

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

MOBIL CHEMICAL COMPANY
MT. PLEASANT, TENNESSEE

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. HE 79-108- 647

December 1979

I. SUMMARY

On June 8, 1979, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate a potential health hazard for laboratory technicians exposed to vapors from herbicide chemicals (Merphos, Bifenox, and Ethoprop) released into a quality control laboratory from gas chromatograph (GC) ejection ports at the Mobil Chemical Company in Mt. Pleasant, Tennessee. To investigate the extent of this potential hazard, NIOSH conducted a site visit to the laboratory, interviewed laboratory personnel, and evaluated the laboratory ventilation systems. No adverse health effects were noted for any of the laboratory personnel, and general laboratory ventilation was adequate. Exhaust air velocity was measured at the face of the laboratory ventilation hoods. Face velocities were below recommended minimums (100-150 feet per minute) for all 4 laboratory hoods. The face velocity for hoods No. 1 and No. 2 was 60 feet per minute (fpm); for No. 3, 78 fpm; and for No. 4, only 26 fpm.

II. TOXICITY DETERMINATION

On the basis of the data obtained in this investigation, NIOSH determined that laboratory hood exhaust capacity should be increased. The herbicide vapors released from the gas chromatographs are generated from liquid sample volumes of 1 microliter or less and therefore are not sufficient to present a health hazard for laboratory technicians. Recommendations for improving laboratory ventilation and a suggested method for directing GC vapors away from laboratory personnel are discussed on page 5 of this report.

III. INTRODUCTION

The Occupational Safety and Health Act of 1970*, authorizes the Secretary of Health, Education, and Welfare, following a written request by any 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. NIOSH received such a request from a Mobil

*Section 20(a)(6), 29 U.S.C. 669(a)(6)

Chemical Company laboratory technician, an authorized representative of two additional laboratory employees. The requestor complained that previously GC ejection port vapors had been vented to an exhaust system but the company had disconnected the vent lines and there was nothing planned for correcting the problem. The requestor stated that the employees' main concern was Merphos, which they believed was a suspected carcinogen.

On July 16-17, 1979, an initial survey was conducted by the Regional Industrial Hygienist from NIOSH, Region IV. Following an opening conference with management representatives, the NIOSH investigator was given a walk-through tour of the entire plant. A description of the procedures used for analyzing samples in the quality control laboratory was provided by the laboratory supervisor. Confidential interviews were conducted with five laboratory employees to determine if they had experienced health problems from working in the laboratory with various herbicide chemicals. The laboratory ventilation system was evaluated and the results of this evaluation were provided to management representatives at the closing conference. Recommendations to improve the exhaust efficiency of the laboratory hoods were also discussed.

IV. HEALTH HAZARD EVALUATION

A. Background

The Mobil Chemical Company, Crop Chemicals Division at Mt. Pleasant, Tennessee, manufactures agricultural herbicides. The products are Merphos, Ethoprop, and Bifenox, but only two can be produced at any one time. At the time of this survey, Merphos production was closing down and the plant was being prepared to start producing Ethoprop. The plant is also producing diethylhydrogen phosphite (DEF), a chemical intermediate used by the Stouffer Chemical Company for the manufacture of a fire retardant. Mobil plans to complete production of DEF during the first quarter of 1980 and has no plans to produce DEF beyond that date. Ethoprop and Bifenox are sold as technical products to formulators to be used in preparing the herbicides Mowcap (containing Ethoprop) and Mowdown (containing Bifenox). Merphos is mixed with xylene at Mobil and sold under the trade name Folex, a cotton defoliant. Under normal production schedules, Merphos is manufactured 2 months/year during the summer and Ethoprop and Bifenox 10 months/year.

The plant has been in operation for 10 years and employes 33 administrative and 75 production personnel. The plant operates three shifts per day, 7 days per week, and production workers rotate from shift to shift according to the following schedule:

7 days on - 2 days off
7 days on - 1 day off
7 days on - 4 days off

The plant has a very active health and safety program and all employees, including laboratory personnel, receive an annual physical examination which includes blood tests, urine analysis, and pulmonary function tests. Blood cholinesterase levels are checked quarterly and once every 3 weeks for workers formulating Ethoprop.

Twelve people work in the quality control (QC) laboratory: 2 supervisors, 2 chemists, and 8 lab technicians. Seven of the eight lab technicians work a rotating schedule. The laboratory is set up as shown in the attached drawing (see Figure 1). The GC's are used to analyze process samples which are brought to the lab by the production workers. Ninety-seven analyses were performed each day on Merphos production samples. Twenty seven of these samples were Merphos, some containing unreacted raw materials. A Bifenox and Ethoprop samples analysis schedule was not available at the time of this survey. Process samples for these products would also contain Bifenox or Ethoprop and unreacted raw materials. Bifenox samples are diluted by a factor of 10 with methyl ethyl ketone (MEK). When open, the sample containers are under laboratory ventilation hoods. The GC injection volumes used for all sample analyses are:

1. Bifenox Samples - 1 microliter
(10% sample-90% MEK)
2. Merphos Samples - 0.2 microliters
3. Ethoprop - 0.5 microliters

At one time the GC ejection ports had been connected via copper tubing to a plastic exhaust pipe leading to the ventilation hood No 1 exhaust system. The copper tubing was removed because the vapors from the GC's were condensing in the tubing and blocking the GC ejection ports. Considering the small sample volumes injected into the GC's, the company concluded that the overhead ceiling exhausts were adequate to remove GC vapors from the work area.

B. Evaluation Methods

Face velocities and exhaust duct velocities of the laboratory ventilation hoods were measured with a Kurz Model 441 Air Velocity Meter. The face velocities were measured at 12 points and averaged (see Figure 2). The duct velocities for hoods No. 1 and No. 3 were measured by traversing the air velocity meter detector probe along the inside diameter of the exhaust ducts. The measurements were taken through a port hole located approximately 2-3 duct diameters from the exhaust fan.

C. Evaluation Criteria

The NIOSH Criteria Document for "Manufacture and Formulation of Pesticides" has classified pesticides into 3 groups (Group I, II or III). Pesticides in Group I are the most toxic. Pesticides in

Group I produce acute effects at extremely low dose levels or serious, irreversible effects. Certain pesticides in this group have been classified based on irreversible effects including probable carcinogenicity; potential teratogenicity, mutagenicity, or neurotoxicity; and reproductive effects as demonstrated in animal test systems and human epidemiologic studies. Pesticides which inhibit cholinesterase have been identified. Merphos, and Ethoprop are classified by NIOSH as Group I pesticides¹. In order that laboratory personnel can be better informed regarding the toxic and hazardous properties of the chemicals contained in the samples they analyze, a listing of the chemicals and toxicity information on Merphos, Bifenox, and Ethoprop is presented in Table. 1.

The environmental criteria which should be used for evaluating the potential adverse health effects for workers exposed to these chemicals is presented in Table 2. Listed in Table 2, for each chemical substance, is the recommended environmental limit and reference source for the recommended limit, the level which is immediately dangerous to life and health, the limit established by Mobil Chemical, the current OSHA standard, and the principal health effects or symptoms underlying each recommended limit.

D. Results and Discussion

A summary of the air velocity measurements is presented in Table 3. The exhaust velocities for the laboratory hoods were below recommended minimums. NIOSH recommends that the average exhaust face velocity for controlling Class I and Class II contaminants should be at least 100 fpm, and for Class III contaminants at least 150 fpm⁶ (see Table 4 and 5). The average face velocities for the hoods in the Mobil QC laboratory were 80, 60, 78, and 26 fpm for hoods No. 1, 2, 3, and 4, respectively. Class III contaminants such as benzene had been used by the research chemist under hood No. 4, yet this hood was the least efficient of all. The duct velocity measurements obtained for hoods No. 1 and No. 3 were used to determine the approximate exhaust volume for these two hoods. For a 9" duct, the exhaust volume for the two systems was inadequate to maintain recommended face velocities. For example, to maintain a 100 fpm face velocity for a hood having a sash opening of 5 ft. x 2.5 ft. requires an exhaust volume of at least 1250 cubic feet per minute (cfm). The exhaust volumes for hoods No. 1 and No. 3 were only around 650 cfm.

None of the 5 laboratory employees interviewed during the initial survey reported health problems which they believed were work-related. One individual had reported a previous problem with wheezing and nasal irritation while working in the Field Formulation Lab, but had not noticed any problems since working in the main lab. One other employee, interviewed by telephone, complained of occasional headaches, sneezing and coughing, and also about the objectionable odor in the lab when running samples containing mercaptans

E. Recommendations

1. The laboratory hood exhaust systems should be evaluated and corrective actions taken to increase the exhaust volumes to insure that adequate face velocities are maintained. Reduced performance could be caused by such things as reduced fan speed, dust accumulation in ducts or on fan blades, broken joints, too many exhaust ports on one system, restrictions in ducts, or poor design and improper fan selection. Until the systems are improved, the moveable sash should not be opened more than halfway. This will reduce the area of the face or sash opening and thereby increase the face velocity.

2. The Mobil Engineering Staff should be asked to design a chimney (approximately 3 feet long) which could be mounted around the GC ejection ports. This chimney would direct the vapors away from the lab technicians' breathing zone and toward the ceiling exhaust. The diffusers on the ceiling exhaust should be removed to improve capture efficiency.

V. REFERENCES

1. Criteria for a Recommended Standard, "Occupational Exposure During the Manufacture and Formulation of Pesticides", DHEW (NIOSH) Publication No. 78-174 (July 1978).
2. NIOSH/OSHA Pocket Guide to Chemical Hazards, DHEW (NIOSH) Publication No. 78-210 (September 1978).
3. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1979.
4. Summary of NIOSH Recommendations for Occupational Health Standards, DHEW (NIOSH) Publication (October 1978).
5. Occupational Diseases, A Guide to Their Recognition, Revised Edition, DHEW (NIOSH) Publication No. 77-181 (June 1977).
6. Recommended Industrial Ventilation Guidelines, DHEW (NIOSH) Publication No. 76-162 (January 1976).

VI. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by: Stanley A. Salisbury
Regional Industrial Hygienist
NIOSH Region IV
Atlanta, Georgia

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

Report Typed by: Barbara Rice
Secretary
NIOSH, Region IV
Atlanta, Georgia

VII. DISTRIBUTION AND AVAILABILITY

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 ninety (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 the NIOSH Publications Office at the Cincinnati, Ohio address.

Copies of this report have been sent to:

- a) Mobil Chemical Company, Mt. Pleasant, Tennessee
- b) Authorized Representative of Employees
- c) U.S. Department of Labor, OSHA, Region IV
- d) Tennessee Department of Labor, Nashville, Tennessee

For the purpose of informing the approximately 12 "affected employees", the employer will promptly "post" the Determination Report for a period of thirty (30) calendar days in a prominent place(s) near where the affected employees work.

TABLE 1

Mobil Chemical Company
Mt. Pleasant, Tennessee

Crop Chemicals Manufactured

I. MERPHOS

A. Manufacturing Process Chemicals

1. Hexane - raw material
2. Phosphorus Trichloride (PCl₃) - raw material
3. Butyl Mercaptan - raw material
4. Acetic Anhydride - additive for odor control
5. Cuprous Chloride - additive, anti-oxidizer
6. Hydrochloric Acid - by-product
7. Sodium Hydroxide - raw material

B. Toxicity Information

Merphos (S,S,S - Tributyl Phosphorotrithioite) has been classified by NIOSH as a Group I pesticide. NIOSH has designated Merphos as an organophosphorous pesticide which can cause irreversible neurotoxic effects.* The Environmental Protection Agency has placed Merphos on the Rebuttable Presumptions Against Registration (RPAR) list because of reported delayed neurotoxicity in hens. There were no reports of carcinogenic effects in the literature.

II. BIFENOX

A. Manufacturing Process Chemicals

1. 2, 4 Dichlorophenol (DCP) - raw material
2. Dimethylformamide (DMF) - raw material
3. Methyl Chloride - raw material
4. Potassium Hydroxide (KOH) - raw material
5. Methanol - raw material
6. Nitrated Methyl Meta Chlorobenzoate (NBE) - raw material
7. Potassium Chloride - by-product

B. Toxicity Information

Bifenox (Methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate) is relatively non-toxic with an oral LD 50 of 6400 mg/kg. Bifenox has been registered by EPA as a Class III pesticide. No long term inhalation studies or adverse health effects in humans have been reported. There were no reports of carcinogenic effects in the literature.

Note: The NIOSH Criteria Document* has Bifenox classified as a Group I pesticide by mistake. This error was verified by the NIOSH Division of Criteria Documentation and Standards Development (DCDSD) through personal communications on December 5, 1979, between the Project Officer and DCDSD personnel.

TABLE 1 Continued

III. ETHOPROP

A. Manufacturing Process Chemicals

1. Sodium Hydroxide - raw material
2. Ethanol - raw material
3. Hexane - raw material
4. Hydrochloric Acid - by-product & raw material
5. Phosphorus Oxychloride (POCl₃)
6. Propyl Mercaptan - raw material
7. Chloridate - chemical intermediate

B. Toxicity Information

Ethoprop (O-Ethyl-S, S-Dipropyl Phosphorodithioate) has been classified by NIOSH as a Group I pesticide. NIOSH has designated Ethoprop as an organophosphorous pesticide.* Ethoprop is a cholinesterase inhibitor. Warning symptoms include weakness, headaches, tightness of chest, blurred vision, nonreactive pinpoint pupils, salivation, sweating, nausea, vomiting, diarrhea, and adominal cramps. There were no reports of carcinogenic effects in the literature.

* Refer to DHEW (NIOSH) Publication No. 78-174, Criteria for a Recommended Standard, "Occupational Exposure During the Manufacture and Formulation of Pesticides," (July 1978).

TABLE 2

Evaluation Criteria
 Mobil Chemical Company
 Mt. Pleasant, Tennessee

Substance	Recommended Environmental Limit/Source	IDLH	Mobil Std.	OSHA Std.	Health Effects Considered
Hexane	100 PPM TWA / NIOSH 510 PPM C / NIOSH	5000 PPM	500 PPM	500 PPM	skin, nervous system effects
Phosphorus Trichloride	0.5 PPM TWA / ACGIH	50 PPM	0.5 PPM	0.5 PPM	eye nose & throat irritation, pulmonary edema, skin & eye burns
Butyl Mercaptan	0.5 PPM TWA / ACGIH	2500 PPM	0.5 PPM	10 PPM	disagreeable odor, eye, skin & upper respiratory irritation, nervous system effects at high concentrations
Acetic Anhydride	5 PPM C / ACGIH	1000 PPM	5 PPM	5 PPM	conjunctivitis, photophobia, eye lacrimation, nose & throat irritation at high concentrations; contact & allergic dermatitis
Sodium Hydroxide	2mg/M ³ TWA / NIOSH	200mg/M ³	-	2mg/M ³	skin & eye burns, nasal irritation, pneumonitis
2, 4 Dichlorophenol	NONE AVAILABLE	-	NONE	NONE	skin dermatitis
Dimethyl Formamide	10 PPM TWA / ACGIH	3500 PPM	10 PPM	10 PPM	skin dermatitis, colic, nausea, vomiting, liver damage
Methyl Chloride	100 PPM TWA / ACGIH	10000 PPM	100 PPM	100 PPM	dizziness, nausea, headache, blurred vision, slurred speech, liver & kidney damage
Potassium Hydroxide	NONE AVAILABLE	-	NONE	NONE	Skin & eye burns, nasal irritation, pneumonitis

TABLE 2 Continued

Substance	Recommended Environmental Limit/Source	IDLH	Mobil Std.	OSHA Std.	Health Effects Considered
Methanol	200 PPM TWA / NIOSH 800 PPM C / NIOSH	25000 PPM	200 PPM	200 PPM	eye irritation, headache, lightheadedness, vision disturbances blindness, metabolic acidosis
Nitrated Methyl Meta Chlorobenzoate (NBE)	NONE AVAILABLE	-	NONE	NONE	no toxicity data available
Ethanol	1000 PPM TWA / ACGIH	-	1000 PPM	1000 PPM	eye & nasal irritation at high concentrations; headache, drowsiness, tremor & fatigue at prolonged exposures
Phosphorus Oxychloride	0.5 PPM TWA / MOBIL	50 PPM	0.5 PPM	NONE	toxicity similar to phosphorus trichloride
Propyl Mercaptan	NONE AVAILABLE	-	NONE	NONE	disagreeable odor, eye, skin & upper respiratory irritation
Chloridate	NONE AVAILABLE	-	NONE	NONE	no toxicity information available
Heptane	85 PPM TWA / NIOSH 440 PPM C / NIOSH	4250 PPM	400 PPM	500 PPM	skin & nervous system effects
Xylene	100 PPM TWA / NIOSH 200 PPM C / NIOSH	10000 PPM	100 PPM	100 PPM	central nervous system depressant, airway irritation
Chlorine	0.5 PPM C / NIOSH	25 PPM	1 PPM	1 PPM C	eye & airway irritation

PPM = Parts per million parts of air

TWA = Time weighted average concentration for an 8 or 10 hour work shift exposure

C = Ceiling limit

IDLH = Immediately dangerous to life and health (see reference 2)

ACGIH = American Conference for Governmental Industrial Hygienists (see reference 3)

NIOSH = National Institute for Occupational Safety and Health (see reference 4 & 5)

TABLE 3

Laboratory Vent Hood Measurements
 Mobil Chemical Company
 Mount Pleasant, Tennessee

July 16-17, 1979

HOOD FACE VELOCITIES (see Figure 2)

<u>Hood No. 1</u>				<u>Hood No. 2</u>			
65	75	80	75	40	80	120	100
50	50	75	60	30	60	60	80
40	60	50	20	35	35	20	50
(Avg. = 60 fpm)				(Avg. = 60 fpm)			
<u>Hood No. 3</u>				<u>Hood No. 4</u>			
100	100	70	75	30	40	25	15
100	100	85	50	25	50	20	10
80	75	40	60	25	25	20	25
(Avg. = 78 fpm)				(Avg. = 26 fpm)			

Recommended face velocity* (see Table 4 & 5)

LAB HOOD EXHAUST DUCT TRAVERSE MEASUREMENTS

<u>Duct No. 1</u>	<u>Duct No. 3</u>
1300	2200
1300	2200
1400	2000
1450	1800
1450	1650
1500	1250
1450	800
1450	700
1400	900
1400	-
Avg. Velocity = 1450 fpm	Avg. Velocity = 1500 fpm

Duct Diameter = 9 in.

Duct Area = 0.4418 sq. ft.

Exhaust Volume = Duct Area x Duct Velocity

Exhaust Volume = 641 cfm

Exhaust Volume = 663 cfm

Recommended Exhaust Duct Velocity = 2000 fpm*

*"Recommended Industrial Ventilation Guidelines," DHEW (NIOSH) Publication No. 76-162, Page 157 (January 1976).

- NOTES: 1. fpm = linear feet of air per minute
 2. cfm = cubic feet of air per minute

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TABLE 4

Minimum Exhaust Velocity Requirements*

Contaminant Class	Laboratory Hood
I	Face velocity: 100 fpm avg. 50 fpm min.
II	Face velocity: 100 fpm avg. 75 fpm min.
III**	Face velocity: 150 fpm avg. 125 fpm min.

* Minimum exhaust face velocities shall be based on the maximum hood face area.

**For cancer-suspect agents, these requirements supplement (are in addition to) control requirements prescribed for specific materials in 29 CFR 1910.1000.

NOTE: Adapted from recommendations presented in DHEW (NIOSH) Publication No. 76-162, "Recommended Industrial Ventilation Guidelines," Page 166, (January 1976).

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TABLE 5

Classification of Contaminant Substances

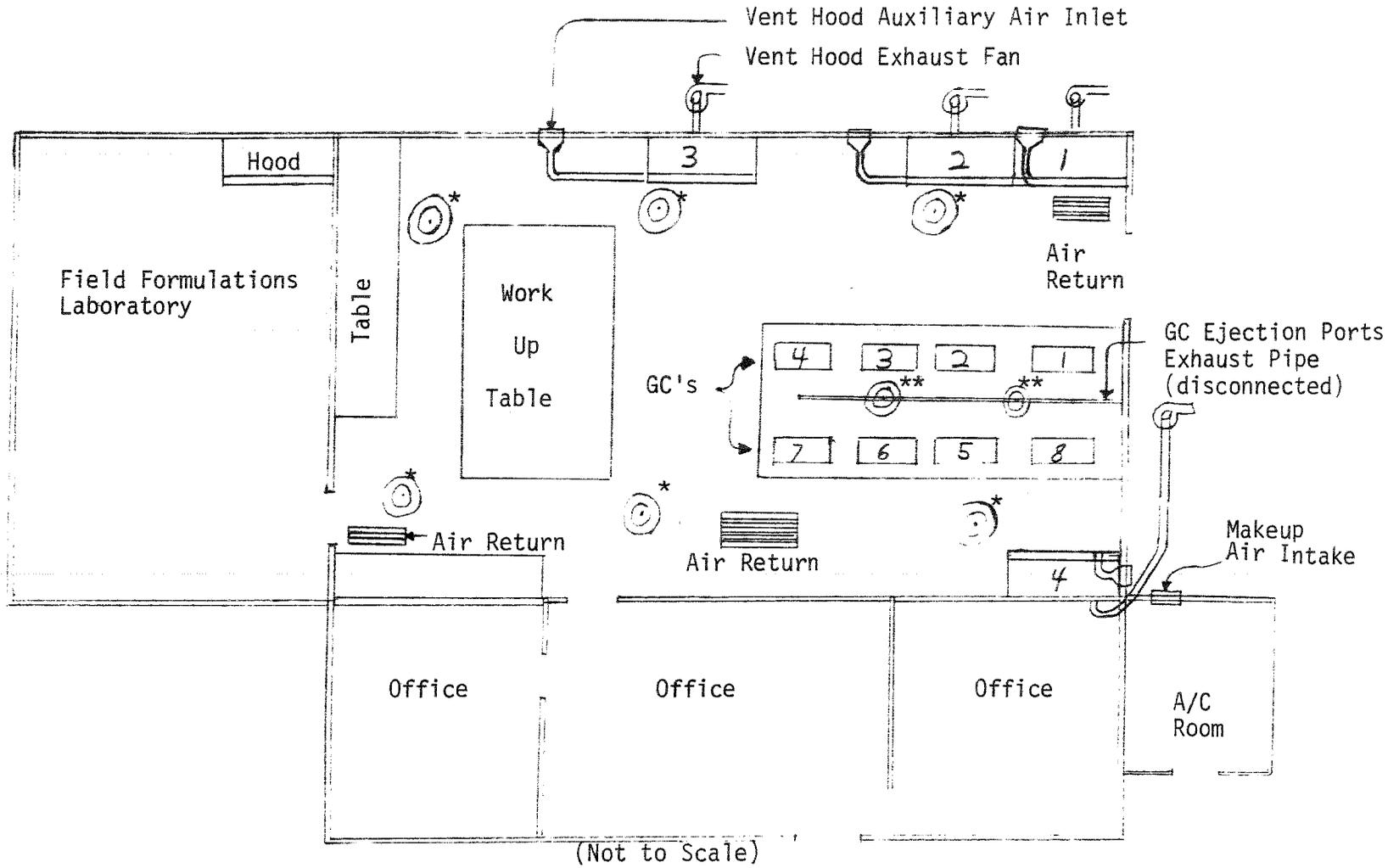
Contaminant Class	Contaminant Substances	
	Gases & Vapors	Dusts, Fumes & Mists
I	Substances with exposure limits of 100 ppm and above	Substances with exposure limits of 10 mg/M ³ and above
II	Substances with exposure limits of 1 ppm and above (up to 100 ppm)	Substances with exposure limits of 0.1 mg/M ³ and above (up to 10 mg/M ³)
III	Substances with exposure limits below 1 ppm; also, radioisotopes, carcinogens, and cancer-suspect agents	Substances with exposure limits below 0.1 mg/M ³ ; also, radioisotopes, carcinogens, and cancer-suspect agents

NOTES: This classification does not include biological agents.

The above recommendations are taken from DHEW (NIOSH) Publication No. 76-162, "Recommended Industrial Ventilation Guidelines," Page 167 (January 1976).

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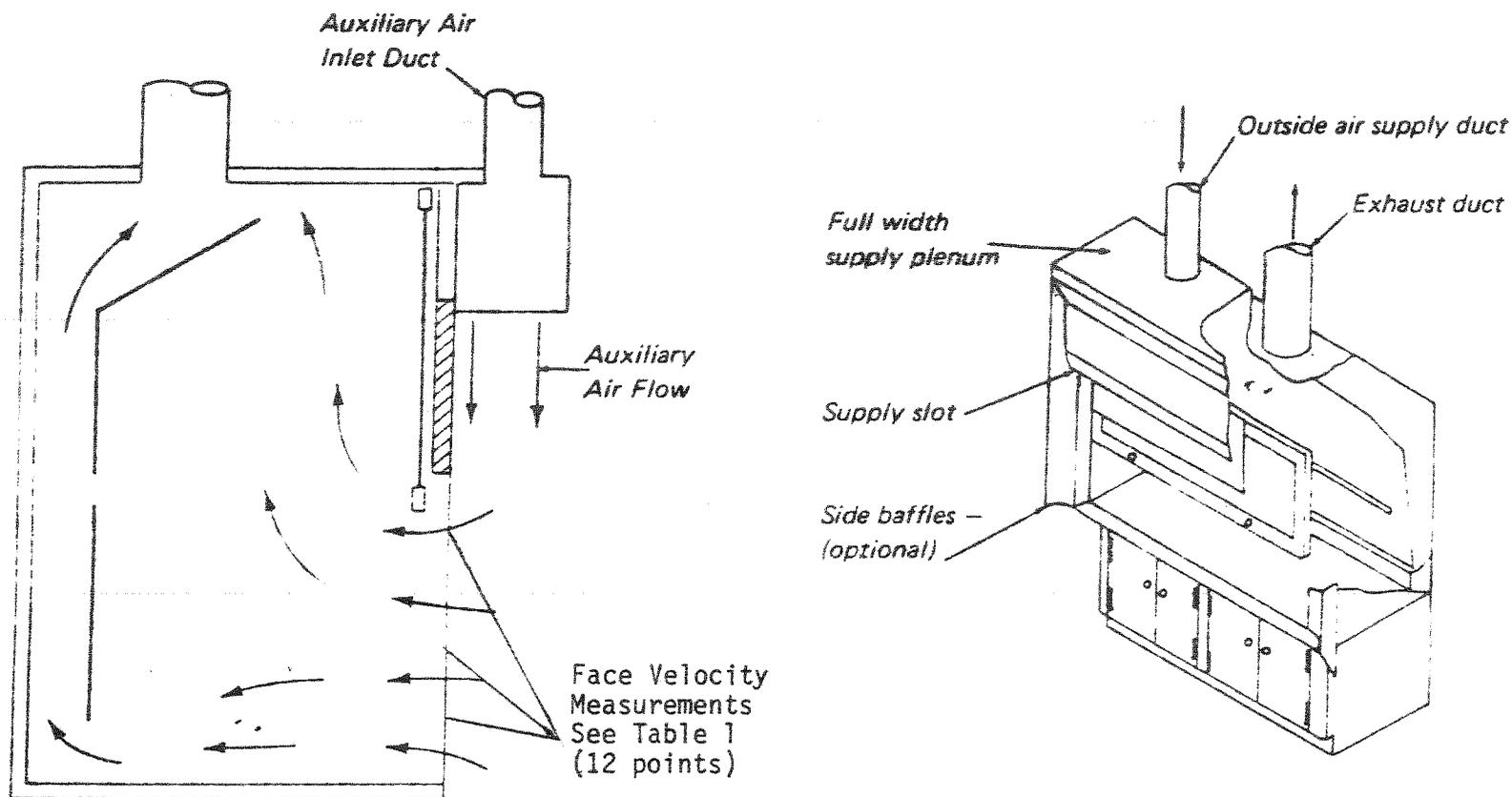
FIGURE 1
Laboratory Floor Plan



* Ceiling Diffuser - Supply Air
**Ceiling Diffuser - Exhaust Air (to vent hood #1 exhaust fan)

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FIGURE 2



LABORATORY HOOD WITH AUXILIARY AIR SUPPLY