obtained on the first site visit. At that time, Atrazine was being formulated and bottled, Bidrin drummed and most other operations were in change-over to begin producing/formulating Pydrin<sup>®</sup>, Azodrin<sup>®</sup> and Nudrin<sup>®</sup>. The results reveal that during the survey there were no excessive exposures to identified contaminants although as seen in Table V, trace amounts of pesticides were found. This isn't surprising but does show that continued health and safety surveillance programs are necessary to help maintain a safe working environment, particularly since dermal routes of entry could be the main source of exposure. Strict personal hygiene and good work practices must be continually stressed and enforced.

Tables VI-X contain the data from the follow-up survey. There were a couple of excessive exposures on those dates but most were well below any exposure criteria. The exposures should be kept to a minimum, however, because chloroform, in particular, is a suspected human carcinogen. All local exhaust ventilation controls were found to be within recommended practices criteria.

During the second survey problems arose in the Azodrin® area when lines were not flushed out and Azodrin® solidified in the lines. Upon steaming the lines, a valve had been inadvertently left open and a spill occurred in the "quad" drumming area. The response and clean-up overall appeared adequate but some contract employees in the area were not properly protected in a timely manner.

Shell maintenance personnel who repaired a leaking pump seal in a different area were well protected utilizing impervious clothing, boots, gloves, and full-face supplied air respiratory equipment. In general, the facility appears to have a good health and safety program but continued effort in follow-up in ensuring that written policy and programs are functioning is needed. There were some gas canisters missing in some of the emergency equipment boxes and the contract laborers in some areas didn't seem to adequately know or weren't properly trained in matters relating to their health and safety. Indicator tube samples for methanol being used to wipe off Pydrin® cans ranged from 100-200 in the employee's breathing zone. Upon finding this, Shell personnel changed to a solution containing isopropyl alcohol, thus, there appeared to be a need for better communication between health and safety staff and production personnel as to what is being used at any given time in a particular operation.

## V. CONCLUSION/RECOMMENDATIONS

### A. Conclusion

It was found that some employees who were exposed to DBCP and who were evaluated by Shell did have reduced or no sperm counts due to a toxic effect of the substance on testicular function. Whether or not the effect is reversible is not clearly known at this time, particularly since contract laborers who may have had the highest exposures have not been evaluated to-date at either of the Shell facilities. The one contract employee who was evaluated was found to be "subfertile" ( $24 \times 10^6$  sperm/ml) with only 3-4 months exposure to DBCP. Thus it is substantiated that DBCP is a very toxic agent which affects testicular function and to-date it is unknown if the effects are reversible particularly since all exposures have ceased for at least 3 years.

Additional analytical developments are required before accurate exposure data to various substances and pesticides used at this facility can be evaluated. The chronic effects from low level exposures to these substances are not clearly elucidated in humans at this time and thus warrant strict controls and surveillance. It should be noted, however, that airborne exposures would be expected to be low due to the vapor pressure of the pesticides.

#### B. Recommendations

The following recommendations are made to help ensure employee health and safety.

1. All employees must observe strict personal hygiene and maintain good work practices in order to keep their exposures to a minimum. Drinking, eating and smoking must not be done outside of designated areas and then only after washing of hands. All employees must be properly trained and the training must be routinely re-emphasized. This should be done for all aspects of the routine job requirements, emergencies, and personal hygiene.

2. Management is encouraged to continue development and refinement of its health and safety programs, particularly an employee educational awareness program. This will help in developing better understanding and alleviation of fears and or uncertainty about health and safety matters, especially those about what is the "stuff", what can it do, what isn't known about it, and what is being done to protect "our" health.

3. A strict routine maintenance program should be continuously reviewed and revised as experience is gathered. Employee input is critical because they become more familiar with daily operations than do the engineers that design and upgrade processes.

4. Medical data obtained on employees should be routinely explained to them and hard copy provided. The employees seemed to feel that something wasn't being revealed about their routine blood tests, etc., thus this recommendation can help reduce uncertainty and could be very informative. The release and discussion of medical results could possibly be incorporated into the employee educational awareness program.

5. A toxicological informational manual should be developed for employees as well as customers and the general public similar to what American Cyanamid has published about its organophosphate pesticides. The booklet is listed in the Reference Section of this report. The booklet will help to inform people on Shell pesticide products which will help to reduce fears resulting from uncertainty, etc.

6. If it is desired that the potential pesticide exposures be re-evaluated in the future, NIOSH will need at least 6 months to 1 year advance notice in order to program in the analytical methods development manpower, budget, etc.

#### REFERENCES

1. NIOSH Manual of Sampling Data Sheets, DHEW (NIOSH) Publication No. 77-159, Cincinnati, Ohio.
2. Air Sampling Instruments for Evaluation of Atmospheric Contaminants, American Conference of Governmental Industrial Hygienists, Fifth Edition, Cincinnati, Ohio 1978.
3. NIOSH Manual of Analytical Methods, Vol. 1, Second Edition, DHEW (NIOSH) Publication No. 77-157A, Cincinnati, Ohio 1977.
4. NIOSH Manual of Analytical Methods, Volume 2, Second Edition, DHEW (NIOSH) Publication No. 77-157B, Cincinnati, Ohio 1977.
5. NIOSH Manual of Analytical Methods, Vol. 3, Second Edition, DHEW (NIOSH) Publication No. 77-157C, Cincinnati, Ohio 1977.
6. NIOSH Manual of Analytical Methods, Vol. 4, Second Edition, DHEW (NIOSH) Publication No. 78-175, Cincinnati, Ohio 1978.
7. Whorton, David and Thomas H. Milby. Health Hazard Evaluation Determination Report No. 77-103-474, DHEW, CDC, NIOSH, Cincinnati, Ohio 1978.
8. Dibromochloropropane (DBCP): Final Position Document, Special Pesticide Review Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, D.C. 1978.
9. Glass, Roger and R., Lyness, et.al., Sperm Count Depression in Pesticide Applicators Exposed to Dibromochloropropane, DHEW (NIOSH) Publication, Cincinnati, Ohio 1977.
10. NIOSH, A Recommended Standard for Occupational Exposure to Dibromochloropropane, DHEW (NIOSH) Publication, Cincinnati, Ohio 1977.
11. NIOSH Criteria for a Recommended Standard ... Occupational Exposure During the Manufacture and Formulation of Pesticides, DHEW (NIOSH) Publication No. 79-174, Cincinnati, Ohio 1978.

12. Toxicological Information Cyanamid Organophosphate Pesticides, Third Edition, American Cyanamid Company, Princeton, New Jersey 1977.
13. The Merck Index, Ninth Edition, Merck and Co., Inc., Rahway, New Jersey 1976.
14. Occupational Diseases - A Guide to Their Recognition, DHEW (NIOSH) Publication No. 77-181, Cincinnati, Ohio 1977.
15. NIOSH Criteria for a Recommended Standard ... Occupational Exposures to Ketones, DHEW (NIOSH) Publication No. 78-114, Cincinnati Ohio 1978.
16. NIOSH Criteria for a Recommended Standard ... Occupational Exposures to Chloroform, DHEW (NIOSH) Publication No. 75-114, Cincinnati Ohio 1975.
17. NIOSH Criteria for a Recommended Standard ... Occupational Exposures to Isopropyl Alcohol, DHEW (NIOSH) Publication No. 76-142, Cincinnati, Ohio 1976.
18. NIOSH Criteria for a Recommended Standard ... Occupational Exposures to Methyl Alcohol, DHEW (NIOSH) Publication No. 76-148, Cincinnati, Ohio 1976.
19. NIOSH Criteria for a Recommended Standard ... Occupational Exposures to Toluene, DHEW (NIOSH) Publication No. HSM73-11023, Cincinnati, Ohio 1973.
20. Industrial Ventilation ... A Manual of Recommended Practice, Fifteenth Edition, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio 1978.

ACKNOWLEDGEMENTS

Report Prepared By:

Gary L. White, M.S.  
Project Officer  
Industrial Hygiene Section  
Hazard Evaluations and  
Technical Assistance Branch  
Cincinnati, Ohio

Donald Whorton, M.D.  
Contract Medical Officer  
Environmental Health Associate  
Berkeley, California

Originating Office:

Jerome P. Flesch  
Acting Chief  
Hazard Evaluations and  
Technical Assistance Branch  
Cincinnati, Ohio

Environmental Evaluation:

Bobby J. Gunter, Ph.D.  
Industrial Hygienist  
NIOSH, Region VIII  
Denver, Colorado

Clifford Moseley, M.S.  
Dawn Tharr, M.S.  
Industrial Hygienists  
Industrial Hygiene Section  
Hazard Evaluations and  
Technical Assistance Branch

Medical Evaluation:

Thomas Milby, M.D.  
Donald Lassiter, Ph.D.  
Environmental Health Associates  
Berkeley, California

Technical Information Assistance:

Robert Delmage  
Technical Information Specialist  
Information Retrieval and Analysis Section  
Cincinnati, Ohio

U.S. Environmental Protection Agency  
Special Pesticide Review Division  
Office of Toxic Substances  
Washington, D.C.

Environmental Sample Analysis:

G S. Bajwa  
Katherine Dennett  
John Reynolds  
Jim Snarr  
Karen Stephensen  
Chemists  
Measurement Support Branch  
Cincinnati, Ohio

Report Typed By:

Sandra L. Kerdolff  
Clerk-Typist  
Industrial Hygiene Section  
Hazard Evaluations and  
Technical Assistance Branch  
Cincinnati, Ohio



Table I  
Results of Air Sampling for Organic Vapors  
Shell Chemical Company  
Denver, Colorado  
January 26-27, 1978  
HE 77-126

Environmental Conditions: Temperature 28-34<sup>0</sup>F, R.H. - 60%, B.P. 624 mmHg, 1630 Hour

<u>Sample Number</u>	<u>Time</u>	<u>Description</u>	<u>Results (mg/M<sup>3</sup>)*</u> <u>Chloroform</u>
CT-1	1540-2202	Personal Sample (P.S.) Operator Bldg. 516	1.3
CT-2	1534-2202	P.S. Operator Bldg. 514	1.1
CT-3	1530-2135	P.S. Utilityman Bldg. 514	0.9
CT-4	1422-2156	General Area (G.A.) Bldg. 516 2nd Floor Desk	2.5
CT-5	1459-2155	G.A. Bldg. 471 2nd Floor	0.5
CT-6	1436-2204	G.A. Bldg. 514 4th "	1.3
CT-7	1527-2201	P.S. Chlorination Operator Bldg. 514 2nd Floor (Unit down)	1.3
CT-8	1507-2154	P.S. Operator Bldg. 471	0.4
CT-9	2133-2251	P.S. Atrazine barrel dumper Bldg. 515E	0.5
CT-20	0843-1430	P.S. Instrument man Bldg. 516	1.5
CT-21	0831-1226	P.S. Pipefitter Zone 1	0.7 <sup>1</sup>
CT-22	0836-1427	P.S. Electrician	1.9 <sup>1</sup>
CT-23	0809-1053	P.S. Drummer Bldg. 451 55 gal. line	N.D. <sup>2</sup>
CT-26	0750-1120	P.S. Bottle Filler Bldg. 532	0.8
CT-126	0750-1120	" "	1.2
CT-27	0722-1322	P.S. Tank Farm Outside Utilityman Bldg. 514 area	1.0 <sup>2</sup>
CT-28	0755-1334	P.S. Bottle Wiper Bldg. 532	N.D. <sup>2</sup>

\* Approximate milligrams of substance per cubic meter air

1. Minimum amount present due to possible break through

2. Not Detected - The limit of detection for these samples was 0.01 mg/tube

The NIOSH Recommended Standard for Occupational Exposure to Chloroform is 9.78 mg/M<sup>3</sup> air for an 8 or 10 hour Time Weighted Average (TWA) daily exposure.

Table II

## Results of Air Sampling for Particulate Herbicides

Shell Chemical Company  
Denver, Colorado

January 26-27, 1978

HE 77-126

Environmental Conditions: Temperature 28-34°F, R.H. - 60%, B.P. 624 mmHg, 1630 Hour

<u>Sample Number</u>	<u>Time</u>	<u>Description</u>	<u>Results (mg/M<sup>3</sup>)*</u>	
			<u>Atrazine</u>	<u>Bladex</u>
FG-1	2133-2251	Personal Sample (P.S.) Atrazine Barrel Dumping Building 515	0.24	0.01
FG-2	0745-1200	P.S. Atrazine Barrel Dumping (Started dumping at 1045 and ended approximately 1130) Building 515	0.1	0.02

\* Approximate milligrams of substance per cubic meter of air

Table III  
Results of Air Sampling for Organic Pesticides

Shell Chemical Company  
Denver, Colorado

January 26-27, 1978

HE 77-126

Environmental Conditions: Temperature 28-34°F, R.H. - 60%, B.P. 624 mm Hg, 1630 Hour

Sample Number	Time	Description	Results (mg/M <sup>3</sup> )*					
			Azodrin	Bidrin	Ciodrin	Nudrin	Atrazine	Bladex
F-1	1433-2204	General Area (GA) Bldg 514, 4th floor	N.D. <sup>1</sup>	0.06	N.D. <sup>3</sup>	0.01	N.D. <sup>5</sup>	0.001
F-20	0807-1053	Personal Sample (PS) Drum Filler Bldg 451 55 gallon line	N.D.	N.D. <sup>2</sup>	N.D.	N.D. <sup>4</sup>	N.D.	N.D. <sup>6</sup>
F-21	0755-1333	PS Atrazine Bottle Wiper Bldg 532	N.D.	N.D.	N.D.	N.D.	0.001	.003
F-22	0750-1330	PS Atrazine Bottle Filler Bldg 532	N.D.	N.D.	N.D.	0.001	0.007	.002
F-25	0745-1200	PS Atrazine Barrel Dumping Bldg 515	N.D.	N.D.	N.D.	0.0002	N.D.	0.001

\*Approximate milligrams of substance per cubic meter of air.

1. Not Detected: The limit of detection for these samples was 0.5 ug/tube; the recovery efficiency was 9.7%.
2. Not Detected: The limit of detection for these samples was 0.3 ug/tube; the recovery efficiency was 2.1%.
3. Not Detected: The limit of detection for these samples was 0.08 ug/tube; the recovery efficiency was 30%.
4. Not Detected: The limit of detection for these samples was 0.05 ug/tube; the recovery efficiency was 81%.
5. Not Detected: The limit of detection for these samples was 0.06 ug/tube; the recovery efficiency was 93%.
6. Not Detected: The limit of detection for these samples was 0.07 ug/tube; the recovery efficiency was 94%.

Table IV

## Results of Air Sampling for Organic Pesticides

Shell Chemical Company  
Denver, Colorado

January 26-27, 1978

HE 77-126

Environmental Conditions: Temperature 28-34°F, R.H. - 60%, B.P. 624 mm Hg, 1630 Hour

Sample Number	Time	Description	Results (mg/M <sup>3</sup> )*						
			Azodrin	Bidrin	Ciodrin	Vapona	Nudrin	Atrazine	Bladex
Imp 1	1422-2156	General Area (GA) Bldg 516 2nd Floor	N.D. <sup>1</sup>	0.0001	N.D. <sup>3</sup>	N.D. <sup>4</sup>	0.006	N.D. <sup>6</sup>	0.013
Imp 2	1428-2207	GA Bldg 514 2nd Floor (S.E.)	N.D.	0.0001	N.D.	0.0004	0.014	N.D.	0.001
Imp 3	1429-2210	GA Bldg 514 2nd Floor (N.E.)	0.0004	0.0005	N.D.	0.0005	0.001	0.001	0.001
Imp 4	1440-2216	GA Bldg 514 3rd Floor	0.0004	0.0033	N.D.	N.D.	0.029	N.D.	0.068
Imp 5	1458-2155	GA Bldg 471 2nd Floor	N.D.	N.D. <sup>2</sup>	N.D.	0.039	N.D. <sup>5</sup>	N.D.	N.D. <sup>7</sup>
Imp 6	0855-1422	GA Warehouse 347 Bay #24	N.D.	0.00005	N.D.	0.0007	N.D.	N.D.	N.D.
Imp 21	0735-1305	GA Atrazine Barrel Dumping Bldg 515	N.D.	N.D.	N.D.	0.003	0.002	1.6	0.059
Imp 22	0748-1334	GA Atrazine Bottle Filling Bldg 532	N.D.	N.D.	N.D.	0.0005	N.D.	0.26	0.053
Imp 23	0805-1350	GA Bldg 451, 55 Gallon line	N.D.	.0021	N.D.	0.03	N.D.	0.003	0.021

\*Approximate milligrams of substance per cubic meter air

1. Not Detected: The limit of detection for these samples was 0.04 ug/sample; the extraction efficiency was 13%.
2. Not Detected: The limit of detection for these samples was 10 ng/sample; the extraction efficiency was 46%.
3. Not Detected: The limit of detection for these samples was 9 ng/sample; the extraction efficiency was 53%.
4. Not Detected: The limit of detection for these samples was 0.2 ug/sample; the extraction efficiency was 11%.
5. Not Detected: The limit of detection for these samples was 0.44 ug/sample.
6. Not Detected: The limit of detection for these samples was 0.56 ug/sample.
7. Not Detected: The limit of detection for these samples was 0.45 ug/sample.

Environmental Conditions: Temperature 28-34<sup>0</sup>F, R.H. - 60%, B.P. 624 mm Hg, 1630 Hours

Results (ng/filter)\*

Sample Number	Description	Azodrin	Bidrin	Ciodrin	Vapona	Nudrin	Atrazine	Bladex	Trimethyl Phosphite
Swipe 1	Lunchroom Table S471	-	-	N.D. <sup>3</sup>	N.D. <sup>4</sup>	-	-	-	N.D. <sup>8</sup>
Swipe 2	Lunchroom Table Bldg 471	-	-	N.D.	N.D.	-	-	-	N.D.
Swipe 3	Table Bldg 451	N.D. <sup>1</sup>	69	N.D.	N.D.	-	-	-	N.D.
Swipe 4	Zone #1 Maintenance lunchroom Table	75	N.D.	N.D.	N.D.	-	-	-	N.D.
Swipe 5	Lunchroom Table Bldg 514	-	28	N.D.	N.D.	-	-	-	N.D.
Swipe 6	Lunchroom Table Bldg 516	76	11	N.D.	N.D.	-	-	-	N.D.
Swipe 7	Contractor Lunchroom Table Bldg 511	N.D.	8	N.D.	N.D.	700	21800	6370	N.D.
Swipe 8	Lunchroom Table 515 W Annex	N.D.	N.D.	-	-	N.D. <sup>5</sup>	31900	4290	-
Swipe 9	Main Lunchroom Table Bldg 515	N.D.	N.D.	-	-	N.D.	N.D. <sup>6</sup>	N.D. <sup>7</sup>	-
Swipe 10	Lunchroom Table Maintenance Shop Bldg 534	N.D.	N.D.	N.D.	N.D.	-	-	-	N.D.
Swipe 11	Lunchroom Laboratory	N.D.	30	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Swipe 12	Bldg 451 Central Drumming Fork Lift Steering Wheel	384	445	N.D.	N.D.	-	-	-	N.D.

\*Approximate nanograms of substance per swipe filter.

1. Not Detected: The limit of detection for these samples was 51 ng/sample; the recovery efficiency was 114%.
2. Not Detected: The limit of detection for these samples was 7 ng/sample; the recovery efficiency was 108%.
3. Not Detected: The limit of detection for these samples was 2.2 ng/sample; the recovery efficiency was 103%.
4. Not Detected: The limit of detection for these samples was 0.11 ng/sample; the recovery efficiency was 78%.
5. Not Detected: The limit of detection for these samples was 0.22 ug/sample; the recovery efficiency was 100%.
6. Not Detected: The limit of detection for these samples was 0.5 ug/sample; the recovery efficiency was 100%.
7. Not Detected: The limit of detection for these samples was 0.39 ug/sample; the recovery efficiency was 98%.
8. Not Detected: The limit of detection for these samples was 0.5 ng/sample; the recovery efficiency was 78%.

Table VI

## Results of Sampling for Airborne Organic Vapors

Shell Chemical Company  
Denver, Colorado

May 16, 1978

HE 77-126

Environmental Conditions: Temperature 75°F, R.H. - 40%, B.P. 639 mm Hg

Type Sample	Time	Description	Building No.	Results (Mg/M <sup>3</sup> )*		
				DBCP <sup>1</sup>	Chloroform	Xylene
Charcoal	0726-1133 <sup>2</sup>	Personal Sample (P.S.) Reduction	514	--	1.0	--
"	1134-1403 <sup>2</sup>	Neutralization Operator			2.5	--
Charcoal	0728-1136 <sup>2</sup>	P.S. Toxification-Solvent Removal	514	--	2.7	--
"	1138-1445	Operator			N.D**	--
Charcoal	0725-1145	P.S. Inside Utility Operator	514	--	0.71	--
"	1146-1455	"	"	--	74	--
Charcoal	0805-1129	P.S. Operator #1	516	--	10	--
"	1130-1435	"	"	--	42	--
Charcoal	0910-1403	P.S. General Utility Operator -	514/516	--	0.78	--
		Tank Farm				
Charcoal	0859-1443	P.S. Outside Utility Operator -	514/516	--	0.53	--
		Tank Farm				
Charcoal	0749-1128	General Area (G.A.) Diketene Reactor	516	--	32	--
"	1128-1433	2nd Floor			17	--
Charcoal	1046-1348	P.S. Pydrin can cleaner	422	--	--	N.D**
Charcoal	1039-1425	G.A. 2nd floor	471	N.D**	--	--

\* Approximate milligrams of substance per cubic meter air

\*\* Not Detected

1. Dibromochloropropane

2. Minimum amount present due to possible breakthrough of backup section of tube

Table VII  
Results of Sampling for Airborne Organic Vapors

Shell Chemical Company  
Denver, Colorado

May 17, 1978

HE 77-126

Environmental Conditions: Temperature 48-68°F, R.H. = 45-100%, B.P. 617 mm Hg, windy, rain 1435 Hr

Type Sample	Time	Description	Building No.	Results (mg/M <sup>3</sup> )*				
				Ac <sup>1</sup>	DBCP <sup>2</sup>	Chloroform	IPA <sup>3</sup>	Toluene
Charcoal	0908-1314	Personal Sample(P.S.) Operator #1 DDVP side	471	--	N.D.**	--	--	--
Charcoal	0910-1314	P.S. Operator #1 Pydrin side	471	--	N.D.	--	--	--
Charcoal	1016-1313	P.S. Maintenance Zone #2 3rd floor	471	--	N.D.	--	--	--
Charcoal	1143-1536 <sup>4</sup>	P.S. Pydrin can cleaner	422	--	--	--	6.4	N.D. <sup>5</sup>
Charcoal	1150-1535	P.S. Pydrin can cleaner - 1940 cans (1 gal.)	422	--	--	--	N.D.	716 <sup>5</sup>
Charcoal	1152-1534	P.S. Pydrin can capper	422	--	--	--	4.2	N.D.
Charcoal	0852-1142	P.S. Formulated Azodrin Drummer (5 gal.cans)	451	N.D.	--	--	--	--
Charcoal	1143-1432	"	"	8.8	--	--	--	--
Charcoal	0857-1159	P.S. Formulated Azodrin Cap, stack cans	451	N.D.	--	--	--	--
"	1200-1431	" " wipe cans "	451	5.0	--	--	--	--
Charcoal	0736-0935	P.S. Outside Utility Operator	514/516	--	--	0.38	--	--
Charcoal	0740-1210	P.S. Pipefitter Zone 1	514/516	--	--	0.67	--	--
Charcoal	1007-1359	P.S. Electrician all over	471,515,525,Det	--	--	N.D.	--	--
Charcoal	0837-1214 <sup>4</sup>	P.S. Technical Azodrin Drummer (5 gal.quads)	514	--	--	0.91	--	--
"	1216-1430	"	"	--	--	N.D.	--	--
Charcoal	0839-1250	P.S. Technical Azodrin Drummer (rotates)	514	--	--	0.34	--	--
"	1250-1430	"	"	--	--	0.91	--	--
Charcoal	0841-1300	P.S. Technical Azodrin Drum stacker	514	--	--	N.D.	--	--
"	1301-1431	"	"	--	--	N/D.	--	--
Charcoal	0840-1220	P.S. Technical Azodrin Drummer	514	--	--	8.3	--	--
"	1221-1437	"	"	--	--	1.3	--	--

\* Approximate milligrams of substance per cubic meter air

\*\* Not Detected

1. Acetone

2. Dibromochloropropane - Considerable amounts of some lower boiling unknowns eluted

3. Isopropyl alcohol

4. Pump failed

5. Minimum concentration due to possible breakthrough on backup section of tube

Table VIII  
Results of Sampling for Airborne Organic Vapors

Shell Chemical Company  
Denver, Colorado

May 18, 1978

HE 77-126

Environmental Conditions: Temperature 48-67°F R.H. - 25%, B.P. 624 mm Hg, 1315 HR

Type Sample	Time	Description	Building No.	Results (mg/M <sup>3</sup> )*				
				Chl <sup>1</sup>	Hex. <sup>2</sup>	IPA <sup>3</sup>	MIBK <sup>4</sup>	Tol <sup>5</sup>
Charcoal	0808-1253	Personal Sample (P.S.) Pydrin can cleaner	422	--	--	7.9	--	282 <sup>6</sup>
Charcoal	0740-1441	P.S. Centrifuge Operator	515	--	N.D.**	--	N.D.	--
Charcoal	0744-1440	P.S. Crystallization and Recovery Operator	515	--	N.D.	--	N.D.	--
Charcoal	1031-1440	P.S. Stripper - Reactor Operator	515	--	N.D.	--	N.D.	--
Charcoal	0841-1416	General Area (G.A.)-Replacing MMCAA pump agitator	514/516	0.54	--	--	--	--
Charcoal	0850-1417	G.A. Indoor Storage Tanks	514/516	0.14	--	--	--	--
Charcoal	0754-1431	P.S. Column Operator	525	--	--	--	6.4	--
Charcoal	0754-1430	P.S. Outside Utility Operator	525	--	--	--	N.D.	--
Charcoal	0755-1434	P.S. Reactor Operator	525	--	--	--	N.D.	--

\*Approximate milligrams of substance per cubic meter of air

\*\*Not Detected

1. Chloroform
2. Hexane
3. Isopropyl Alcohol
4. Methyl Isobutyl ketone
5. Toluene
6. Minimum concentration due to possible breakthrough on backup section of tube
7. Pump failed and was replaced



Table IX

## Results of Sampling for Airborne Organic Vapors

Shell Chemical Company  
Denver, Colorado

May 19, 1978

HE 77-126

Environmental Conditions: Temperature 70°F, R.H. - 42-45%, B.P. 632 mm Hg, 1000 HR

Type Sample	Time	Description	Building No.	Results (mg/M <sup>3</sup> )*			
				Ac <sup>1</sup>	Chl <sup>2</sup>	Hex <sup>3</sup>	MIBK <sup>4</sup>
Charcoal 1233-1534		Personal Sample (P.S.) Azodrin-5 Drummer	451	N.D.**	--	--	--
Charcoal 1235-1537		P.S. Azo-5 Drummer	451	N.D.	--	--	--
Charcoal 1237-1535		P.S. Azo-5 Drummer (rotates wipetops)	451	8.2	--	--	--
Charcoal 0814-1445 <sup>5</sup>		P.S. Technical Azodrim Drummer	514	--	N.D.	--	--
Charcoal 0753-1430		General Area (G.A.) 3rd floor centrifuge	515	--	--	1.9	0.8
Charcoal 0750-1428		P.S. Outside Utility	515	--	--	3.1	3.1
Charcoal 0754-1428		P.S. Centrifuge Operator	515	--	--	0.77	N.D.
Charcoal 0722-1422		P.S. G.A. Nudrin Reactor 2nd floor	525	--	--	--	0.43
Charcoal 0735-1420 <sup>6</sup>		P.S. Outside Utility Operator	525	--	--	--	1.1
Charcoal 0740-1421		P.S. Reactor Operator	525	--	--	--	N.D.

\*Approximate milligrams of substance per cubic meter of air

\*\*Not Detected

1. Acetone
2. Chloroform
3. Hexane
4. Methyl Isobutyl Ketone
5. Pump failed
6. Pump failed and was replaced

Table X

## Results of Sampling for Airborne Organic Vapors

Shell Chemical Company  
Denver, Colorado

May 22, 1978

HE 77-126

Environmental Conditions: Temperature 72°F, R.H. - 25%, B.P. 620 mm Hg

Type Sample	Time	Description	Building No.	Results (mg/M <sup>3</sup> )*				
				DBCP <sup>1</sup>	Chl <sup>2</sup>	Hex <sup>3</sup>	MIBK <sup>4</sup>	Xyl. <sup>5</sup>
Charcoal	0826-1237	General Area (G.A.) Bay - 1 West side	335	N.D.**	--	--	--	--
Charcoal	0951-1528	Personal Sample (P.S.) Instrument man	Det/422	--	--	--	--	N.D.
Charcoal	0712-1316	P.S. MMCAA Drummer	514	--	2.0	--	--	--
Charcoal	0800-1542	P.S. Instrument man	515/525	--	--	--	N.D.	--
Charcoal	0803-1541	P.S. Instrument man	514	--	3.9 <sup>6</sup>	--	--	--
Charcoal	1350-1508	P.S. Nudrin Drummer - 26 drums @ 175 lbs	515	--	--	N.D.	N.D.	--

May 23, 1978

Environmental Conditions: Temperature 70°F, R.H. - 35%, B.P. 626 mm Hg, 0940 HR

Charcoal	0724-1145	P.S. Outside Utility Operator	515	--	--	0.18	2.7	--
Charcoal	0727-1146	P.S. Shift Foreman	515	--	--	N.D.	N.D.	--
Charcoal	0735-1135	P.S. Inside Utility Operator	525	--	--	--	26	--

\*Approximate milligrams per cubic meter of air

\*\*Not Detected

1. Dibromochloropropane
2. Chloroform
3. Hexane
4. Methyl Isobutyl Ketone
5. Xylene
6. Minimum concentration due to possible breakthrough on backup section of tube

I. Background

The Shell Chemical Company facility located in the Rocky Mountain Arsenal near Denver, Colorado, previously had been a manufacturer of dibromochloropropane (DBCP). In the summer of 1977 during the concern over the health effects of DBCP, Shell initiated medical evaluations for some of the personnel. During the initial stage of this evaluation there were such serious problems with the laboratory examinations that the initial semen analyses were invalid. During the Fall Shell contracted with Dr. Larry Lipshulz, University of Texas and Baylor at Houston, to provide urological evaluations of the men. The problems with the laboratory examinations appeared resolved with the new team. Also, the Union, the Oil, Chemical, Atomic Workers Local 4-277, requested a Health Hazard Evaluation from NIOSH for an independent evaluation of the problem.

Shell produced DBCP (nemagon) at the Denver facility from 1956 to 1976, when it discontinued DBCP production. Shell has produced a variety of other pesticides and chemicals at this facility. The chemicals produced are included in Appendix B (as provided by Shell).

Shell curtailed all production of DBCP by June of 1976 and moved production to the Shell facility in Mobile, Alabama.

## II. Task Order One

### A. Investigation

We had copies of the summary data for the medical evaluations for both the exposed and control populations at the Shell Denver plant. This summary included case number, sperm density for the first, second, and third test, plus the mean sperm density, percent motility for each test plus the mean, and the results of FSH, LH, and testosterone done by the Reproductive Research Laboratory, Baylor College of Medicine. After a careful review of these data we decided that the most expeditious manner to evaluate further the biological data was to obtain more detailed summaries of these data. In early March we requested that Shell have the previously examined employees sign medical releases so that the summary data could be sent to us for evaluation. The summary data were sent to us promptly. For the individuals who did not sign the release form, their data were blanked out.

After an analysis of these more complete medical data, we decided that we had to verify the exposure data and the medical records. On April 4, 1978 we (Drs. Thomas Milby, Donald Lassiter, and Donald Whorton) traveled to Denver to obtain the necessary data. We had an opening meeting with the following: Arnold C. Dreier, Manager Safety, Wanda E. Himes, Nurse, J.B. Plummer, Manager Operations, J.H. Krauss, Plant Manager, and Charles P. Burnett, Manager Employee Relations, from Shell; Tom Neel, Pipe-fitter, from OCAW; Ray Osborn, Electrician, from IBEW; and

D.E. McCord, from I.U.O.E.

At the meeting we stated our purpose and needs. We wanted: 1) a plant tour of the area where DBCP had been produced, drummed, and stored; 2) an explanation of how the people were selected for the DBCP study; 3) an explanation of how the controls were obtained; 4) an explanation of the contract laborers; 5) a description of how exposure times were determined; 6) a review of a random selection of medical records (selected by us) for validation; 7) a brief exposure history from all the nonvasectomized men who participated in the study; 8) collection of environmental sampling data; and 9) a discussion or evaluation of other potentials for exposure.

Accompanied by both management and union personnel, we toured Building 471 where DBCP had been previously produced. We were shown the various processes of DBCP production. We observed that most of the DBCP manufacturing equipment and machinery had been removed. We also toured the drumming area and were taken to an area of current storage of previously canned DBCP.

Drs. Milby and Whorton took a twenty percent random sample of the medical records (again selected by us) to verify that our summary information was the same as that contained in the medical records. This was done in a private office without any Shell employees present.

Dr. Lassiter was shown how the personnel records were kept and how exposure hours were estimated. There were

detailed records on hours of work with specific compounds for cost accounting purposes. These dated back to the 1950's.

On April 5, 1978 Drs. Milby and Whorton interviewed 77 men to obtain information about their work exposure. Each of the men was asked to sign a new release form specifically for the DBCP study related medical records. The interviewed men included both exposed and controls. We also answered many questions and concerns raised by some of the men.

Dr. Lassiter reviewed the personnel records for exposure times. At that time he was given a list of 11 salaried employees who had revised their previous DBCP exposure estimate. He was told that there were not specific recorded hours for salaried employees; thus, the estimate was by memory. This was contrasted to hourly employees where hours per compound were known and kept for cost accounting purposes. Dr. Lassiter was also given copies of sampling data.

#### B. Discussion

On returning to California, employee medical history data and company work history data were compared to the previous summary data provided by Shell. There appeared to be large discrepancies in the exposure data with some workers reported with only ten percent of their total exposure hours, and others with twenty, fifty, sixty, seventy, etc. percent of total exposure hours reported. A telephone call from Wanda Himes, the plant nurse, to Dr. Lassiter, informed him

that a discrepancy had been discovered by Shell concerning the total exposure hours for exposed employees as compared with the hours reported on the summary data sheet originally supplied to EHA by Shell. A telephone call to Mr. Arnold Dreier, Safety Supervisor, confirmed our speculations that exposures had been weighted for various job categories according to some scheme. Although the scheme was not supplied to us at the time of our visit to the Denver facility, Mr. Dreier said during the telephone conversation that the weighting factors for given job categories ranged from ten percent to 100 percent of the total exposure hours. The rationale for weighting exposure hours was not clear and Mr. Dreier stated that he believed that total exposure hours would be more appropriate when considering the exposure of a given individual. In addition, employee work histories obtained as a part of the medical interview revealed, in some cases, a much greater exposure history than was documented on company work history data records.

In addition, of the 24 men considered controls, eight gave histories of definite DBCP exposure, and thirteen gave no history of exposure.

The random review of the medical records showed a good correlation between the summarized data and the data contained within the medical records. Both of us (Drs. Whorton and Milby) believe the summaries to be accurate.

When we requested from Shell a listing of all plant employees including identification of those with known DBCP exposure, we received a computer printout with approximately 320 names which constituted the entire plant workforce. In addition, a list of names of 89 individuals exposed to DBCP but never examined was included, together with information for each about job classification and exposure hours. These 89 were subdivided into two groups: (1) 65 who had signed a medical release form, and (2) 24 who had not signed a release form.

The then current population at the plant can be defined as the following:

"Exposed"

172	83 examined by Shell
	89 not examined by Shell

"Controls"

37

<u>209</u>	Total "Exposed" and "Controls"
<u>111</u>	No Information
320	Total Plant Population

Thus, in the "exposed" group of men identified by Shell, 83 of 172 (48.3 percent) had been examined. Of the exposed-not examined group, 50 of 89 (56.2 percent) are operators, some with many hundreds of exposure hours. Based on these data, it appears that less than half of the truly exposed population has been evaluated.



One of the problems in interpreting the biological implications of the exposure data is the broad spectrum of time over which the population had been exposed. Also, there is the variable of time-since-last-exposure. In our analyses of the data for both the operators and the maintenance craftsmen, we standardized annual exposure hours by dividing total hours exposed by number of years exposed and compared this to years since last exposure. Table I shows this comparison. (In each matrix cell the numbers are sperm counts.) We believe that this shows an informative pattern. However, one of the problems is the fact that there are no individuals with heavy average annual exposure spanning more than four years since last exposure. In fact, there are few individuals with much exposure at all more than five years prior to 1977.

Another variable that needs to be examined is the number of hours spent in Building 471. Since trace amounts of DBCP are still found within the building, one must assume that there were substantially higher levels during the period that DBCP was produced. Analyzing the data with this variable added could prove to be instructive.

In our May 9, 1978, addendum to our interim report of April 14, 1978, we concluded that if NIOSH wished to know the extent of DBCP-related health effects, then: (1) the 89 exposed but not examined must be offered an examination; (2) the work histories of the 111 with no information must be evaluated and some of the men offered examinations if

appropriate; (3) all work history records must be reviewed to determine exposure hours; (4) all workers who participated in the study but have not yet been interviewed should be interviewed; and, (5) differences between work histories obtained from individuals and those contained within company records should be reconciled. As required by our contract, we informed NIOSH that all of this entailed a much larger study than called for in our Task Order One agreement.

### III. Task Order Two Activities

In April 1978, Gary White, NIOSH Industrial Hygienist for this HHE, sent questionnaires to 127 DBCP contract workers who worked for Nankin. He received 24 replies (18.9 percent) from men who expressed interest in being examined. On November 20, 1978, we were asked to submit a protocol for the examination of these 24 men which we did on November 27, 1978. After several protocol modifications by NIOSH, a contract was signed effective 15 March, 1979.

We made arrangements with Eugene Heller, M.D., a Board-certified Denver urologist to complete the following work-up on each of the 24 present or former Nankin employees:

- (a) review and clarify the self-administered medical and work history;
- (b) conduct a urological examination;
- (c) conduct a semen analysis (and then have the remaining semen frozen);

- (d) obtain blood for an FSH test (serum to be frozen for shipment to California); and
- (e) send us copies of results or responses from (a), (b), and (c).

One of us (DW) personally visited Dr. Heller in Denver to make final arrangements.

The list of the 24 men who expressed a desire for the examination was obtained from Mr. White. Each man was sent a letter of explanation, a consent form, plus a medical and occupational history form (see Appendix C). Three letters were returned as "Not deliverable, unable to forward." Only three of the remaining 21 called Dr. Heller's office for an appointment; only one man showed up and was examined (0.8 percent of the original 127). Based on the lack of response and the original small numbers (24 of 127), we contacted our project officer, Dr. Xinteras and recommended that the study be terminated. This recommendation was accepted.

#### IV. Conclusion

The evaluation of the Shell Denver data showed a definite adverse effect on testicular function of the exposed population with 7.8 percent azoospermic and 14.1 percent oligospermic ( $< 20 \times 10^6$  sperm cells/ml semen). Approximately half of the exposed population was examined, the other half declined. In our opinion, there is no valid reason to repeat the examination on those previously examined.

The near total lack of response from the current and former Nankin contract workers precluded any evaluation of their health status. Clearly, they had no desire to participate in a NIOSH examination.

TABLE I

## SPERM COUNT

BY MEAN HOURS PER YEAR EXPOSURE BY YEARS SINCE EXPOSURE

HOURS/YEAR OF EXPOSURE	200+	106, 18, 0, 0. (11)	0, 0, 0.06, 56		65 (11)			
	150-199		51	174				
	100-149		95					
	80-99							
	60-79	28, 21, 143, 96						214
	40-59	166, 118	134, 34	41		30		
	20-39		190	238	60		82	72, 117
	0-19	26, 251	37, 87 53	10, 19 84, 65			125	
		1	2	3	4	5-6	7-9	≥ 9

YEARS SINCE EXPOSURE

SOURCE: Shell Denver, 1977-78

BUILDING USAGE  
1952-1977

BUILDING		YEAR
422 (South)	Aldrin	1952-1955
424A (Control House)	Aldrin	1955-1974
424C	Aldrin	1959-1974
422 (North)	Aldrin (drumming)	1952-1974
451 (Central drumming)	AZODRIN*, BIDRIN*, CIODRIN*, PHOSDRIN*, and VAFONA* Insecticides, NEMAGON* Soil Fumigant, and DIBROM	1965-1977
471	AZODRIN	1964
	DIBROM	1962-1970
	NEMAGON	1955-1975
	VAFONA	1964-1977
	PYDRIN* Insecticide	1976-1977
	SUPONA* Insecticide	1965-1967
473	DDVP (drumming)	1965-1977
512	Endrin	1952-1954
514	AZODRIN, BIDRIN, CIODRIN	1965-1977
	Ethyl parathion	1964-1966
	Methyl parathion	1957-1967
	VAFONA	1960-1964
	Endrin	1954-1957
	PHOSDRIN	1957-1973
515	Endrin	1957-1965
	PLANAVIN* Herbicide	1966-1975
	BLADEX* Herbicide (production)	(Intermittent) 1970-1971
	NUDRIN* Insecticide	1973-1977
515E	BLADEX (formulation)	1974-1977
	Atrazine	1977
516	Dieldrin	1952-1973
525	AKTON* Insecticide	1967
	BIDRIN	1962
	CIODRIN	1962
	PHOSDRIN	1956
	LANDRIN* Insecticide	1969
	SUPONA	1963-1965
	GARIDONA* Insecticide	1966-1968
	RABON*/RAVAP* Insecticides (formulation)	1971
526	Aldrin filters	1952-1973
532	BLADEX (bottling)	1974-1977
	Atrazine (bottling)	1977

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Donald Whorton, M.D., MPH  
Diplomate American Board  
of Internal Medicine  
Diplomate American Board  
of Preventive Medicine in  
Occupational Medicine

## APPENDIX C

Thomas H. Milby, M.D., MPH  
Diplomate American Board  
of Preventive Medicine in  
Occupational Medicine

Practice limited to occupational medicine,  
internal medicine, epidemiology, toxicology

2150 Shattuck Ave. Suite 414  
Berkeley, CA 94704  
(415) 548-1888

Last year you received a letter from Mr. Gary White, an Industrial Hygienist from the National Institute for Occupational Safety and Health (NIOSH) asking if you desired to be examined at no cost to you for possible health effects resulting from your employment for Harkin at the Shell Chemical Company plant. You responded that you would indeed be interested in such an examination.

Arrangements have been made for you to be examined by Eugene Heller, M.D., a urologist. You should call his office at (303) 388-9321 for an appointment. I have enclosed a short medical questionnaire and release form that you should complete prior to your appointment with Dr. Heller and take with you to his office.

Because the major concern about exposure to Nemagon is the adverse effect on the testicles, Dr. Heller will want to obtain both a sperm (semen) sample and a blood sample from you. Dr. Heller will provide you with instructions about the semen sample. The most important point concerning this sample is that you must not have sex or an ejaculation for 72 hours prior to producing the sample.

After the examination is completed, I will write you a letter providing you with your results and an explanation of their meaning. Any further medical evaluation will not be paid for by NIOSH.

If you have any questions, please contact Dr. Heller or me.

Thank you for your participation.

Sincerely yours,

Donald Whorton, M.D.

DW/lh

CONSENT FORM

I, \_\_\_\_\_,  
voluntarily agree to participate in a Health Hazard Evaluation  
of the Shell Chemical Company, Denver, Colorado, conducted by  
the National Institute for Occupational Safety and Health  
(NIOSH). This evaluation is conducted under the authority of  
Section 20(a)(6) of the Occupational Safety and Health Act and  
in accordance with Federal Regulations (42, Code of Federal  
Regulations, Part 85).

I understand that I will be examined by Eugene  
Heller, M.D., a Denver urologist. I understand that Dr. Heller  
will send a copy of my examination results to Donald Whorton,  
M.D., and Thomas H. Milby, M.D., Berkeley, California, for  
further evaluation. I understand that at any time during the  
study I have the right to ask questions and that I am free to  
withdraw my consent and discontinue participation in the study  
at any time without prejudice to myself.

Any information gathered in this evaluation will  
not be disclosed in a manner which will identify me except with  
my written permission or except that which is required by law.  
The information will be used by NIOSH primarily for purposes  
of the Health Hazard Evaluation and also for occupational  
health research.

\_\_\_\_\_  
Date

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Witness



DATE: \_\_\_\_\_

NAME: \_\_\_\_\_

BIRTH DATE \_\_\_\_\_

ADDRESS: \_\_\_\_\_

PHONE NUMBER: (     ) \_\_\_\_\_

MARITAL STATUS:    Married \_\_\_\_\_ Divorced \_\_\_\_\_ Single \_\_\_\_\_ Other \_\_\_\_\_

Children you have fathered (birth dates and sex):

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

# I. WORK HISTORY

	<u>Start</u> (Month/year)	<u>Finish</u> (Month/year)	<u>Job Category</u>
Time worked for Nankin	_____	_____	_____
Time worked at Shell Plant for Nankin	_____	_____	_____
Amount of time worked with Nemagon	_____	_____	_____

Jobs prior to Nankin:

	<u>Employer</u>	<u>Dates</u>	<u>Job Category</u>
1)	_____	_____	_____
2)	_____	_____	_____
3)	_____	_____	_____
4)	_____	_____	_____
5)	_____	_____	_____

Employment after Nankin:

	<u>Employer</u>	<u>Dates</u>	<u>Job Category</u>
1)	_____	_____	_____
2)	_____	_____	_____
3)	_____	_____	_____
4)	_____	_____	_____
5)	_____	_____	_____

## II. MEDICAL QUESTIONNAIRE

A. Please check if you have ever had any of the following and give dates for occurrence:

	<u>Dates</u>
a) Diabetes	_____
b) Thyroid problems	_____
c) Prostatitis	_____
d) Epididymitis	_____
e) Mumps	_____
f) Gonorrhea	_____
g) Syphilis	_____
h) Tuberculosis	_____
i) Undescended testicle	_____
j) Injury to testicle	_____
k) Bladder infection	_____
l) Kidney infection	_____
m) Swelling of testicle	_____
n) Blood in urine	_____
o) Other problem with testicle (specify)	_____

Have you ever been hospitalized? If so, when and for what?

\_\_\_\_\_

\_\_\_\_\_

Have you had previous surgery? If so, when and for what?

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Have you had a previous sperm count? If so

When \_\_\_\_\_

Why \_\_\_\_\_

Results \_\_\_\_\_

What type of birth control do you or your spouse use?

---

Do you want more children?

---

Have you been trying to have a child during the last year?

---

Has your wife had any miscarriages? If so, when?

---

Have you had any loss of

facial hair \_\_\_\_\_

body hair \_\_\_\_\_

head hair \_\_\_\_\_

Have you lost more than 15 pounds during the last year? \_\_\_\_\_

Have you had any swelling or discomfort of breasts during the  
last 5 years? \_\_\_\_\_

Have your testicles changed in size during the past 5 years? \_\_\_\_\_

If so, how? \_\_\_\_\_

Have you had a loss of sex drive during the last 5 years? \_\_\_\_\_

Have you had a loss in ability to have sex during the past  
5 years? \_\_\_\_\_

For what conditions have you been treated by a physician during  
the last 5 years? \_\_\_\_\_

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