NIOSH

TECHNICAL REPORT

Extent-of-Exposure Survey of Monochlorobenzene

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

EXTENT-OF-EXPOSURE SURVEY OF MONOCHLOROBENZENE

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
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DISCLAIMER

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PREFACE

NIOSH has been granted the authority and responsibility under the "Occupational Safety and Health Act of 1970" to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 22(e) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with SRI International to perform an extent-of-exposure study of monochlorobenzene. The funding for this work was provided by the Division for Cancer Cause and Prevention, National Cancer Institute, through the Interagency Agreement on Research on Occupational Carcinogens (Y-01-CP-60605).

ABSTRACT

Following preliminary, walk-through, industrial hygiene surveys of U.S. plants in which monochlorobenzene is used and produced, three facilities were selected for further surveying of human exposures to the chemical. Fifty-eight full-shift personal samples for monochlorobenzene covering workers in 20 job classifications, and area samples of 30 different sites at these three facilities were collected and analyzed. The findings were reported separately for the three plants. This report consolidates the findings for the individual plant surveys.

The report includes--in addition to background information on production and uses, toxicity and human exposure standards, and production processes--descriptions of operations and jobs, exposure control efforts, health and safety programs, air sampling data collected, summary tables of worker exposure levels to monochlorobenzene and associated substances (benzene, dichlorobenzene, and nitrochlorobenzene), sampling and analytical procedures and methods, evaluation of findings, and recommendations.

Results of the survey showed time-weighted-average personal exposures to monochlorobenzene for normal operations ranging from below the detectable limit to 4 ppm--all well below current permissible levels of 75 parts per million. All but two of personal samples for other substances were well below permissible limits. (Two benzene samples at one plant showed concentrations of 15.7 and 21.1 ppm, above the OSHA standard and ACGIH recommended level of 10 ppm).

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INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry (see Preface), NIOSH contracted with SRI International to conduct an industrial hygiene study of exposure to four chlorinated hydrocarbons. Chlorinated hydrocarbons were selected as an area for study because vinyl chloride has been shown to be a human carcinogen and because a growing number of the compounds have been shown by research to be known animal carcinogens and suspected human carcinogens. The four compounds selected for study--benzyl chloride, monochlorobenzene, methylene chloride, and methyl chloride--were chosen on the bases of: the industry in which the compound is produced or used; history of production and use; processes and related new materials involved; and numbers of workers potentially exposed. The report that follows concerns industry exposures to monochlorobenzene.

OBJECTIVES AND SCOPE OF THIS STUDY

The objectives of this industrial hygiene study were to:

- Review and summarize the toxic effects of monochlorobenzene.
- Document and describe selected workplaces, including information on the production and use of monochlorobenzene.
- Identify job types and describe specific jobs.
- Describe current industrial hygiene and safety practices, including engineering controls, work practices, administrative controls, and biological and environmental sampling and control procedures.
- Document (1) job-function exposures to monochlorobenzene and (2) relevant process or production changes occurring during the survey that could affect the evaluation of job-function exposures.
- Describe analytical procedures for collection and analysis of monochlorobenzene.

Detailed industrial hygiene surveys reflecting these objectives were made at three U.S. facilities where monochlorobenzene is produced and/or used. The detailed surveys, all of which had been preceded by preliminary surveys, were conducted during the period November 1978 to June 1979 by the contractor and by NIOSH.

LIMITATIONS OF STUDY

The industrial hygiene surveys represent singular evaluations of worker exposures to monochlorobenzene which do not reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures for each job type as encountered during all work shifts. These studies were made during periods of normal production. No abnormal exposure situations were encountered during the sampling periods; therefore, the reported exposure measurements are considered to represent only those exposures associated with normal operating conditions.

BACKGROUND

Monochlorobenzene, or MCB, is a colorless liquid with a penetrating odor of almonds. The chemical formula, synonyms, and some chemical and physical properties of MCB are given in Table 1.

Table 1. Chemical and physical data for monochlorobenzene

Synonyms: chlorobenzene, chlorobenzol, phenylchloride, benzene monochloride	
Chemical formula: C_6H_5Cl	
Some chemical and physical properties:	
Molecular weight	112.56
Saturated vapor concentration (vol., 20°C)	11,900 ppm
Melting point	-45°C
Boiling point (101.3 kPa)	132°C
Critical temperature	359.2°C
Liquid density	1.10118 kg/L
Explosive limits (vol. in air, 101.3 kPa)	1.3 - 7.1%
Flash point (closed cup)	28°C
Heat of vaporization	333.1 J/g

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5. New York, Wiley-Interscience, 1979, p. 799.

PRODUCTION AND USES

Large quantities of monochlorobenzene were once used in the production of DDT insecticide and phenol; however, because of a restriction on the use of DDT, and because MCB was replaced by cumene in the manufacture of phenol, the production and use of MCB in the United States has declined. Estimated production volumes for the latest three years for which data are available were 170 million kilograms in 1976, 148 million kg in 1977, and 134 million kg in 1978.[1]

Monochlorobenzene is currently used mainly as a solvent, (e.g., in the manufacture of pesticides and for degreasing) and in the production of nitrochlorobenzenes (used as intermediates for dyes, herbicides, and insecticides). The U.S. consumption pattern for MCB, based on data for 1976, is approximately as follows:[1]

Solvent (e.g., pesticides, degreasing)	49%
Manufacture of nitrochlorobenzene	30
Diphenyloxide	8

DDT	7
Other	6
	100%

HUMAN EXPOSURE STANDARDS AND TOXICITY

The current Occupational Safety and Health Administration permissible limit of exposure to MCB is 75 parts per million (ppm) as a time-weighted average (TWA) for eight hours.[2] The Threshold Limit Value recommended by the American Conference of Governmental Industrial Hygienists is also 75 ppm,[3] "... [in the belief that] this limit is low enough to prevent narcotic effects or chronic poisoning."[4] The American Industrial Hygiene Association, in a 1971 publication, indicated that, based on unpublished data, a "...somewhat lower concentration may be more appropriate."[5]

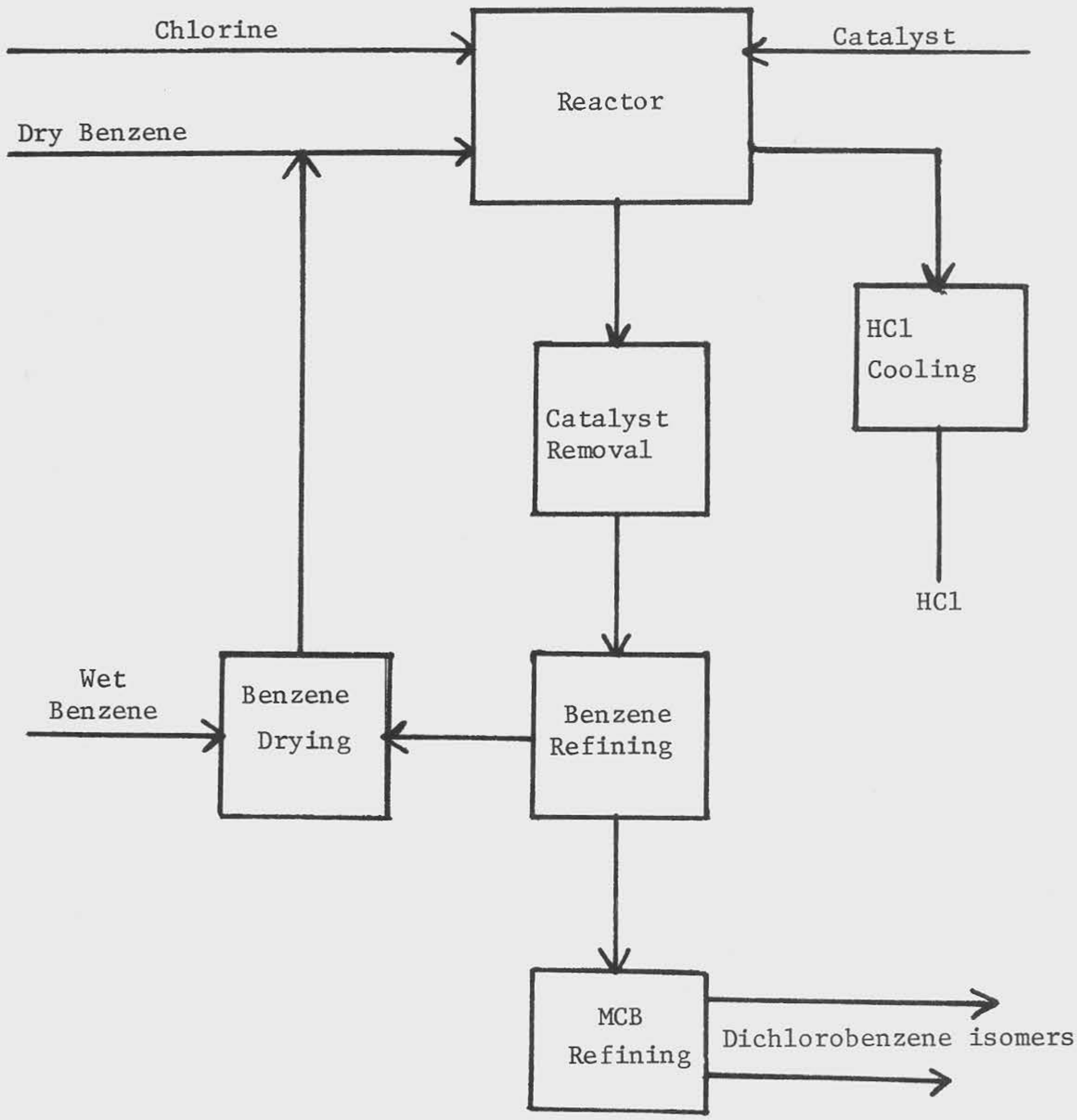
Monochlorobenzene can enter the body through inhalation of its vapor and by percutaneous absorption of the liquid. Typically, as a chlorinated benzene, MCB is irritating to the skin, conjunctiva, and mucous membranes of the upper respiratory tract, and prolonged or repeated contact with the liquid may cause skin burns. An acute exposure to the compound can cause drowsiness, incoordination, and unconsciousness. Animal experiments have indicated histological changes in the liver, kidneys, and lungs after chronic exposure.[6] In one such experiment, for example, animals were exposed to inhalation doses of 0, 75, or 250 ppm of MCB for seven hours, 5 days per week, for 24 weeks, and subtle hematological and histological changes, together with a decrease in food utilization, were observed at the 75 ppm and 250 ppm exposure levels.[7] No such changes were observed among controls.

BASIC PROCESS FOR PRODUCING MCB

The 12 chlorinated benzenes, including monochlorobenzene, are formed by replacing the hydrogens of benzene with chlorine atoms. Monochlorobenzene is produced by chlorinating benzene in the presence of a catalyst, usually ferric chloride. The chemical reaction involved is:

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(chlorine)}}{Cl_2} \xrightarrow{\text{catalyst}} \underset{\text{(MCB)}}{C_6H_5CL} + \underset{\text{(hydrogen-chloride)}}{HCl}$$

The ferric chloride catalyst is either added as such or generated during the reaction by exposing a large surface of iron to the liquid being chlorinated.[1,8] Two major isomers of dichlorobenzene, ortho- and para are also formed, as is a small amount of the meta- isomer. As chlorination continues, tri-, tetra-penta-, and hexachlorobenzenes are formed. The degree of chlorination can be controlled by the catalyst used, temperature, and ratio of benzene to chlorine, but since each of the previous compounds, except hexachlorobenzene, can be further chlorinated, those compounds are always a mixture of chlorinated benzenes. Pure compounds are obtained by distillation and crystallization. A simplified, block, diagram of the basic process for manufacturing MCB is shown as Figure 1.



Abstracted from: Dylewski, SW: Emission Control Options for the Synthetic Organic Chemicals Manufacturing Industry: Chlorobenzenes Product Report (Draft). Prepared for Environmental Protection Agency, Research Triangle Park, N.C., August 1978.

Figure 1. A simplified, block, diagram of the basic process for manufacturing monochlorobenzene.

FACILITIES AND PERSONNEL SURVEYED

Three facilities at which monochlorobenzene is produced and/or used in further chemical production were surveyed. In an attempt to provide as much of an exposure cross-section as possible, the following criteria were used for plant selection: the number of persons potentially exposed; level of exposure experienced, as determined by preliminary area sampling; type of operation (continuous or batch); exposure situations limited primarily to the target chemical; and a process representative of a major use of the substance.

The facilities are designated as Plants A, B, and C. They are briefly described below, followed by discussions of their process and control operations, descriptions of personnel and jobs in which potential exposure to MCB occurs, and descriptions of health and safety programs that have been established.

DESCRIPTION OF FACILITIES

The following are brief overviews of the three facilities at which in-depth exposure surveys were made for purposes of this report.

Plant A--Overview

Both monochlorobenzene and nitrochlorobenzene (derived from MCB) are manufactured at this facility. The facility is one production unit of a plant that produces a number of different chemical compounds. Both the MCB and nitrochlorobenzene manufacturing operations were surveyed in this study.

Plant B--Overview

Plant B is a long-time (over 30 years) producer of MCB in a part batch, part continuous, operation. The plant, which also manufactures several other chemical compounds, is located on the site of a larger chemical manufacturing facility.

Plant C--Overview

The chlorobenzene production unit is located in a large Midwest, chemical-producing and -using facility. The MCB production unit, which covers 23 acres, has been in operation since 1922, and most plant additions and technology changes have been continuous and relatively minor over the years since that date. An exception is in the chlorinator technology; a new chlorinator unit was recently installed and the old unit put on standby.

PROCESS AND CONTROL OPERATIONS

All three of the plants surveyed used the fundamental process for producing monochlorobenzene as described briefly in the preceding chapter ("Background"), including the use of ferric chloride as a catalyst. The nature of the process is such that the structures utilized are not enclosed. Comments and observations on the process operation at each of the three plants are given below as appropriate.

Plant A--Process and Control

As noted previously, both monochlorobenzene and nitrochlorobenzene are produced at Plant A, and production of both was included in this survey. The process/control operations involved in their production are discussed below.

Monochlorobenzene Manufacturing--

Monochlorobenzene is produced at Plant A by the continuous chlorination of benzene. Benzene for the process is pumped by pipeline from a reception terminal to in-plant bulk storage, from which it is then pumped to the manufacturing area. Chlorine is vaporized and pumped to the manufacturing area from another department at the plant site.

The benzene (both unreacted and recycled) is dried and passed into a series of three chlorinators, where it reacts with vaporized chlorine and the ferric chloride catalyst. The catalyst is added to the system once each day by an operator who manually empties the needed amount into a slurry tank. Hydrogen chloride gas created during chlorination is separated from the other reaction products, cooled, and passed to an absorber from which it is recovered as a usable byproduct.

The crude chlorinated benzene and the unreacted benzene pass from the chlorinator to the first of three separatory stages. The first stage removes the catalyst; in the second stage, unreacted benzene is separated by distillation (and returned for reintroduction to the process); in the third stage, MCB and residual amounts of dichlorobenzene are passed into a unit, called the mono-column, where the final MCB product is separated. (The dichlorobenzene is pumped to another department for recovery.)

Nitrochlorobenzene Manufacturing--

Nitrochlorobenzene is manufactured by the reaction of monochlorobenzene and nitric acid in the presence of sulfuric acid. Monochlorobenzene for the manufacturing process is received by pipeline from the MCB manufacturing unit at Plant A. Nitric acid is received by rail car.

The MCB is pumped, from underground storage, to a surge tank, then to the first of three nitrators, to which nitric acid and sulfuric acid are also added. The three nitrators agitate the material as it cascades through them, and para-nitrochlorobenzene, ortho-nitrochlorobenzene, hiboilers, and sulfuric acid are produced from this reaction. The mixture is then separated into acid and organics in two separators. The acid is concentrated and recycled. The organic fraction is washed with caustic to remove any residual acid. The washed organics are then introduced to a dehydrator, where entrained water from the washing sequence is removed.

The crude nitrochlorobenzene is stripped of excess monochlorobenzene in a distillation column. The botton of the stripper contains the finished crude product; the overhead contains MCB, which is pumped back to the surge tank.

Plant B--Process Control

The manufacturing of MCB at Plant B is a part batch, part continuous operation. The process begins with the introduction of vaporized chlorine and dry benzene into one of two batch-operated chlorinators, which contain the catalyst. Water runs continuously onto the reaction vessels, reportedly for cooling the system. Hydrogen chloride gas created during chlorination is separated from the other reaction products and is transferred to an area where it is recovered as a usable product.

The crude reaction mixture is pumped to storage tanks, from which it is drawn for refining in the continuously operated refining unit. Plant B has two sets of fractionization (stripping) columns, only one set of which is used at a time, the other set being reserved as a backup (such as during general maintenance). After the benzene is stripped from the monochlorobenzene, the MCB is pumped to intermediate storage tanks (and the benzene is pumped to a storage tank for recycling to the chlorinators). Crude MCB from the intermediate storage tank is pumped to a second stripping column, where it is further refined by the removal of dichlorobenzenes and other polychlorobenzenes. The refined MCB then leaves the stripper for storage.

A potential for exposure to MCB exists during quality-control sampling or when system maintenance is required. At the time of this survey, open-spout sampling ports were in the process of being changed to a closed-system type. At the open-spout ports, spillage or drips were caught in buckets beneath the ports. This effluent would contain quantities of MCB or a combination of MCB and other chlorobenzenes. Gloves are worn by the operators during sampling, and operators are instructed to wear respirators equipped with organic vapor/acid gas cannisters. The survey team observed, however, that some of the operators were not wearing respirators during the collection of samples.

In early 1978, Plant B began a program of engineering and process changes in the MCB unit to reduce airborne benzene levels to 1 ppm as an eight-hour time-weighted average. At the time of this survey, most of these changes had been completed. They include:

- Installation of improved condensers for the fractionating columns to achieve better condensing and cooling;

- Repositioning and manifolding of vents to reduce total emissions and installation of refrigerated cooling-water units on certain vents to increase condensing capacity; and

- A process change for removing benzene contaminant during the neutralization of crude product that will reduce corrosion and the consequent need to open lines and vessels for maintenance.

Plant C--Process and Control

Monochlorobenzene is manufactured at Plant C by a continuous, closed, process in fundamentally the same way as previously described in this report. The manufacturing facility includes two buildings--one, containing a control room, in the Chlorinator (reactor) area and one in the Badger (recovery) area containing a control room and a gas chromatograph (GC) room. All other structures and equipment involved with MCB production are open to the air. The Plant C layout is shown in Figure 2.

The production area offers potential exposure to benzene, chlorine, sodium hydroxide, hydrogen chloride, and hydrochloric acid, and to mono-, di-, tri-, and tetra-chlorobenzenes. However, since the production process is closed and continuous, exposures should be minimal around most equipment under normal operating conditions. During start-up, maintenance, or if system leaks occur, exposures would be expected to be greater. (Data supplied by Plant C dating back to 1972 show no samples exceeding the 75 ppm TWA standard for MCB.)

PERSONNEL AND THEIR ACTIVITY

Plant A--Personnel

There are 14 persons at Plant A who are involved in the production of monochlorobenzene; 15 persons work in nitrochlorobenzene production. (This workforce is supplemented by contract maintenance laborers who, in general, are not assigned to a fixed work area but work in a number of areas, including the production facilities. These workers assist with the maintenance of the facilities and are not directly involved in the operation of chemical production equipment.)

Monochlorobenzene Personnel--

There are four principal job classifications involved with monochlorobenzene production:

- Premium Operators
- Day Operators
- Repairmen
- Porters

Most of the time, these individuals are indoors, in a control-room blockhouse located at grade level in the middle of the monochlorobenzene facility. Those workers whose duties include checking the operation, cleanup, and maintenance of the equipment make frequent, short-duration, trips outdoors to various

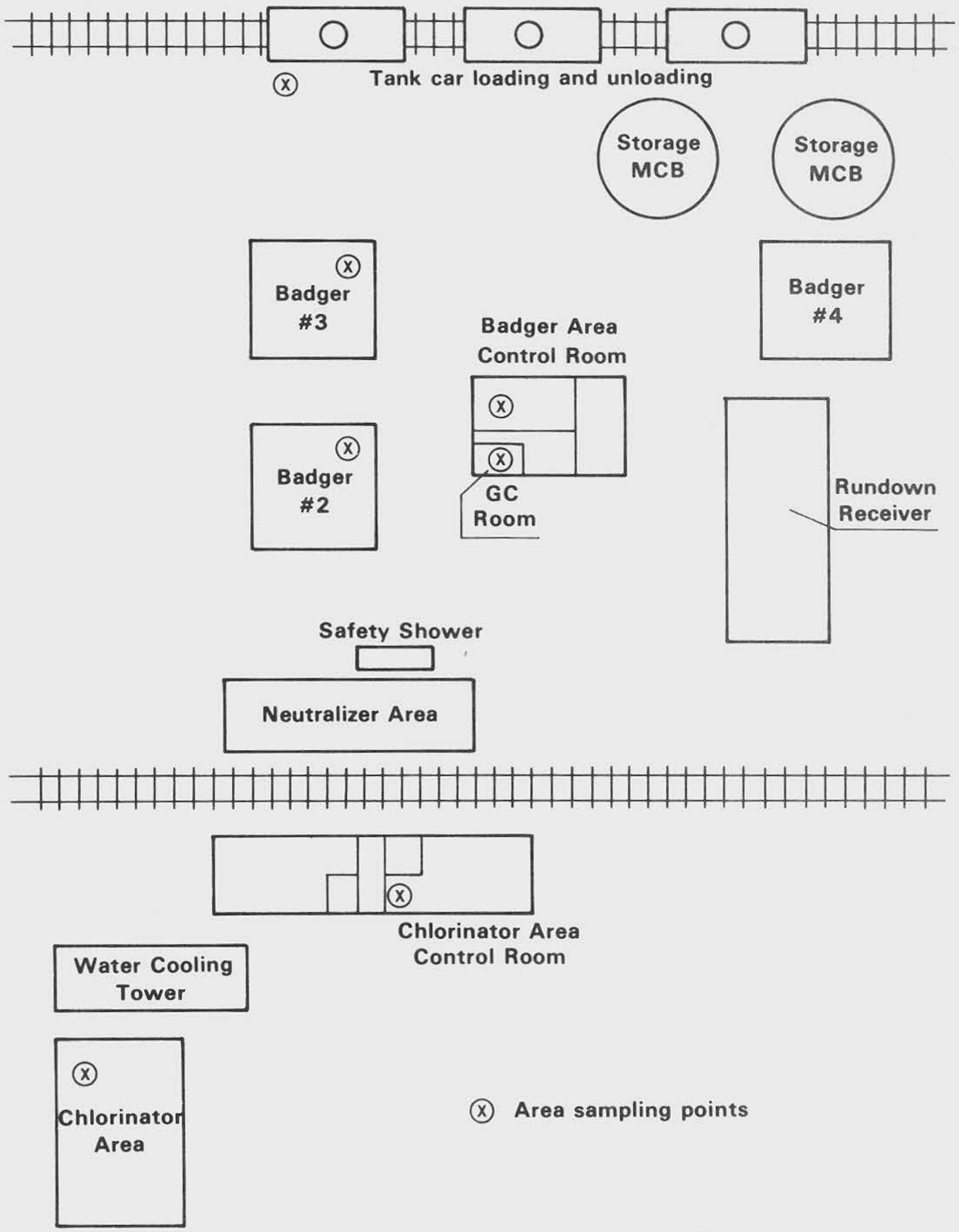


Figure 2. Layout of the MCB manufacturing facility at Plant C.

reactors, chlorinators, storage tanks, and associated equipment.

The duties of the four job classifications associated with the production of monochlorobenzene are as follows:

Premium Operator--Responsible for operating the department, process equipment, and auxiliaries. Controls inventories of raw materials, finished goods, intermediates, and products in storage tanks and processing equipment. Disposes of the waste material and adds oil to the refrigeration systems as necessary.

Day Operator--Initiates the transfer of wet benzene by pipeline to the process area and also receives benzene from terminal storage. Responsible for loading and unloading of monochlorobenzene, ortho-dichlorobenzene, para-dichlorobenzene, and benzene from tank cars and trailer trucks; this includes the connecting and disconnecting of loading, unloading, or steam lines to tank-car or trailer-truck coils. Responsible for drumming of products and assists the Premium Operator in the disposal of waste material. Also drains water from wet benzene and cleans equipment. Assists Repairmen in the cleaning of reboilers, heat exchangers, and condensers (or any other equipment normally cleaned by two Repairmen) on the day when only one Repairman is present. Often assists Repairmen in their duties.

Repairman--Responsible for cleaning reboilers, heat exchangers, condensers, and water jets; also performs general repair work as directed by the supervisor.

Porter--Performs custodial services in control room offices and repair area.

Nitrochlorobenzene Personnel--

The nitrochlorobenzene manufacturing area employs a nitration operator, washer operator, utility day operator, repairmen, porters, and an hourly foreman (on day shift). Descriptions of these job classifications follows:

Nitration Operator--Monitors and controls continuous nitration of monochlorobenzene, separation of crude nitrochlorobenzene from spent acid, and dehydration of the spent acid. Performs most of these tasks from the control room. Makes periodic trips to the process area to sample, check equipment, clear lines, clean up operation area, and clean equipment for maintenance work.

Washing Operator--Monitors and controls the continuous neutralization, washing, dehydrating, and MCB stripping of the new MCB crude generated in nitration process. Performs most tasks from the control room. Makes periodic trips to the process area to sample, check equipment, clear lines, clean up operating area, and clean equipment for maintenance work.

Utility Day Operator--Unloads from tank truck or tank car (or receives by pipeline) the raw materials used, which include sulfuric acid, nitric acid, and monochlorobenzene. Loads tank trucks and tank cars, and then transfers by pipeline the finished products made in the department (p-nitrochlorobenzene and o-nitrochlorobenzene). Also makes up batches of mixed nitric and sulfuric acids for another department at the plant site.

Repairman--Performs repairs throughout the department and performs other operation assistance such as inserting and pulling blanks, installing pressure gauges, disconnecting lines for clean-out, opening equipment for inspection or clean-out, and making minor modifications. Repairs steam traps and tracing, applies temporary insulation to lines, patches small leaks in lines and vessels, replaces small lines, etc.

Porter Helper--Performs typical porter duties in the control rooms, offices, and toilet areas in the department; also performs some pickup and cleanup in the process area.

Plant B--Personnel

Twelve employees work within the monochlorobenzene manufacturing area at Plant B, and an additional 16 employees handle MCB on an intermittent basis. The job titles and number of workers that work in the MCB manufacturing unit are as follows:

Job Title	Number per Shift	Total Force
Senior Operator	1	4
Distillation Operator	1	4
Process Helper*	1	4
Material Handler--Loading (on day or swing shift only)	1	2

*This employee works in the MCB manufacturing area on the average of 25% of the time.

In addition to the employees just mentioned, there are an additional 40 mechanics, laboratory technicians, and supervisory staff who may be exposed to MCB intermittently. Senior Operator and the Distillation Operator are the principal job classifications that are directly involved with the MCB process area and that receive a continuous exposure to MCB. The duties of these two operators are as follows:

Senior Operator--Responsible for operating the chemical processing equipment to produce chlorinated benzene, nitric acid, and purified polychlorobenzene. Directs the other operators, material handlers, and the process helper. Checks all gauges and meters and adjusts flows of material as needed. Also takes samples as required and assists the maintenance crew during repairs.

Distillation Operator--Maintains equilibrium conditions in the continuous fractionating columns and in the drying system. Checks all temperature and pressure instruments, flowmeters, and operating pumps and valves. Also takes samples and assists the maintenance crew during repairs.

Plant C--Personnel

At Plant C, 12 hourly employees are assigned to work each day in the monochlorobenzene manufacturing unit, which comprises two major areas--Clorinator (reactor) and Badger (recovery). Hourly employees work eight-hour shifts on a standard (four-shift rotation) schedule. The job titles and number of workers in the MCB unit are as follows:

Job title	Per shift	Total
Chlorobenzol Operator	2	6
Alternate (day shift only)	1	1
Badger Operator	1	3
Plant Mechanic (day shift only)	1	1
Transfer Man	1	1

The process-operator and transfer-man job classifications are directly involved with the MCB process and receive the most continuous exposure to the chemical. Other mechanics, as well as laboratory technicians and supervisory staff, may be exposed intermittently. The duties of the Operators and Transfer Men are as follows:

Clorobenzol Operator--Responsible for operating the chemical processing equipment to produce chlorinated benzene. Monitors all process control equipment and makes necessary adjustments. Also takes process samples as required.

Badger Operator--Responsible for maintaining equilibrium conditions in the continuous fractionating columns and associated equipment. Monitors all process control equipment and adjusts process variables as necessary.

Transfer Man--Responsible for unloading trucks and rail tank cars of raw materials for the process and for loading rail tank cars with the finished product for shipment. This includes taking quality control samples of both incoming and outgoing shipments.

HEALTH AND SAFETY PROGRAMS

Plant A--Health and Safety

Plant A has a formalized safety program, which includes an environmental health group composed of health and safety professionals. Medical assistance is available on the plant site from a physician, and there is a fulltime nurse on each shift. Pre-employment and annual physicals are required by Plant A for all of its employees.

The company requires that each employee in the manufacturing areas wear overalls, safety shoes, hard hat, and safety glasses at all times. All employees also have at their disposal additional safety equipment, which includes respirators (fitted with chemical cannisters suitable for organic vapors and acid gases), Scott Air-Paks®, gloves, goggles, boots, rubber aprons, face shields, and other safety equipment. In the monochlorobenzene facility, all personnel are required to wear rubber work shoes or overshoes and to carry respirators at all times. Written procedures have been established for proper protection of employees who execute potentially high-exposure tasks, such as opening process lines or other equipment.

Biological monitoring has been performed at the Plant for phenols in urine.

Plant B--Health and Safety

Pre-employment physicals are required for each employee at Plant B. These physicals include job and family medical history, chest x-ray, audiograms, and blood and urine analysis. Complete blood tests are also performed annually by a nearby clinic.

The Plant has a formalized safety program, directed by one of its salaried employees who has received some training in industrial hygiene technology. Industrial hygiene functions at the plant are augmented by a regional industrial hygienist. Each foreman is required to be trained in first aid. A hospital, about one-half mile away, is available in case of emergencies.

Every employee is required to wear Plant-supplied work clothing, safety hat, safety shoes, safety glasses, and NIOSH-certified respirators equipped with organic vapor/acid gas cannister. Gloves, face shields, and rubber boots are supplied when a specific task warrants extra personal protection, and air-supplied respirators are also available for high-risk exposures. Locker rooms with showers are available for the employees.

Plant C--Health and Safety

Health and safety programs at Plant C are provided by the corporation that operates the monochlorobenzene operation at the chemical complex. The Medical Department, directed by a physician, has a staff of six physicians and 20 registered nurses who handle problems 24 hours a day, seven days a week. The Safety Department has a staff of 15, including the manager. The Industrial Hygiene program is conducted by a manager and a staff of 25 hygienists.

Emergency medical personnel on every shift respond with a radio-dispatched van to requests for medical assistance. An Occupational Health Team consisting of a medical doctor, safety engineer, and industrial hygienist has been assigned to each area of the chemical facility where exposures to chemicals might occur. Industrial hygienists have access to a wide array of sampling and analytical equipment that includes a computerized system of continuous air monitoring, gas chromatographs, and mass spectrometers.

Safety showers are strategically located within the site. Employee safety equipment provided by Plant C includes coveralls, shoes, hard hats, safety glasses, respirators, and gloves. Plastic monogoggles are also required in the chlorobenzol area. Showers, a locker room, and an isolated eating area are provided for employees.

SURVEY PROCEDURES AND METHODS

The procedures and sampling and analytical methods employed in this survey of exposure to monochlorobenzene are described in this chapter of the report. Personal samples taken at all three plants were analyzed for benzene and dichlorobenzene, in addition to monochlorobenzene, and area sampling was performed at Plant A for the presence of nitrochlorobenzene. The detailed surveys at each of the three plants had all been preceded by walk-through surveys to identify suitable facilities for more in-depth study. In-depth sampling at Plants A and B was conducted by the contractor, Plant C by NIOSH industrial hygiene personnel without the assistance of SRI.

GENERAL SURVEY PROCEDURES

At Plant A, the survey team sampled every operator working in the monochlorobenzene and nitrochlorobenzene manufacturing units for the presence of MCB, benzene, and dichlorobenzene. Breathing zone samples were taken with charcoal tube/sampling pump assemblies for approximately eight hours on all shifts. Area monitoring was performed with charcoal tube/sampling pump assemblies and a Century Systems Total Organic Vapor Analyzer. The Century analyzer was used at several locations throughout the MCB facility where there seemed to be a chance for exposure, such as near valves, flanges, pumps, and quality-control sampling ports.

Area samples for nitrochlorobenzene were also taken around the nitrochlorobenzene manufacturing unit. These samples were collected in large-size silica gel tubes using a Bendix monitoring pump. Sampling times were approximately eight hours.

At Plant B, every operator working in the monochlorobenzene manufacturing unit was monitored for the presence of MCB, as well as benzene and dichlorobenzenes. Eight-hour TWA breathing zone, charcoal-tube samples were collected. Personal samples were also taken to determine ceiling concentrations during those operations where there was a potential for short-term, high-level exposure to MCB, benzene, or dichlorobenzene.

Area charcoal-tube samples were collected at locations with potential higher-than-normal MCB exposure, such as near quality-control sampling ports.

Most of the regular-shift employees at Plant C were monitored for MCB, dichlorobenzene, and benzene. A new recovery unit was being constructed in an area adjacent to the Plant's chlorinator, and two of the construction workers were also monitored for MCB exposure. Charcoal tubes were used for the personal sampling, as well as for the area samples that were taken.

SAMPLING AND ANALYSES

Personal sampling employed charcoal tubes and monitoring pumps--Bendix BDX-44 at Plants A and B, MDA Accuhaler® at Plant C--which were attached to the clothing and belts of the workers. The pumps were connected to the sampling media by Tygon® tubing.

At Plants A and B, the sampling medium was a large-size charcoal tube (600 mg) containing a 400-milligram adsorbing section backed up by a 200-mg section to determine breakthrough of the substances being sampled. The sections are separated by a portion of urethane foam and are analyzed separately. The charcoal tubes used at Plant C were standard-size, 150 mg (100 mg adsorbing section and 50 mg backup section). The sampling pumps drew air through the tubes at nominal rates of 100 milliliters per minute at Plants A and B and 20 milliliters per minute at Plant C.

While sampling was performed for somewhat less than the full eight-hour shift for most of the workers surveyed, the nature of the operations are such that the exposure for individuals would not be expected to vary. Hence, the TWA calculated was on an eight-hour basis. The calculation for MCB concentration was as follows:

$$C = \frac{(24{,}450) \times (W)}{(MW) \times (V)}$$

where: C = Concentration of MCB, ppm

W = Mass of MCB collected, mg

MW = Molecular weight of MCB, 112.56 g/gmol

V = Volume of air sampled, L

The Plant A and B samples were analyzed for monochlorobenzene, benzene, and dichlorobenzene according to NIOSH-approved analytical technique S133 with a minor adjustment in technique: The NIOSH method calls for desorption of the charcoal using 1 ml of carbon disulfide: however, since large charcoal tubes were used, 2 ml of carbon disulfide were used to desorb. Samples collected at Plant C were analyzed for MCB, dichlorobenzene, and benzene according to NIOSH method P & CAM 127 (modified)[9]. All samples were analyzed by gas-liquid chromatography with flame ionization detection. Four area samples that were taken at Plant A for nitrochlorobenzene were analyzed according to NIOSH method S218[9].

RESULTS AND RECOMMENDATIONS

Results of the in-depth exposure surveys carried out at Plants A, B, and C, together with summaries and recommendations, are presented in this chapter.

RESULTS OF SURVEY--PLANT A

Time-weighted average exposures of workers at Plant A to monochlorobenzene are shown in Table 2 in the form of concentrations for each job classification, by work shift, together with geometric means* for the job categories. Individual personal sample results, together with results of long-term area sampling, are shown in Appendix Table A-1.

Variations among personal samples can be caused by such factors as: (1) small operational changes, and (2) different operators doing the same task in different ways--some get closer to the equipment, some take longer or shorter times to complete a task, etc. For all job classifications, there is inevitably some variation in exposure levels from shift to shift, even though the operations are nominally continuous and constant overall.

Personal exposures to concentrations of MCB in both the monochlorobenzene and nitrochlorobenzene work areas ranged from less than 0.1 ppm to 4 ppm, a range that is well below the OSHA standard and ACGIH recommended Threshold Limit Value (both 75 ppm). The mean MCB exposure concentration for all jobs in MCB manufacturing was 0.19 ppm. The actual highest mean concentration was for MCB Operator (0.24 ppm). As can be seen in Table 2, the difference between average exposures for jobs in the MCB production area were very small. The highest concentration of MCB for a job category in the nitrochlorobenzene manufacturing area was 4 ppm (Day Operator). The mean concentration for all jobs in this area was 0.46 ppm. As compared with the monochlorobenzene manufacturing area, somewhat higher mean concentrations of MCB were recorded for all job categories in the nitrochlorobenzene area, except for the Washing Operator. The difference in mean MCB exposures between the three work shifts was not great.

The MCB found in long-term area samples in the monochloro- and nitrochlorobenzene work areas ranged from 0.2 to 2.4 ppm (Appendix Table A-1).

Personal exposure (TWA) and area concentrations of benzene and o-dichlorobenzene are shown in Appendix Table A-2. The TWA personal concentrations of benzene taken in the MCB production area ranged from 0.8 to 21 ppm, with 2 out of 15

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*Geometric mean = antilog $\frac{1}{n} \left(\sum_{i-1}^{n} \log x_i \right)$

Table 2. Job and work-shift TWA concentrations of monochlorobenzene at Plant A, November 1978.

Job title	TWA concentration (ppm)			
	Day Shift	Evening Shift	Night Shift	Geometric Mean
Monochlorobenzene production				
MCB Operator	0.9,0.2	0.1	0.2	0.24
HCl Operator	0.1,1.1	0.1,0.2	0.1	0.19
Day Operator	0.1,0.2 0.1,0.1			0.12
Repairman	0.5,0.1			0.22
Nitrochlorobenzene production				
Nitration Operator	1.2,0.3	0.2	0.9	0.50
Washing Operator	0.5,0.1	0.1	0.3	0.20
Day Operator	4.0			
Porter	0.5			
Repairman	1.5,0.6			0.95

samples registering above the OSHA and ACGIH standards (10 ppm). The geometric mean for the benzene personal samples was 1.9 ppm, and the seven area samples ranged from 0.3 to 3 ppm. Three out of 15 personal samples for o-dichlorobenzene showed concentrations above the limit of detection (they were 0.1, 0.1, and 0.3 ppm). However, all area samples were at or below the detection limit.

Four long-term area samples for nitrochlorobenzene were taken in the nitrochlorobenzene manufacturing unit, all four of which were determined upon analysis to be below the level of detection for the substance (Appendix Table A-3).

Simultaneously with the SRI survey team, Plant A conducted personal sampling for MCB and for benzene using a 3M passive sampler as the collection medium for the samples. As with the SRI charcoal-tube samples, the Plant A samples were analyzed using desorption with carbon disulfide and analysis by gas chromatography with flame ionization detection. The results of this side-by-side sampling are shown in Appendix Table A-4.

RESULTS OF SURVEY--Plant B

Time-weighted-average exposures of workers at Plant B to monochlorobenzene are shown in Table 3, where concentrations and geometric means for each job classification, by shift, are given. Individual personal sample results, and the results of long-term area sampling, are shown in Appendix Table B-1.

Personal MCB exposure concentrations ranged from 0.1 to 2.9 ppm, which is well below the current OSHA standard and ACGIH recommended Threshold Limit Value. The highest concentration, for a Distillation Operator, was 2.9 ppm. (The mean concentration of MCB for all jobs was 0.8 ppm.) The Senior Operator job classification received the highest mean concentration, which was 1.1 ppm. (See Table 3.)

Long-term area samples for MCB were taken during the day shift on the second day of the survey. The concentrations of MCB found in these samples ranged from 3.1 to 14.2 ppm (Appendix Table B-1).

Table 3. Job and work-shift TWA concentrations of monochlorobenzene at Plant B, January 1979.

Job title	TWA concentration (ppm)			
	Day Shift	Evening Shift	Night Shift	Geometric Mean
Senior Operator	2.7,0.5	2.8	0.4	1.11
Distillation Operator	0.2,1.8	0.1	2.9	0.57
Material Handler	0.8,0.5	0.7		0.65

Personal and area concentrations of benzene and o-dichlorobenzene at Plant B also were determined, and the sampling results are presented in Appendix Table B-2. Personal TWA benzene levels ranged from 0.1 to 3.5 ppm, with a geometric mean concentration of 0.6 ppm. This is below the current OSHA standard and ACGIH recommended TLV of 10 ppm. Material handlers received the greatest exposure to benzene, a geometric mean concentration of 2.4 ppm. Concentrations of dichlorobenzene were below 10 ppm for all personal samples.

RESULTS OF SURVEY--PLANT C

Time-weighted-average exposures of workers at Plant C to monochlorobenzene, by job classification and work shift, are presented in Table 4. Individual personal sample results, and results of area sampling, are shown in Appendix Table C-1. All of the sample results at Plant C were well below the current OSHA standard and ACGIH recommended Threshold Limit Value.

Table 4. Job and work-shift concentration of monochlorobenzene at Plant C, June 1979.

	TWA Concentration (ppm)			
Job Title	Day Shift	Evening Shift	Night Shift	Geometric Mean
Chlorobenzol area				
Operator	--*,-- --,--	--,--	--,--	--
Mechanic	--			
Maintenance Worker (adjacent area)	--,--			
Construction Worker	--			
Badger area				
Operator	0.42,0.59	0.36	0.25	0.39
Transfer Man	1.79,1.90			1.84

*Below detection limit (less than 10 micrograms).

Of the 18 personal samples taken, only 6 showed detectable levels of MCB. All six were collected in the Badger (recovery) area on the Operators and the Transfer Man; no MCB was detected for workers in the chlorobenzol (reactor) area. Concentrations of MCB for four Badger Operators ranged from 0.25 ppm to 0.59 ppm, with a mean (geometric) of 0.39 ppm. The two Transfer-Man samples in the Badger area showed concentrations of 1.79 ppm and 1.90 ppm (mean, 1.84).

Results of area sampling for MCB (20 samples) presented in Appendix Table C-1 are similar in level to the personal results. The areas monitored in the chlorobenzol area yielded no detectable MCB. In the Badger area, both the control room and GC room yielded detectable levels of MCB--0.21 ppm and 0.22 ppm in the control room, and 0.40 ppm in the one sample in the GC room. Five area samples for MCB at Badgers 2 and 3 yielded detectable levels ranging from 0.62 ppm to 2.35 ppm (mean, 1.02). Two samples at the tank car loading truck showed 3.15 ppm and 10.5 ppm MCB.

As noted on Table C-1, 30,000 gallons of MCB were being loaded during the sampling period on day one, and 40,00 gallons were loaded during the sampling period on the second day.

Results of analyzing samples for benzene and dichlorobenzene at Plant C are shown in Appendix Table C-2. In the 18 personal samples, detectable levels of benzene were found in 11, the highest of which was 0.82 ppm (well below the current OSHA standard of 10 ppm). Levels of benzene in area samples, and levels of dichlorobenzene in personal and area samples, were also well below the OSHA standard and the ACGIH Threshold Limit Value.

The ranges of mean exposures to MCB for job categories at Plants A, B, and C, together with the mean personal exposure for all jobs at each plant, are shown in the following tabulation (figures are parts per million):

	Plant A	Plant B	Plant C
Range of mean job-category exposures to MCB	0.12-0.95	0.57-1.11	<detect.-1.84
Mean personal exposure for all job categories	0.27	0.74	0.11

SUMMARY AND RECOMMENDATIONS

From the data collected during this survey, the following summaries and recommendations are made:

- Eight-hour TWA concentrations of monochlorobenzene from personal monitoring at all of the three facilities included in this survey were well below the current OSHA permissible level and ACGIH Threshold Limit Value (see Chapter II--"Background"). Low concentrations are due to combinations, according to each plant, of the following factors: the processes are performed in closed systems that minimize the possibility of MCB release into the work atmosphere; the processes are highly automated, demanding little time of operators in the process area; and processes in relatively open structures.

- Personal, eight-hour-TWA concentrations of monochlorobenzene at Plant A ranged from 0.1 ppm to 4 ppm in the two manufacturing areas surveyed--monochlorobenzene production and nitrochlorobenzene production. The geometric mean concentration of MCB for all job categories in the monochlorobenzene facility was 0.1 ppm; for job categories in the nitrochlorobenzene facility the average was <0.5 ppm. Eight-hour-TWA personal concentrations of MCB at Plant B ranged from 0.1 to 2.9 ppm, with a mean concentration of 0.8 ppm for all job classifications. Plant B was operating at a low capacity during the survey, and it is not known if personal exposures would remain below the current permissible (or ACGIH recommended) level during full-capacity operating conditions. At Plant C, personal TWA exposures to MCB were well below current exposure standards, ranging from below-detectable (12 of 18 samples) to 1.90 ppm. Long-term area samples for MCB at the three plants were also low (the highest level was a 14.2 ppm concentration at Plant B).

- Personal concentrations of benzene and dichlorobenzene were also determined from air samples taken during the survey. Forty-two of the 44 benzene personal samples at the three plants ranged from 0.02 ppm to 3.5 ppm. The remaining two samples (2 of 15 at Plant A) showed concentrations of 15.7 ppm and 21.1 ppm. (The current OSHA standard and ACGIH recommended Threshold Limit Value is 10 ppm). Personal concentrations of o-dichlorobenzene ranged from below-detectable to 2.28 ppm (well below the current OSHA standard of 50 ppm). Four samples for para-nitrochlorobenzene, taken at Plant A, yielded concentrations that were below the detectable limit.

- The plants should maintain their vigilance on exposures of personnel to monochlorobenzene (and other toxic substances). This should include maintaining ventilation and other physical control measures and a personnel exposure monitoring program. Also, instruction of employees, particularly new employees, in the toxic nature of the substances with which they work, and work practices that are in consort with process operations and production rates that exist at any given time should be implemented or continued.

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Table A-1. Individual personal and area TWA concentrations of monochlorobenzene at Plant A, November 1978.

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Monochlorobenzene production		
MCB Operator	100C	0.2
	112C*	0.9
	120C	0.1
	126C	0.2
HCl Operator	101C	0.1
	111C	0.1
	121C	0.1
	122C	0.2
	128C	1.1
Day Operator	104C	0.1
	110C+	0.2
	127C	0.1
	134C	0.1
Repairman	109C	0.5
	130C	0.1
Blank	129C	--
Nitrochlorobenzene production		
Nitration Operator	102C	0.9
	107C	1.2
	117C	0.2
	132C	0.3
Washing Operator	103C	0.3
	105C	0.5
	119C	0.1
	123C	0.1
Day Operator	131C‡	4.0
Porter	108C	0.5
Repairman	106C	1.5
	124C	0.6
Area samples		
MCB storage--day tanks on stairway	114C	0.9
Grade level--#3 chlorinator	116C	2.4

(continued)

Table A-1. (continued)

Job title/location and sample number		TWA concentration (ppm)
Grade level--below benzene stripper	114C	0.9
Grade level--crude liquor transfer	118C	1.1
Grade level--near chlorinator cooler	125C	0.2
1st level--between #2 & #3 chlorinators	133C	1.4
1st level NCB--acid dehydrator	113C	0.2

*A trainee--was wearing an organic-vapor-cartridge respirator while gathering quality-control product samples.

+Operator was preparing equipment for maintenance.

‡Operator was transferring MCB.

Table A-2. Individual personal and area TWA concentrations of benzene and ortho-dichlorobenzene at Plant A, November 1978.

Job Title/location and sample number		TWA concentration (ppm) Benzene	o-dichloro-benzene
Personal samples--monochlorobenzene production			
MCB Operator	100C	1.3	--*
	112C+	21.1	--
	120C	1.2	--
	126C	2.0	--
HCl Operator	101C	1.0	--
	111C	1.2	--
	121C	1.1	--
	122C	1.4	
	128C	1.4	
Day Operator	104C	2.1	--
	110C±	15.7	--
	127C	2.5	0.3
	134C	1.3	--
Repairman	109C	0.8	--
	130C	1.0	--
Blank	129C	BD	BD
Area samples--monochlorobenzene and nitrochlorobenzene production areas			
MCB Storage--Day tanks, on stairway	114C	1.3	--
Grade level--#3 chlorinator	116C	1.3	--
Grade level--below benzene stripper	115C	0.3	--
Grade level--crude liquor transfer	118C	0.9	--
Grade level--near chlorinator cooler	125C	0.5	--
1st level--between #2 & #3 chlorinators	133C	3.0	--

*Below 0.1 ppm.
+A trainee--was wearing an organic-vapor-cartridge respirator while gathering quality-control product samples.
±Operator was preparing equipment for maintenance.
Note: BD = Below Detection.

Table A-3. Area concentrations of para-nitrochlorobenzene at Plant A, November 1978.

Location and sample number		Time (min)	Volume (liter)	Concentration* (ppm)
Above underground PNCB storage tank	S1	415	70.5	--*
Below #1 Nitrator (on OC booth)	S2	406	71.7	--
Between #1 and #2 separators	S3	401	77.7	--
Grade level, near NCB pumps	S4	375	62.2	--

*All were below detectable limit (less than 10 micrograms).

Table A-4. Results of side-by-side personal sampling for monochlorobenzene and benzene conducted by Plant A and SRI International, November, 1978.

	Monochlorobenzene			Benzene		
	$\bar{X}g$	Sg	N	$\bar{X}g$	Sg	N
SRI*	0.2 ppm	3.8	27	1.8 ppm	2.8	15
Plant A+	0.2 ppm	2.5	18	1.5 ppm	2.8	14

*Charcoal tubes used as collection medium.

+The collection medium was a 3M passive sampler. All samples (SRI and Plant A) were analyzed using desorption with carbon disulfide and analysis by gas chromatography with flame ionization detection.

Table B-1. Individual personal and area TWA concentrations of monochlorobenzene at Plant B, January 1979.

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Senior Operator	2C	0.5
	5C	2.8
	10C	0.4
	13C	2.7
Distillation Operator	1C	0.2
		0.1
		2.9
		1.8
Material Handler	3C	0.8
		0.7
		0.5
Boilermaker--replacing MCB primary condenser and removal of drums	4C	0.4
Distillation Operator--QC sampling at Azeo #1, MCB receiving	15C	2.8
Blank	6C	--*
Area Samples		
Near column "B" at bottoms sampling port+	14C	14.2
Near column "D" bottoms pump	16C	4.6
Walkway between MCB and benzene sampling ports	17C	3.1±

*Below detectable limit (less than 10 micrograms).
+Column B was not operating
±Sampling pump stopped operating--results are questionable.

Table B-2. Individual personal and area TWA concentrations of benzene and ortho-dichlorobenzene at Plant B, January 1979.

Job title/location and sample number		TWA concentration (ppm) Benzene	O-dichloro-Benzene
Personal samples			
Senior Operator	2C	0.3	0.1
	5C	0.8	0.8
	10C	0.1	0.1
	13C	0.8	0.2
Distillation Operator	1C	0.2	0.1
		0.1	0.1
		0.3	0.2
		1.2	0.1
Material Handler	3C	3.5	0.1
		3.0	0.1
		1.4	0.1
Area samples			
Boilermaker--replacing MCB primary condenser and removal of drums	4C	0.1	0.1
Distillation Operation--QC sampling at Azeo #1, MCB receiving	15C	1.6	0.1
Blank	6C	--*	--*
Area--near column "B" at bottoms sampling port†	14C	5.5	0.6
Area--near column "D" bottoms pump	16C	0.6	0.4
Area--walkway between MCB and BZ sampling ports	17C	1.3‡	0.3‡

* Below detectable limit (less than 10 micrograms).
† Column B was not operating.
‡ Sampling pump stopped operating--results are questionable.

Table C-1. Individual personal and area TWA concentrations of monochlorobenzene at Plant C, June 1979.

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Operator (chlorobenzol)	964	--*
	966	--
	982	--
	987	--
	989	--
	980	--
	992	--
	999	--
Mechanic (chlorobenzol)	951	--
Maintenance Worker (adjacent area)	956	--
	996	--
Construction Worker (new construction around chlorinator)	105	--
Badger Operator	961	0.42
	975	0.36
	985	0.25
	994	0.59
Transfer Man (Badger area)	960	1.79
	108	1.90
Area samples		
Chlorinator--control room	950	--
	976	--
	109	--
Chlorinator--north end	952	--
	972	--
	102	--
Badger--control room	963	0.21
	973	0.22
	997	--
Badger--GC room	962	0.40
	970	--
	991	--
Badger #3--N.E. corner	967	0.62
	977	0.86
	100†	1.04
Badger #2--N.E. corner	953	0.85
	974	2.35

(continued)

Table C-1. (Cont'd) Individual personal and area TWA concentrations of monochlorobenzene at Plant C, June 1979.

Job title/location and sample number		TWA concentration (ppm)
Area Samples		
MCB tank car loading rack--West end	957‡	3.15
	104§	10.50
Interim benzene unloading station	101†	--

*Below detectable limit (less than 10 micrograms)

†Sampling pump stopped working--results questionable.

‡30,000 gal. MCB loaded (day 1 of survey).

§40,000 gal. MCB loaded (day 2 of survey).

Table C-2. Individual personal and area TWA concentrations of benzene and dichlorobenzene at Plant C, June 1979.

Job title and sample number		TWA concentration (ppm) Benzene	Dichloro-Benzene
Personal samples			
Operator	964	0.17	0.54
	966	0.09	--
	982	--	--
	987	0.03	--
	989	0.03	--
	980	--	--
	992	0.05	--
	999	--	--
Mechanic	951	--	--
Maintenance Worker (adjacent area)	956	--	2.28
	996	--	1.30
Construction Worker (new construction around chlorinator)	105	--	--
Badger Operator	961	0.30	--
	975	0.36	--
	985	0.25	--
	994	0.28	--
Transfer Man	960	0.82	0.23
	108	0.24	--
Area samples			
Chlorinator--control room	950	0.04	--*
	976	--	--
	109	--	--
Chlorinator--north end	952	0.08	--
	972	--	--
	102	--	--
Badger--control room	963	0.21	--
	973	0.34	--
	997	0.33	--
Badger--GC room	962	0.23	--
	970	0.30	--
	991	0.08	--
Badger #3--N.E. corner	967	0.21	--
	977	0.34	0.33
	100†	0.15	--

(continued)

Table C-2. (Cont'd) Individual personal and area TWA concentrations of benzene and dichlorobenzene at Plant C, June 1979.

Job title and sample number		TWA concentration (ppm) Benzene	Dichloro-Benzene
Area samples			
Badger #2--N.E. corner	953	0.15	0.33
	974	0.11	0.75
MCB tank car loading rack--West end	957‡	0.07	--
	104§	0.09	--
Interim benzene unloading station	101†	0.20	--

*Below detection limit--0.001 for benzene; 0.01 for dichlorobenzene.

†Sampling pump stopped working--results questionable.

‡30,000 gal. MCB loaded (day 1 of survey).

§40,000 gal. MCB loaded (day 2 of survey).

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