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

HEALTH HAZARD EVALUATION DETERMINATION REPORT
HE 78-90-739

FMC CORPORATION
SPECIALTY CHEMICALS DIVISION
NITRO, WEST VIRGINIA

September 1980

I. SUMMARY

In May 1978 the National Institute for Occupational Safety and Health (NIOSH) received a request from an authorized representative of employees to evaluate the exposures of Mechanical Department workers at the FMC plant in Nitro, West Virginia to phosphorus trichloride (PCl_3) and phosphorus oxychloride ($POCl_3$). Workers were reportedly experiencing respiratory problems due to exposures while working on equipment.

Environmental samples for PCl_3 and $POCl_3$ were collected on the $PCl_3/POCl_3$ operators, two tank yard workers and one maintenance employee on May 23 and 24, 1979. All air sample results for PCl_3 and $POCI_3$ were below the lower analytical limit of detection with two exceptions: (1) a tank yard operator was exposed to approximately 6 mg/M^3 of PCl_3 during a one-hour truck loading operation, and (2) a maintenance employee was exposed to approximately 4 mg/M^3 of $POCl_3$ during the pulling off of a pump in a 25-minute period. Upon calculation of an 8-hour time weighted average concentration, the tank yard operator was not found to be exposed above the evaluation criterion of 3 mg/M^3 for PCl_3. No evaluation criterion exists for $POCl_3$.

The medical study included a questionnaire and pulmonary function tests on 37 exposed and 22 unexposed employees. Exposed employees had a significantly higher prevalence (65%) of occasional respiratory discomfort than unexposed employees (5%), but no consistent association between pulmonary function parameters and exposure to $PCl_3/POCl_3$ could be documented.

The data from this study suggest that there are intermittent exposures to $PCl_3/POCl_3$ which can cause acute respiratory symptoms. Recommendations concerning respiratory protection are provided on page 6.

II. INTRODUCTION

Under the Occupational Safety and Health Act of 1970*, NIOSH investigates the toxic effects of substances found in the workplace. In May 1978, NIOSH received such a request from an authorized representative of employees, Local 12757, of the United Steelworkers of America. It was asked that NIOSH evaluate the exposures of Mechanical Department (Maintenance) employees to two chemicals - phosphorus trichloride and phosphorus oxychloride - manufactured at the facility. It was felt that the two chemicals had caused employees to suffer from respiratory problems due to overexposures while working on equipment. Certain young non-smokers also seemed to be suffering from respiratory disease of occupational origin.

III. BACKGROUND

The process under evaluation was the production of PCl_3 and $POCl_3$, both corrosive, musty smelling, clear liquids. The production of PCl_3 and $POCl_3$ began at the facility in 1960. At the time of the survey, there were about 150 operators, maintenance and service employees at the facility, with nine working directly in $PCl_3/POCl_3$ production areas. There are approximately 40 maintenance personnel who work in all areas of the facility, not only the $PCl_3/POCl_3$ area. There are three work shifts per day for the production employees and one for maintenance workers.

Production of $PCl_3/POCl_3$ takes place in closed systems as they react violently with water and give off hydrogen chloride gas and phosphorous acid in ordinary atmospheres. Vaporized chlorine from tank cars is sprayed into a phosphorus trichloride-phosphorus mixture in a reactor under a specific temperature and pressure. The heat of reaction vaporizes PCl_3 through a distillation column. The distilled product, after being sent through condensers, is pumped to storage for sales or in-plant use to manufacture $POCl_3$.

$POCl_3$ is produced in a batch operation in a reactor by air oxidation of PCl_3. The $POCl_3$ product is also pumped to product storage for sales or in-plant use.

Two operators per shift oversee the closed system production of PCl_3 and $POCl_3$. Their duties include (1) collecting product samples in eight-ounce glass bottles, (2) adjusting valves settings during the changing of chlorine tank cars, and (3) draining lines prior to maintenance operations.

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*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 and Human Services 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 tank yard personnel are responsible for attaching loading lines to tank cars and trucks for $PCl_3/POCl_3$ shipment. While the product is pumped through fittings on the tops of the tanks, generated gases and vapors are exhausted from the man head entry into a flexible exhaust duct. Suction is created by a water jet. Exposure to $PCl_3/POCl_3$ may occur when connecting or disconnecting any of these lines.

Maintenance personnel are involved in repair of the lines and pumps used to transfer the $PCl_3/POCl_3$. Maintenance personnel are also involved in the "clean-out" of 64-inch diameter reflux columns that make up part of the closed production system. This operation may occur for about three days every four to six months. Personal protective equipment - rubber suits, gloves, and respirators - are supplied to the employees during this operation or whenever potential exposures may occur.

The company maintains three types of respirators for use in the $PCl_3/POCl_3$ area: (1) a gas mask for protection against chlorine, (2) a 30-minute self-contained breathing apparatus, and (3) a mouthpiece respirator for protection against chlorine and acid gas (escape or short-duration exposures).

IV. EVALUATION DESIGN AND METHODS

A walk-through survey of the $PCl_3/POCl_3$ production areas and storage facilities was conducted on June 21, 1978.

NIOSH mailed questionnaires to 37 maintenance employees exposed to $PCl_3/POCl_3$, whose names and addresses were provided by the union. Of the 16 who returned the questionnaire, six had respiratory symptoms. NIOSH also reviewed the company's pulmonary function testing data on 35 maintenance employees. Eight had a low* one-second forced expiratory volume (FEV-1), forced vital capacity (FVC), or FEV-1/FVC ratio.

A follow-up environmental-medical survey was conducted on May 22-25, 1979. Environmental samples for PCl_3 and $POCl_3$ were collected on the operators, tank yard personnel and maintenance employees. Samples for PCl_3 were collected using midget impingers containing distilled water at a flowrate of 200 cc/minute. Samples for $POCl_3$ were taken on charcoal tubes at flowrates of 50 cc/minute and 200 cc/minute. Both PCl_3 and $POCl_3$ samples were analyzed colorimetrically.

On the basis of the findings of the mailed questionnaire the follow-up medical survey survey included an interviewer-administered respiratory questionnaire and pulmonary function tests. The questionnaire was based, in part, on the survey instrument developed by the Medical Research Council of Great Britain.[1] FEV-1 and FVC were measured with an Ohio Medical Model 842* dry rolling seal spirometer. Three properly performed - as judged by the pulmonary function technician - exhalation maneuvers were obtained on each participant, and the best FEV-1 and FVC was used for subsequent calculations. Predicted normal values for FEV-1 and FVC were calculated according to the Morris formula;[2] the predicted normal values for black participants were calculated by multiplying the Morris predicted value by 0.85.[3-5] An individual's predicted FEV-1/FVC was calculated directly from his predicted FEV-1 and FVC.

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*An FEV-1 or FVC <80% predicted normal, or FEV-1/FVC <0.7 was considered "low."

All maintenance employees whose job involved exposure to $PCl_3/POCl_3$ were invited to participate in the medical survey, as were a comparable number of unexposed employees.

V. EVALUATION CRITERIA

PCl_3 and $POCl_3$ are potent skin, eye, throat and respiratory tract irritants. Repeated exposure to these substances can lead to chronic cough, wheezing and bronchitis.[6-7]

Airborne exposure limits for the protection of the health of workers have been recommended or promulgated by several sources. These limits are established at levels designed to protect workers occupationally exposed to a substance on an 8-hour day, 40-hour per week basis over a normal working lifetime. For this investigation, the criteria used to assess the degree of health hazards to workers were selected from two sources:

1. Threshold Limit Values (TLV): Guidelines for Airborne Exposures Recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for 1979.

2. OSHA Standard: The air contaminant standards enforced by the U.S. Department of Labor - Occupational Safety and Health Administration - as found in the Federal Register - 29 CFR 1910.1000 (Table Z-1).

The ACGIH TLV and the OSHA standard for PCl_3 is 3 mg/M^3. A permissible exposure limit for $POCl_3$ has not been established.

VI. RESULTS AND DISCUSSION

A. Environmental

Results of air sampling are presented in Table 1. The $PCl_3/POCl_3$ operators, two tank yard and one maintenance employees were monitored during two working days under normal operating conditions. All air samples were below the lower analytical limit of detection with two exceptions: (1) a tank yard operator was potentially exposed to approximately 6 mg/M^3 of PCl_3 during a one-hour truck loading operation, and (2) a maintenance employee was potentially exposed to approximately 4 mg/M^3 of $POCl_3$ during the pulling off of a pump in a 25 minute period. Both employees were wearing proper respiratory protection (chlorine gas masks) while performing these duties. No other known exposures occurred through the work shift for either employee. The tank yard operator thus had a TWA exposure to PCl_3 of approximately 0.8 mg/M^3. This concentration is well below the permissible exposure limit of 3 mg/M^3. The tank yard operator would have to repeat the same job at least three more times during the same work day for his potential TWA exposure to exceed the permissible exposure limit. It is likely that a proposed standard for $POCl_3$ would be comparable to the standard for PCl_3 due to the similarity of the two substances. Therefore, for the same reasons as outlined above, the maintenance employee's exposure to $POCl_3$ was probably not excessive.

B. Medical

Thirty seven $PCl_3/POCl_3$-exposed employees - all except one were maintenance workers - participated in the study. They had worked in the exposure areas from 2 to 38 years (median 9, mean 14). Twenty two persons with no history of $PCl_3/POCl_3$ exposure also participated. The two groups had a similar age distribution - exposed: 22-62 years, median 35, mean 39; unexposed 24-63 years, median 40, mean 42.

Respiratory symptoms were more prevalent among the $PCl_3/POCl_3$-exposed employees. Eleven (30%) of the 37 had symptoms suggestive of chronic bronchitis (cough and phlegm, with phlegm production occurring on most days for at least three consecutive months a year for at least two years),[8,9] compared to 3 (14%) of the unexposed employees, a difference not statistically significant ($x^2 = 1.185$, $p>0.2$). Acute respiratory discomfort (chest tightness, wheezing, or difficulty breathing) at least once a month, however, was significantly more prevalent among exposed employees: 24(65%) of 37 vs. 1 (5%) of 22, $X^2 = 18.16$, $p<0.001$. The prevalence of this respiratory discomfort among exposed employees was high in all smoking categories: 11 (69%) of 16 current smokers, 8 (73%) of 11 former smokers, and 5 (50%) of 10 persons who never smoked.

The pulmonary function test results of the $PCl_3/POCl_3$-exposed employees did not differ significantly from those who were unexposed. The mean ($\pm$ standard deviation) percent predicted normal values for FEV-1, FVC, and FEV-1/FVC for the exposed employees were 96 $\pm$ 15, 95 $\pm$ 11, and 101 + 11, respectively; the corresponding results for the unexposed employees were 99 $\pm$ 10, 95 $\pm$ 9, and 105 $\pm$ 8. Smoking history could not account for this lack of difference since the exposed employees had a greater proportion of both current and former smokers (43% and 30%, respectively) than the unexposed employees (27% and 18%). The adverse effect of smoking on pulmonary function should thus have amplified rather than obscured any difference in pulmonary function due to $PCl_3/POCl_3$ exposure.

Among the 37 exposed employees, percent predicted normal FEV-1/FVC was not significantly correlated with years of $PCl_3/POCl_3$ exposure [Spearman rank correlation coefficient(r) = -0.11, p=0.25]. Among the 11 former smokers there was a significant correlation between these parameters ($r = -0.56$, $p = 0.036$), but not among the 16 current smokers ($r = 0.018$, $p = 0.46$) or the 10 non-smokers ($r = 0.085$, $p = 0.41$). In none of the smoking categories, nor among the exposed employees as a whole, was there a statistically significant ($p<0.5$) correlation (Spearman's rank correlation) between years of exposure and either percent predicted normal FEV-1 or percent predicted normal FVC. In the case of FEV-1, which is more likely than FVC to be affected by chronic exposure to a direct irritant, no correlation had a $p<0.1$.

Except for the association between decreased FEV-1/FVC among former smokers, the pulmonary function tests showed no apparent chronic effects from intermittent exposure to $PCl_3/POCl_3$. However, these tests would not necessarily detect acute, reversible damage after it has been repaired, and thus do not negate the questionnaire finding of an increased prevalence of acute respiratory symptoms among exposed employees. Furthermore, the detection of a slightly increased risk of chronic respiratory disease might escape detection in a relatively small group of employees.

VII. RECOMMENDATIONS

1. All employees who are likely to be exposed to $PCl_3/POCl_3$ should have preplacement and periodic pulmonary function testing and evaluation of respiratory symptoms. This information should be used to evaluate an employee's ability to use a respirator and to evaluate the effect of potential or actual exposures to $PCl_3/POCl_3$.

2. When working in the $PCl_3/POCl_3$ areas during maintenance or other similar procedures, it is advisable to select air purifying respiratory protection that will afford the greatest protection. In this area, exposures to PCl_3, $POCl_3$, and/or their decomposition products - hydrogen chloride gas, phosphorous acid - can occur when PCl_3 or $POCl_3$ is exposed to the ambient air. The best protection against over-exposures during maintenance or tank yard operations would be through the use of an "acid gas" gas mask. At least one manufacturer advises against the use of a "chemical cartridge" respirator for PCl_3(10). The acid gas type respirator should offer more protection against more air contaminants than the "chlorine" gas mask presently used, as the former has been tested against hydrogen chloride and sulfur dioxide as well as chlorine. However, the choice of acid gas masks on the current market is limited (only two belt-mounted canisters certified as of May, 1979). The current use of a chlorine gas mask does not seem to be protecting the workers adequately.

3. Currently, mouthpiece respirators for protection against chlorine, organic vapors, and acid gases are used throughout the plant during escape or short-duration exposures. If used in the $PCl_3/POCl_3$ areas, their use would leave the eyes open to the irritant effects of the possible contaminants. A full facepiece gas mask would be preferable. Mouthpiece-type escape respirators should only be used when full facepiece gas masks absolutely cannot be fitted in time.

4. The proper selection for protection against specific air contaminants will be of no benefit if proper fit on the face is not obtained. One employee stated that fit testing is only conducted annually. This may not be sufficient to detect defective respirators or changed physical qualities such as increased facial hair. There are qualitative fit tests (such as the banana oil test) which can be doen easily in the field to check on the facepiece seal. Such testing procedures should be implemented.

VIII. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by:

Dawn Gilles Tharr
Industrial Hygienist
Industrial Hygiene Section

Mitchell Singal, M.D.
Medical Officer
Medical Section

Field Evaluation:

William Evans
Industrial Hygienist
Industrial Hygiene Section

Jeffrey Lybarger M.D.
Medical Officer
Medical Section

Originating Office:

Hazard Evaluations and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations and Field Studies
Cincinnati, Ohio 45226

Report Typed by:

Jackie Woodruff
Clerk/Typist
Industrial Hygiene Section

IX. REFERENCES

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X. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this report are currently available, upon request, from NIOSH, Division of Technical Services, Publications Dissemination, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 21161.

Copies of this report have been sent to:

a. FMC, Nitro, West Virginia.
b. Authorized Representative of Employees - United Steelworkers of America, Local 12757, South Charleston, West Virginia.
c. U.S. Department of Labor - Region III.
d. NIOSH - Region III
e. United Steelworkers of America - Safety and Health Department, Pittsburgh, Pennsylvania.

For the purpose of informing the approximately 40 "affected employees" the employer shall promptly "post" for a period of 30 calendar days the Determination Report in a prominent place(s) near where exposed employees work.

Table I

Results of Personal Air Sampling for Phosphorus Chloride (PCl_3) and Phosphorus Oxychloride ($POCl_3$)

FMC Corporation
Nitro, West Virginia

May 23-24, 1979

Date	Job Title	Sample Location	Sample Number	Sample Time	Sample Volume (M^3)①	Concentration (mg/M^3)②
5/23/79	Chief operator	$PCl_3/POCl_3$ Building	CT-1	0655-1410	0.02	N.D.③ - $POCl_3$
"	" "	"	P-1	0710-1410	0.08	N.D. - PCl_3
"	1-O operator	"	CT-2	0657-1410	0.02	N.D. - $POCl_3$
"	"	"	P-2	0715-1410	0.08	N.D. - PCl_3
"	Tank yard operator	Truck landing platform - PCl_3 loading	P-4	1037-1137	0.06	5.7 - $PCl_3$④
"	"	Hooking hose to truck during $POCl_3$ loading	CT-4	1345-1400	0.003	N.D. - $POCl_3$
"	"	Unhooking hose during $POCl_3$ loading	CT-5	1420-1426	0.002	N.D. - $POCl_3$
5/24/80	Chief operator	$PCl_3/POCl_3$ Building	CT-6	0650-1340	0.02	N.D. - $POCl_3$
"	"	"	P-5	"	0.1	N.D. - PCl_3
"	1-O operator	"	CT-7	0655-1355	0.02	N.D. - $POCl_3$
"	"	"	P-6	"	0.08	N.D. - PCl_3
"	Tank yard operator	Truck loading of $POCl_3$ from hooking to unhooking lines	CT-8	0854-1010	0.02	N.D. - $POCl_3$
"	1-MS employee	Pulling "T-8" pump in $POCl_3$ area	CT-10	1010-1035	0.005	4.2 ($POCl_3$)④

Environmental Criteria - PCl_3 - based on an 8-hour TWA concentration:

NIOSH	-
ACGIH (TLV)	3 mg/M^3
OSHA	3 mg/M^3

① M^3 = Cubic Meters of Air.
② mg/M^3 = Milligrams of substance per cubic meter of air.
③ N.D. = Non detectible, the analytical limit of detection was 28 micrograms of PCl_3 and 16 micrograms of $POCl_3$.
④ Employee was wearing chlorine gas mask.