U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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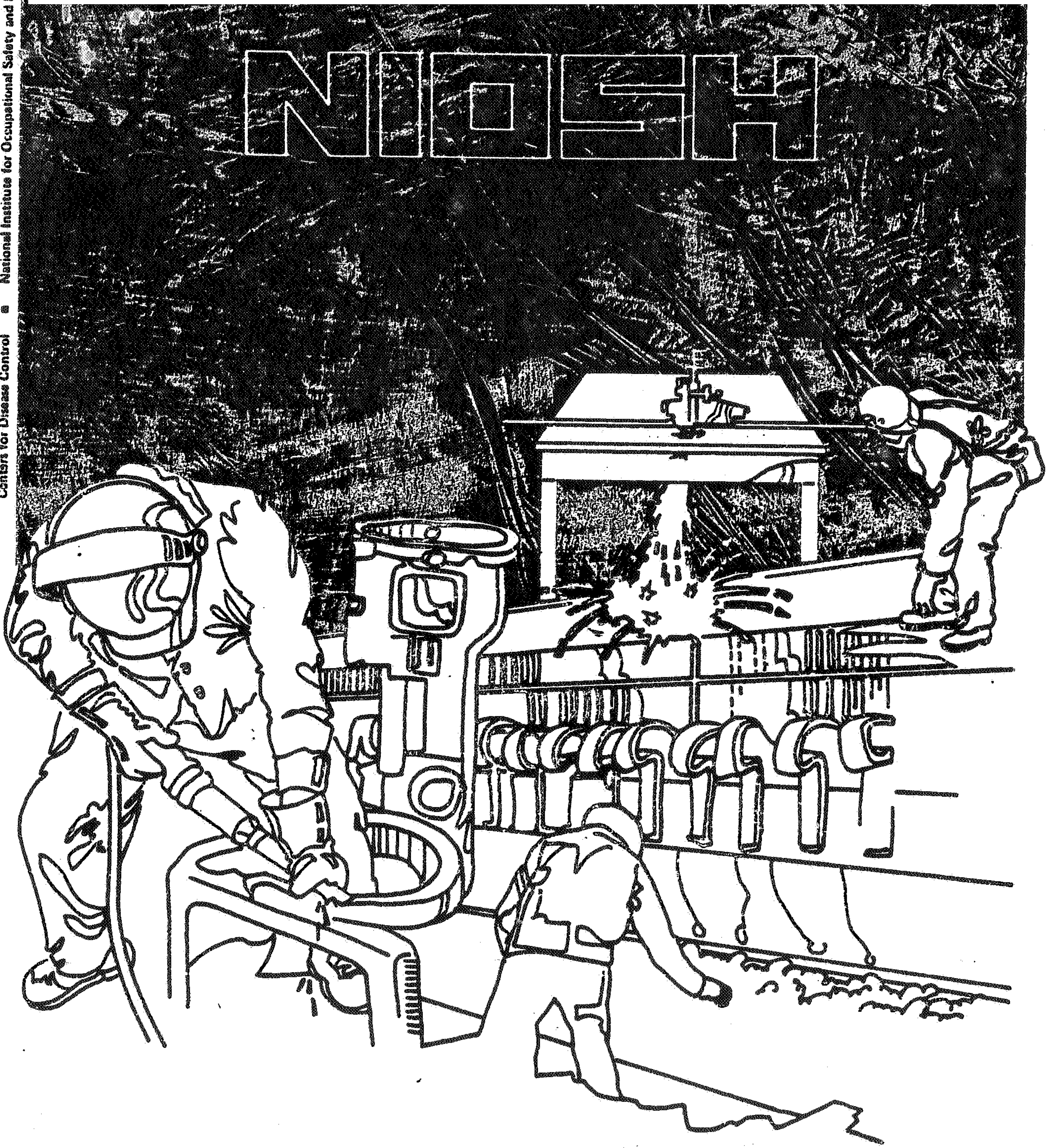

Health Hazard Evaluation Report

HETA 84-311-1575
GRAIN ELEVATORS
SUPERIOR, WISCONSIN
DULUTH, MINNESOTA

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from 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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 84-311-1575
APRIL 1985
GRAIN ELEVATORS
SUPERIOR, WISCONSIN
DULUTH, MINNESOTA

NIOSH INVESTIGATORS:
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I. SUMMARY

On April 27, 1984, the National Institute for Occupational Safety and Health (NIOSH) was requested by the American Federation of Grain Millers, Local 118, to evaluate exposures to grain fumigants and grain dust for workers at grain elevators in Duluth, Minnesota and Superior, Wisconsin. The process involves receiving grain by truck or rail and reloading it on ship or rail for domestic customers or export. Grain may be stored, cleaned, mixed, or treated for pests by the elevators depending upon customer specifications.

The field study was conducted May 14 to 18, 1984, at Archer Daniel Midland grain elevator in Superior, Wisconsin, and International Multifoods Elevator in Duluth, Minnesota. The evaluation consisted of an industrial hygiene survey with personal exposure monitoring of elevator workers for carbon disulfide, carbon tetrachloride, ethylene dibromide, and grain dust. No phosphine exposure monitoring was done as no grain was being or had recently been treated with this compound. Short term sampling to profile fumigant exposures associated with treated grain also was conducted.

Worker exposures to carbon disulfide and carbon tetrachloride were nondetectable. Exposures to grain dust ranged from 0.34 to 38 milligrams per cubic meter (mg/m^3) (median 1.85 mg/m^3, ACGIH TLV® 4 mg/m^3). Short-term sampling of fumigant levels associated with handling treated grain was inconclusive. Elevator screening practices of incoming grain may have contributed to the minimization of fumigant exposures.

Based on the results of this study, NIOSH investigators determined that a health hazard from overexposure to grain dust exists at these grain elevators. Efforts to evaluate fumigant exposure hazards produced inconclusive results for several shipments of treated grain. No exposure of workers to carbon disulfide, carbon tetrachloride, or ethylene dibromide was documented. Recommendations are offered addressing correction of dust overexposures and an approach to handling fumigated grain.

KEYWORDS: SIC 5153 (grain), grain dust, grain fumigants, carbon disulfide - CAS # 75-15-0, carbon tetrachloride - CAS # 56-23-5, ethylene dibromide - CAS # 106-93-4, grain elevators-export.

II. INTRODUCTION

On April 27, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from the American Federation of Grain Millers, Local 118 to conduct a Health Hazard Evaluation (HHE) assessing exposures of their membership to grain fumigants and dust. Local 118 identified eight grain elevators in the Duluth, Minnesota-Superior, Wisconsin area for this study. Discussions with union representatives regarding their concerns and objectives reduced the number of elevators at which the evaluation would be conducted to two.

NIOSH investigators conducted a field study May 14 to 18, 1984. The purpose of this study was to evaluate worker exposures to fumigants present on incoming grain and grain dust, both associated with daily elevator operations.

This current request was initiated as a follow-up to work done in February 1984 by a NIOSH investigator in which the identity of fumigants present in a unit train grain shipment were determined. A letter report for this previous work (HETA 84-194) was sent to involved parties March 15, 1984. The final report (No. 84-194-1549)[1] was distributed in January 1985. No worker exposure monitoring was conducted at that time. Primary fumigants identified as present in the February 1984 study were carbon disulfide and carbon tetrachloride.

III. BACKGROUND

A. Basis of the Request:

Local 118 and Congressman David Obey's office submitted a request to NIOSH February 17, 1984, requesting immediate evaluation of a unit train shipment of treated grain. The concern was that the grain was very heavily treated with fumigants. This concern was based on reported acute health effects experienced by an elevator worker while opening the railcars and conducting routine fumigant determinations. Additionally the workers believed that the extremely cold winter weather retarded the normal volatilization of fumigant from the grain and that this would result in higher fumigant exposures of workers as the grain was handled at the elevator.

Carbon tetrachloride fumigant levels in-the-mass (samples obtained with the sample collection device submerged in the grain) as determined by elevator personnel with direct reading indicator tubes reached or exceeded the maximum concentration of the scale on the tubes (50 parts per million or ppm). The workers also were concerned that ethylene dibromide may be present. Both carbon tetrachloride and carbon disulfide were found to be present in this shipment. The reader is referred to Final Report HETA 84-194-1549[1] for a more in-depth presentation of this previous study.

Local 118 representatives were still concerned about exposure of their membership to fumigants present on incoming grain associated with shipments such as that evaluated in February. Since no opportunity to evaluate worker exposures occurred during the February study, a request for this present study was submitted by the union. The two primary concerns of this second request were the evaluation of the health hazards associated with worker exposure to unknown fumigant levels and exposure to grain dust.

B. <u>Location of the Study</u>:

The current study was conducted at Archer Daniel Midland (ADM) grain elevator in Superior, Wisconsin and International Multifoods Elevator (IMF) in Duluth, Minnesota. These two elevators were chosen from the eight listed in the request after discussions with the requestors. These two elevators were determined to offer the best opportunity for addressing a number of the union's concerns. Some of the considerations in the decision process included activity level, number of workers, different modes of transportation served, presence of engineering controls, elevator size, elevator age, and which elevators were most suitable in providing a range of activities representative of all the elevators in the area.

C. <u>Process Description</u>:

Grain is shipped into the Port of Duluth - Superior by truck or railroad. During the season when the Port is open, most grain is transported out by ship either to domestic lake ports or to foreign ports. Otherwise shipment is by rail.

Most of the grain arriving at the Port has been previously dried and cleaned to some extent and possibly fumigated at inland elevators. The length of storage prior to arrival at the Port varies from rather short for grain coming in after the fall harvest to considerable lengths of time for grain shipped shortly before the harvest which is obtained by emptying storage facilities in preparation for the new harvest.

Since elevators will not accept grain with active pests, it is customary for shippers to fumigate the grain immediately prior to shipping or in transit. Although this is supposed to be done in an approved manner and properly labeled, this is not always the case. Lack of labeling and excessive dosing are reported to occur with moderate frequency. On arrival at the elevators the grain is inspected and graded by State inspectors and elevator workers. Samples are taken by probe from within the load or obtained from a diverter sampler in the inbound grain stream entering the elevator and are then subjected to testing and grading by the State inspectors as well as the elevator's own personnel. Sniff tests are conducted only by State inspectors. The sniff tests requires inspectors to obtain an odor determination by directly smelling the grain. Elevator personnel work throughout the elevators but generally (with the exception of oilers, sweepers, and maintenance work) are limited to certain areas within the facility. These areas are the railcar and truck unloading operations, the inspection laboratory, the scale floor, the diverter or distribution floor, the annexes above the bins, grain cleaners, annex basements under the bins, and grain loading locations (control rooms and loading spouts).

In addition to receiving and shipping, the elevators clean the grain, weigh the grain, mix the grain when indicated, store the grain, and treat the grain with suitable insecticides and fumigants. At ADM the grain is monitored by temperature for weevil activity and turned over or fumigated as indicated. At IMF grain generally is not stored for any length of time due to limited bin space. Grain that remains in the elevator for any length of time may be transferred to another bin ("run through the house") or cleaned. The use of fumigants by the elevators on site to treat infested grain was reported to be very limited.

D. <u>Job Titles and General Job Descriptions</u>:

Workers at the elevators are provided from a labor pool. Workers, with a few exceptions, must be able to do any job in the grain elevator. The two elevators involved in this study have variations in the job titles and job elements of their workforce. A list of the different job titles, some of the job tasks, and the elevator using that job designation or assigning workers to the indicated job is presented in Table I.

E. <u>Elevator Screening Procedures for Fumigated Grain</u>:

The two elevators involved in this study had different approaches to screening incoming grain shipments for the presence of fumigants.

ADM tests all inbound grain shipments with a portable HNU® Photo Ionization Unit. This unit provides a qualitative readout identifying the presence of photoionizable organic (and some inorganic) compounds. Any positive readings on the photoionization unit are followed with a series of detector tube readings. Company protocol dictates obtaining the fumigant sample above the grain mass.

International Multifoods conducts fumigant testing by obtaining detector tube readings in the grain mass of the samples. In colder weather conditions the sample is permitted to warm in the inspection laboratory before the sample is taken. If the fumigant level in-the-mass exceeds the eight-hour Occupational Safety and Health Administration (OSHA) permissible exposure limit, the shipment is not permitted to be taken into the grain elevator.

The two methods of assessing fumigant levels of grain shipments used by the elevators in this study are either direct reading indicator tubes or a direct reading photoionization unit. Although these are among the most expedient methods in attempting to evaulate potential fumigant exposure situation, these systems have the greatest utility as qualitative or semiquantitative screening devices due to their large variations in sensitivity and specificity. Comparing the fumigant contrations obtained with this type of equipment to full shift time-weighted-average exposure limits appears at times to be inappropriate.

During this survey, IMF had received three railcars of grain having carbon tetrachloride levels in-the-mass in excess of 10 parts per million (ppm) determined by indicator tube testing conducted by the company. The management of IMF decided to proceed with dumping this grain, running it through the elevator, and returning it to empty railcars in an effort to determine the effect this would have on fumigant levels. This procedure was conducted after normal working hours May 15, 1984, and all labor was provided by management. There was no union involvement with this activity, as they chose to boycott the effort based on contractual considerations and health concerns. NIOSH investigators also expressed their concerns and reservations regarding management's decision and actions. The primary reason IMF undertook this experiment was to provide an opportunity to obtain data addressing fumigant levels associated with grain movement through the elevator. Their hope was that this would aid in the clarification of the fumigant problem and hopefully provide data useful in developing an industrywide approach to the problem.

F. Description of the Problem of Incoming Fumigated Grain:

Numerous difficulties and unknowns are encountered in both evaluating the problem of fumigated grain and in taking corrective action. The identification of treated, unplacarded grain shipments before an overexposure has occurred is almost impossible under current operating procedures. The loss of placards on treated shipments and failure to remove old placards from untreated shipments increases the uncertainty of using placards alone to designate fumigated grain. Difficulties in identifying the source of fumigated grain due to such things as sales-in-transit and multiple loading and/or railcar pick up points may make determinations of where the grain was treated tedious and unreliable. Non-uniformity in fumigant application procedures and rate (amount used) as well as lack of information on the identity of the fumigant used hinders the evaluation and appropriate handling of treated grain. Fumigation of grain during subsequent storage and shipment periods may result in the presence of higher residual fumigant levels in recently loaded grain shipments even though the grain was not directly treated prior to the last shipment. Ambient and grain temperatures may influence the release of volatile fumigants from the grain. Methods for aerating and/or handling fumigated grain in some manner to make it "safe" for conducting a sniff test remain unproven as to their efficacy. The question of what constitutes sufficient aeration of grain in order to conduct a sniff test is still unanswered. Limited laboratory work undertaken by NIOSH researchers to address what aeration techniques were most productive prior to the sniff test was presented in Technical Assistance Report No. 84-310.[2] Predicting when the movement of fumigated grain is most likely to increase remains subjective. Methods of testing grain to determine if it is free of fumigants or at least will not present a health hazard to workers handling the grain is fraught with questions, inappropriate applications of exposure criteria, and questionable or unproven measurement practices. The interaction of different grains with fumigants as far as fumigant retention and release is concerned is another issue. There does not appear to be a definitive answer as to whether different grains interact similarly or differently when fumigated with the same and different fumigants. Essentially grain shipments arrive at the elevators "as is" with no historical information about the grain or shipment.

In addition to the fumigant health hazard to the central nervous system, the effects, when experienced by samplers accidently exposed to fumigants, present a serious safety hazard. Sure footedness is essential when on top of and around railroad cars and semi-trailers.

Additionally, the reader should keep in mind that any industrial hygiene evaluation of a fumigated grain incident after it has been accidentally or programatically identified or through some fumigant concentration determination, cannot be considered to represent the conditions existing during the preceeding, unevaluated time period. A major factor contributing to this is the nonreproducibility of incoming grain shipments.

G. Other Agency Regulations Concerning Fumigated Grain:

The U. S. Department of Transportation specifies, in the Transportation Safety Act of 1974, that movement of grain by rail that has been treated with flammable liquids or gases in the fumigation process is prohibited until either 48 hours have elapsed after treatment or the carrying vessel has been ventilated "so as to remove danger of fire or explosion due to the presence of flammable vapors" [Section 173.9 para (a)].[3] A placarding procedure is specified for lading which has been fumigated or treated with poisonous liquid, solid, or gas, and the placard states that before unloading and entering, the car must be free of gas [Section 173.9 para (b)].[3] No guidance is given as to how a shipment is determined to be "free of gas" or what constitutes a gas-free lading. Additionally, a railcar must be thoroughly cleaned after poisonous materials are unloaded unless it is used exclusively for the carriage of poisonous materials [Section 174.615).[3] Health issues, other than those associated with immediate death, are not addressed by the regulations. The date and time given on a placard, after which the shipment can be opened, has nothing to do with the safety of the lading as it pertains to fumigant exposure of workers.

The U. S. Environmental Protection Agency currently exempts carbon disulfide, carbon tetrachloride, ethylene dichloride, chloropicrin, chloroform, methylene chloride, and methyl bromide from the requirement of a residue tolerance.[4] This means that there is no fumigant level, which if exceeded in a grain sample, that would prohibit the use of the grain. The agency issued three (C) (2) (B) letters under the Federal Insecticide, Fungicide and Rodenticide Act requesting residue, product chemistry, and toxicology data for carbon tetrachloride, ethylene dichloride, carbon disulfide, methyl bromide, and methylene chloride in March 1984, to registrants of pesticide products containing these active ingredients. This re-evaluation of existing exemptions from tolerances has been undertaken in response to recent findings of ethylene dibromide residues in foods.

IV. METHODS AND MATERIALS

Sampling was conducted using battery powered air sampling pumps and an assortment of sampling media which included sorbent tubes (standard coconut shell charcoal), preweighed 37 millimeter (mm) filters, and 5 liter (L) aluminized mylar sampling bags. The use of direct reading indicator tubes was limited to short-term area and bag sampling. Personal exposure monitoring of elevator workers was conducted for carbon tetrachloride, carbon disulfide, ethylene dibromide, and grain dust. Short-term source and area sampling, along with personal exposure monitoring during the handling of fumigated grain, was conducted for carbon tetrachloride and carbon disulfide.

A. Personal Exposure Sampling and Analytical Methods:

1. Dust: Total dust exposures were collected on pre-weighed polyvinyl chloride filters using closed face cassettes and sampling at a rate of 1.5 to 1.7 liters per minute (Lpm). Samples plus filters were weighed on an electrobalance and the previously determined tare weight for the respective filter was subtracted. Tare and gross weighings were done in duplicate.

   The instrumental precision of weighings done at one sitting is 0.01/mg. Due to variable factors such as overloading, hygroscopicity of samples, humidity, and the physical integrity of the filter itself, the actual precision can be considerably poorer and occasional slight net negative particulate weights are to be expected.

2. Fumigants: Samples for evaluating worker exposure to carbon tetrachloride, carbon disulfide, and ethylene dibromide were obtained using a three tube sampling manifold and SKC Universal Sampling Pumps®. Sampling flow rates for the respective compounds were approximately 100, 100, and 200 cubic centimeters per minute (cc/min). Some additional personal exposure sampling for carbon tetrachloride (both long-and short-term) and carbon disulfide (short-terms) was conducted using low flow Sipin® pumps at a flow rate of 200 cc/min.

   Carbon tetrachloride samples were analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) according to NIOSH Method S-314[5] with modifications. (See Appendix A). The analytical limit of detection was 0.01 milligram per sample (mg/sample).

   Carbon disulfide samples were analyzed by GC equipped with a flame photometric detector using NIOSH Method S-248[5] with modifications (See Appendix A). The analytical limit of detection was 0.01 mg/sample.

Ethylene dibromide samples were analyzed by GC equipped with an electron capture detector. The analytical limit of detection was 19 nanograms per sample (0.000019 mg). See Appendix A for details of the analytical method used.

B. Short-term and Area Sampling for Fumigants:

Short-term sampling was conducted using two different sampling methods. Samples for carbon tetrachloride and carbon disulfide were obtained on standard charcoal tubes using a flow rate of about 1 Lpm. In addition to sorbent tube sampling, bag samples were obtained at many of the same sampling locations. These bag samples were analyzed on site with a portable GC. Short-term personal exposure samples to carbon tetrachloride and carbon disulfide were obtained using personal sampling pumps calibrated at a flow rate of about 200 cc/min.

This sampling (short-term and area) was undertaken in an effort to evaluate fumigant concentrations (specifically carbon tetrachloride and carbon disulfide) associated with railcar grain shipments that were condsidered to be fumigated. During this survey three railcars of grain considered unacceptable for unloading due to high (greater than 10 ppm) carbon tetrachloride levels when sampled in-the-mass by elevator personnel were evaluated.

Samples of both types, sorbent tube and bags, were collected above the grain in the railroad cars, in the grain mass in the rail cars, during dumping of the rail cars at the grain stream, and at locations along the grain flow through the elevator such as transfer points, open belts, and at trippers where the grain enters the bin. Management personnel were monitored with sorbent tube sampling systems for carbon tetrachloride and carbon disulfide. Area samples using sorbent tube sampling trains were placed at locations throughout the elevator along the path followed by the grain.

1. Sorbent Tube Sampling: All charcoal tubes for carbon tetrachloride and carbon disulfide were analyzed as in Subsection A of this section and Appendix A.

2. Short-Term Air Bag Sampling:

   Air samples were collected in aluminized mylar bags above and within the grain mass of two treated grain shipments and at various locations throughout the elevator as this grain was transferred to storage bins. The bags were filled using an SKC Universal Pump® equipped with a bag filling port and an inlet probe of Tygon® tubing fitted with a particulate filter on the probe end. In-the-mass samples are for a single location in the grain. The amount of time required to fill the bags was about five minutes.

Samples were taken to the field laboratory where they were analyzed for carbon tetrachloride and carbon disulfide. These two compounds appear to be the primary constituents of a commonly used grain fumigant generally referred to as "80-20" (80% carbon tetrachloride, 20% carbon disulfide). All bags were letter coded and all bags were flushed with clean (room) air and analyzed for residual fumigant levels prior to reuse. Samples were usually analyzed within a short time after collection, normally less than one hour.

Samples were injected into a gas chromatograph using a microliter gas syringe. Analyses were all run a minimum of two times for each sample. The Photovac Model 10A10 gas chromatograph (Photovac, Inc., Thornhill, Ontario, Canada L3T 1L3) was equipped with a photoionization detector and was operated under the following conditions:

Temperature:	68-74°F (ambient)
Carrier Gas:	Air at 30 psig and 30 cc/minute
Column:	CSP 20, 4' x 1/8", 80-100 mesh

The output was to a strip chart recorder, (Linear Model 142) operated at 100 millivolts full scale and a chart speed of 0.5 cm/minute. The gas chromatograph was operated on an attenuation of 20 or 50 and the injected sample volume ranged from 50 to 400 microliters depending upon fumigant concentration.

Standards were prepared from liquid reagents (carbon disulfide and carbon tetrachloride) by adding microliter quantities to metered volumes of air in aluminized mylar bags.

C. <u>Follow-up Laboratory Comparison of Short-term Sorbent Samples and Bag Sampling:</u>

Due to the experimental nature of the on-site portable gas chromatographic analysis of bag samples coupled with disparate indicator tube readings, the NIOSH investigator chose to await the matching sorbent tube sample results prior to presenting the onsite GC data. The discrepancy between the portable GC results and the sorbent tube data (See Section VI Results and VII Discussion) necessitated additional laboratory work as a means of determining which method provided the best representation of fumigant concentrations in the grain elevator. Appendix B presents a summary of the follow-up laboratory study. The additional lab work involved generation of known carbon tetrachloride concentrations which were sampled and analyzed by the various methods used during the field survey. A comparison of results obtained from use of the different sampling and analytical methods was conducted.

V. EVALUATION CRITERIA AND TOXICITY SUMMARIES

A. Environmental Criteria:

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) The American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) The U. S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In reviewing the exposure levels and the recommendations for reducing those levels found in this report, it should be noted that industry is required by the Occupational Safety and Health Act of 1970 to meet those levels specified by OSHA standards.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8 to 10 hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

Evaluation Criteria used in this report are presented in Table II and the following Toxicity Discussion.

B. Toxicity Discussion:

1. Carbon Disulfide

Carbon disulfide vapor causes narcosis at high concentrations; repeated exposure to low concentrations causes damage to the central and peripheral nervous systems and may accelerate the development of or worsen coronary heart disease. Reproductive disorders may result, such as azospermia, menstrual irregularities, and spontaneous abortion. Other reported effects of exposure to carbon disulfide are ocular changes (retinal degeneration, corneal opacities, disturbances of color vision, corneal anesthesia, diminished pupillary reflexes, microscopic aneurysms (in the retina), gastrointestinal disturbances (chronic gastritis and achlorhydria), renal impairment (albuminuria, microhematuria, elevated blood urea nitrogen, diastolic hypertension), and liver damage. Effects commonly caused by repeated exposure to carbon disulfide vapor are exemplified by a group of workers with a time-weighted average (TWA) exposure of 11.5 ppm (range 0.9 to 127 ppm) who complained of headaches and dizziness. In other workers with a TWA of 186 ppm (range 23 to 378 ppm), complaints also included sleep disturbances, fatigue, nervousness, anorexia, and weight loss. The end-of-day exposure coefficient of the iodine azide test on urine was a good indicator of workers who were or had been symptomatic.[12]

Dermatitis and vesiculation may result from skin contact with the vapor or liquid.[13] Exposure by inhalation of vapor may be compounded by percutaneous absorption of liquid or vapor.[14] Cutaneous exposure of rabbits to carbon disulfide vapor resulted in measurable carbon disulfide concentration in the exhaled air. Carbon disulfide vapor absorbed through the skin was present in solution in the blood and in combined form. The authors of this study concluded that under conditions of grain fumigation, carbon disulfide vapor concentrations may reach a level where skin absorption, as another route of exposure, is a possibility.[15] A study done by Cesaro[16] in which the intact skin of male human subjects was exposed to CS_2 vapors resulted in no detectable CS_2 in exhaled air subsequent to exposure. In this particular study the lowest concentration which could be measured was 10 ppm (30 mg/m^3). No measurements of exposure chamber CS_2 concentrations were obtained. The study assumed that a 20 minute exposure period along with wrapping one arm in CS_2 soaked cotton would sufficiently expose the subjects to a degree where the contaminants of interest would appear in exhaled air.

The current OSHA Permissible Exposure Limit is 20 ppm (62 mg/m^3) for an eight-hour TWA and has an acceptable ceiling concentration of 30 ppm (93 mg/m^3). The acceptable maximum peak above the acceptable ceiling concentration for an eight hour shift is 100 ppm (310 mg/m^3) for 30 minutes and this maximum peak must be included in the eight-hour TWA calculation.[10]

NIOSH recommends a permissible exposure limit of 1 ppm (3 mg/m^3) over a workshift of up to 10 hours (in a 40-hour work week) with a ceiling of 10 ppm (30 mg/m^3) averaged over a 15-minute period. The NIOSH recommended exposure limit is considered to be below levels at which serious health effects would generally be found, specifically those involving the cardiovascular and central nervous systems. Acute toxicity by CS_2 can be avoided by applying the recommended ceiling limit[6].

Carbon disulfide is not known to be an eye irritant and since the odor threshold (7.7 ppm (24 mg/m^3) or less) is below the OSHA PEL it has good warning properties.[12]

2. Carbon Tetrachloride

Carbon tetrachloride (CCl_4) vapor is a narcotic and causes severe damage to the liver and kidneys. In animals the primary damage from intoxication is to the liver, but in humans the majority of fatalities have been the result of renal injury with secondary cardiac failure. In humans, liver damage occurs more often after ingestion of the liquid than after inhaling the vapor. Human fatalities from acute renal damage have occurred after exposure for about one-half to one-hour at concentrations of 1000 ppm to 2000 ppm (6286 to 12571 mg/m^3). Exposure to high concentration results in symptoms of central nervous system depression including dizziness, vertigo, incoordination, and mental confusion; abdominal pain, nausea, vomiting, and diarrhea are frequent. Within a few days, jaundice may appear and liver injury progresses to toxic necrosis. There are several reports of adverse effects in workmen who were repeatedly exposed to concentrations between 25 and 30 ppm (157 and 189 mg/m^3); nausea, vomiting, dizziness, drowsiness, and headache were frequently noted. The effects of CCl_4 in humans who are addicted to alcohol are more severe than usual. No adverse symptoms resulted from repeated exposure to 10 ppm (63 mg/m^3). Hepatomas have been reported in several animal species exposed to carbon tetrachloride; human exposure has also been associated with hepatomas.[12] Liquid CCl_4 can be absorbed through the skin.[17]

The current OSHA PEL for CCl_4 is 10 ppm (63 mg/m^3) over an eight-hour TWA with an acceptable ceiling concentration of 25 ppm (157 mg/m^3) and a maximum acceptable peak of 200 ppm (1257 mg/m^3) for five minutes occurring only once in any four hours and included in the overall TWA calculation.[10]

NIOSH recommends that the TWA exposure limit to CCl_4 be maintained below 2 ppm (12.6 mg/m^3) during the course of a workshift determined during a one-hour sampling period. Maintaining exposures below this level is considered capable of greatly reducing the cancer risk associated with occupational exposure to CCl_4.[7] NIOSH recommends that CCl_4 be regulated as an occupational carcinogen.

Carbon tetrachloride has an odor threshold of about 50 ppm (314 mg/m^3), which is above the PEL and is, therefore, regarded as having poor warning properties. Carbon tetrachloride has been reported as being slightly irritating to the eyes, however, no concentration at which this occurs was given.[12]

3. Ethylene Dibromide

Ethylene dibromide (EDB) vapor is a narcotic, a severe mucous membrane irritant, and a hepatic toxin. Accidental use as a human anesthetic resulted in severe irritation of the conjunctiva and respiratory tract, followed by protracted vomiting and death. Excessive exposure may be expected to cause irritation of the eyes and respiratory tract. The liquid is highly irritating to human skin, causing marked erythema and vesiculation. In a bioassay conducted by the National Cancer Institute, ethylene dibromide was found carcinogenic in rats and mice when fed by gavage. The compound induced squamous cell carcinomas of the fore stomach in rats of both sexes, hepatocellular carcinomas in female rats, and hemangiosarcomas in male rats. In mice of both sexes, the compound induced squamous cell carcinomas of the fore stomach and alveolar/broncheolar adenomas. In NIOSH-sponsored research, laboratory rats exposed to 20 ppm EDB (153 mg/m^3) by inhalation and also receiving a diet containing 0.05% disulfiram experienced exceedingly high mortality levels as well as a high incidence of tumors (including hemangiosarcomas of the liver, spleen, and kidney).[12]

OSHA has proposed a reduction in the EDB PEL from an eight-hour TWA of 20 ppm (154 mg/m^3) to 0.10 ppm (0.77 mg/m^3). OSHA believes that the total risk to health of employees exposed to EDB is the result of the compounded risks from carcinogenicity, mutagenicity, spermatotoxicity, teratogenicity, and damage to the kidneys, liver, spleen, respiratory tract, central nervous system, circulatory system, skin, and eyes warrants this reduction in PEL and substantially reduces risk. The short-term exposure limit would also be revised to 0.5 ppm (3.8 mg/m^3) over a 15-minute period from the current five minute acceptable maximum peak of 50 ppm (384 mg/m^3).[9]

NIOSH has concluded in its comments on the OSHA Proposed EDB Standard that an eight-hour TWA of 0.045 ppm (45 parts per billion or ppb) (0.34 mg/m^3) will greatly reduce the risk of workers developing cancer as a result of a working lifetime exposure to EDB. NIOSH also concludes that a ceiling limit, to accommodate intermittent exposures in certain industries, of 0.130 ppm (130 ppb) (1.0 mg/m^3) as determined in any 15 minute sampling period is appropriate (Internal Memorandum "NIOSH Comments on the Occupational Safety and Health Administration Proposed Standard: Occupational Exposure to Ethylene Dibromide" November 21, 1983).

The odor of EDB is detectable at 10 ppm (77 mg/m^3), well above occupational exposure limits and therefore is considered to have poor warning properties. Ethylene dibromide is also reported to be an eye irritant.[12]

4. Grain Dust

Grain dust inhalation may cause three major respiratory diseases: asthma, chronic bronchitis, and grain fever.

Both immediate and delayed asthmatic reactions have been reported when asthmatic grain handlers were given bronchial challenges of grain dust extracts. Estimation of the prevalence of asthma among grain handlers is difficult due to self exclusion of symptomatic workers from grain dust exposure. The long-time asthmatic grain handlers represent a surviving population.[18]

Workers exposed to grain dust demonstrate a higher prevalence of respiratory symptoms and rhonchi (abnormal chest sounds) than in control populations, regardless of smoking history. Inhalation of grain dust causes coughing, expectoration, wheezing, chest tightness, and shortness of breath. Grain handlers with symptoms had impaired lung functions. This impairment was either of the same magnitude as that of cigarette smoking or of lesser extent. The prevalence of chronic bronchitis with respiratory obstruction was higher in grain handlers regardless of smoking. Chronic bronchitis with evidence of airway obstruction was related to the length of employment. Chronic bronchitis is considered a major occupational health problem among grain handlers. Although smoking is a major contributing factor to this disease, it also occurs in nonsmokers.[18]

The incidence of grain fever has been stated to range from 19 to 40% in grain handlers. Its occurrence is determined largely by excessively dusty conditions, i.e., dust concentrations exceeding 15 mg/m^3.[18]

Grain workers exposed to time weighted average grain dust concentrations of 4 mg/m^3 or less generally do not express respiratory symptoms in excess of those reported among control populations.[18] This is the basis of the recommended time-weighted TLV of 4 mg/m^3 for total dust.

VI. RESULTS

A. Full-shift Exposure Monitoring for Grain Dust:

Grain dust overexposures of elevator personnel occurred at both ADM and IMF. Exposures at ADM ranged from 0.34 mg/m^3 to 38 mg/m^3, with a median value of 1.6 mg/m^3. Three workers (two sweepers and an annexman) had grain dust exposures in excess of the 4 mg/m^3 ACGIH Threshold Limit Value. A total of 17 workers were monitored at ADM for grain dust.

Exposures of elevator personnel at IMF ranged from 0.28 mg/m^3 up to 9.5 mg/m^3. The median value for the 23 samples taken was 1.3

mg/m^3. Four workers (all laborers at the railcar dump) had exposures in excess of 4 mg/m^3.

Table III presents exposure sampling data for total grain dust. Job title and work location are also given.

B. Full-Shift Exposure Monitoring for Fumigants:

All of the workers monitored for carbon tetrachloride, carbon disulfide, and ethylene dibromide had no detectable exposures to these compounds during the survey. This held true at both ADM and IMF.

Using the analytical limit of detection of 0.01 mg/sample for both carbon tetrachloride and carbon disulfide, all personal exposures to these two compounds, if present, were below 0.42 mg/m^3 (0.07 ppm) and 0.41 mg/m^3 (0.13 ppm) respectively. The NIOSH recommended exposure limits for these two compounds are 12.6 mg/m^3 (2 ppm) for carbon tetrachloride - measured as a ceiling over one hour; and 3 mg/m^3 (1 ppm) for carbon disulfide - for an 8 to 10 hour workshift, 40 hour workweek. Table IV presents these results, indicating the location, job, and date the samples were taken.

No worker exposures to ethylene dibromide were documented. All worker exposures to this agent, if present, were below detectable levels which calculates out to an environmental level of less than 0.0003 mg/m^3 (0.00004 ppm). The current NIOSH recommended full shift exposure limit to ethylene dibromide is 0.34 mg/m^3 (0.045 ppm).

Contamination of two of the blanks with a compound that appeared to be ethylene dibromide occurred, however the identity of the compound on the blanks could not be undertaken due to the extremely small amount of material present.

Analysis of selected samples on different chromatographs with different columns and conditions provided slight clarification of the original analytical results, and no improvement in the limits of detection and quantitation.

C. Short-term Fumigant Sampling:

Table V presents the short term fumigant sampling results for sample sets in which fumigants were found on the sorbent tubes. A total of 44 bag samples for fumigants were collected. Twenty-eight (28) of these samples were paired with sorbent tube samples (64%). Of these paired samples, only six (21%) samples had carbon disulfide and/or carbon tetrachloride present on the sorbent tube samples (the remaining 79% of the paired sorbent tube samples were nondetectable (ND). Carbon disulfide concentrations on the sorbent tubes ranged from up to 2.2 mg/m^3 (0.72 ppm) and the paired CS_2 concentrations determined by portable GC ranged from ND to 84 mg/m^3 (27 ppm). Carbon tetrachloride concentrations in this same group ranged from ND up to 49 mg/m^3 (7.8 ppm) for the sorbent tubes and from 19 mg/m^3 (3 ppm) up to 754 mg/m^3 (120 ppm) for bag samples analyzed by portable GC. Referring to Table V, the reader can see that high portable GC values do not correspond to high sorbent tube concentrations. The sorbent tube data has substantially lower fumigant concentrations when compared to the bag sampling data and there does not appear to be any consistency in the difference between sample sets.

D. <u>Follow-up Laboratory Study for Clarification of Field Data:</u>

Follow-up laboratory work undertaken to define the cause of disagreement between the two sampling and analytical methods used during the survey was unable to reproduce discrepancies of the magnitude seen in the field. Using a known concentration of 25 ppm for carbon disulfide and carbon tetrachloride, sorbent tube values averaged 17 and 21% higher respectively when compared to the bag samples collected from the same contaminant generation system. Carbon tetrachloride indicator tubes went off scale (greater that 50 ppm) and CS_2 detector tubes read slightly less than 25 ppm.

At the five (5) ppm carbon tetrachloride concentration the sorbent tubes agreed with the portable GC values very closely (5.17 vs. 5.03 ppm). Indicator tubes produced a dark stain consistently to five (5) ppm with a lighter stain channeling up to 10 to 20 ppm, making the value assigned to the tube reading questionable.

Carbon disulfide values obtained by sorbent tube sampling at the five (5) ppm level averaged 34% higher than the portable GC readings (4.47 ppm vs. 2.95 ppm). Indicator tubes were approximately 30% higher than the sorbent tubes and also presented uncertainty reading the final concentration (stain length) due to the channeling.

There was no indication of bias due to the use of aluminized mylar bags.

An incident which occurred at the beginning of the laboratory experiment resulted in a significant discrepancy between the sorbent tubes and portable GC results. The initial 25 ppm carbon tetrachloride concentration was generated using material that had been sitting in the laboratory hood storage area for two or more years. The portable GC response to this concentration, calculated to be 25 ppm, was 60 ppm. Two sorbent tubes for CCl_4 analyzed by two separate laboratories and obtained at the same time as the portable GC sample had concentrations of 18.1 and 18.9 ppm CCl_4. Cleaning of the generation system and use of a new, unopened bottle of CCl_4 resulted in portable GC responses much closer to the anticipated theoretical concentration of 25 ppm. The preceeding data in this subsection was generated after this change. Disposal of the original standard prevented further analysis for an interfering compound.

VI. DISCUSSION

A. Worker Dust Exposures

Overexposure of workers to grain dust occurred both at ADM and IMF.

At IMF the job title of all overexposed workers was laborer. The exposures occurred during the dumping of railcar shipments.

Workers wore disposable nuisance dust masks, although their suitability in protecting the workers from high dust concentrations is questionable. No local exhaust is present in the grain dumping area.

Two sweepers and an annexman had excessive grain dust exposures at ADM. During the walk-through sweepers were observed knocking dust off of rafters with brooms. Dry sweeping is the standard practice for dust removal and this probably contributes significantly to the exposure of sweepers.

Missing screws, loose panels, open panels, holes, and sheet metal damage to enclosed grain handling structures permitted both grain and dust to escape. A large number of these can significantly reduce the effectiveness of any dust collection system, especially as one moves further away from the fan.

B. Worker Fumigant Exposures:

No worker exposures to carbon disulfide or carbon tetrachloride as grain fumigant constituents were documented during the course of our survey. We had considered mid-May as a better time to conduct fumigant exposure monitoring of workers. Discussion with the union indicated a high level of concern that due to the extremely cold winter and increased fumigant use (including carbon disulfide - carbon tetrachloride based fumigants), fumigant exposures would be greater as the weather (and subsequently the grain elevators and grain) began to warm up. A factor which may account for the fact that no fumigant exposures to CS_2 and CCl_4

were seen is the conservative approach taken by the two elevators surveyed. This was especially noted at IMF where a major portion of our work was conducted.

At ADM grain handling activities were very low resulting in very limited opportunity to assess worker fumigant exposures. Procedures at IMF - sampling in the grain mass for fumigants, allowing the sample to warm if necessary before taking detector tube samples, and contractual language prohibiting the dumping of grain with in-the-mass fumigant concentrations in excess 10 ppm (the OSHA 8 hour time weighted average) as determined by detector tubes provides what appears to be a very conservative approach to handling treated grain. Inspection of all incoming grain shipments for the presence of fumigants may also contribute to the negligible fumigant levels observed during this survey, again because treated grain isn't taken into the elevator.

No fumigant usage by the elevators occurred during the survey. The amount of onsite fumigation done by or for the elevators was reported to be minimal, thus fumigant exposures associated with internal use were not addressed.

C. Short-Term Fumigant Sampling:

Efforts to evaluate airborne concentrations of carbon disulfide and carbon tetrachloride were inconclusive. The initial portable GC data collected in the field lead us to believe that fairly large amounts of these fumigant compounds were being released as the grain was dumped and run through the elevator. Receipt of the comparison sampling method (sorbent tubes) results indicating nondetectable or negligible levels of these compounds during sampling made us question which, if any, of the data was to be considered valid.

This resulted in the conduct of a follow-up laboratory experiment to compare the two methods used with known contaminant concentrations. The results of this study indicated that the two methods, while they do not agree exactly, will produce results in essentially the same range. The exception to this was seen when an old bottle of carbon tetrachloride was used, resulting in much higher GC values when compared to the sorbent tube samples. One plausible explanation for the high values reported in the field by portable GC analysis is the presence of a chemical interference. The carbon tetrachloride used during the survey was taken from an older, previously opened container.

None of the reagents used for standards in the field were available for subsequent analytical work when disagreement between the data collected by different methods was discovered.

VII. CONCLUSION

The data collected during this survey did not demonstrate the existence of a health hazard from exposure to grain fumigants. The low level of grain shipping activity undoubtedly has significant influence upon these findings, as well as the cautious approach taken by workers when accepting fumigated grain shipments. However, the possibility of inadvertent fumigant exposures or overexposures remains. Sampling of fumigated grain during its passage through the elevator was inconclusive. Conventional sorbent tube sampling for fumigants demonstrated negligible fumigant concentrations during grain dumping and at transfer points in the elevator.

A health hazard from over exposures to grain dust was documented at both elevators.

Recommendations addressing dust exposures, and approches to dealing with fumigated grain shipments are offered in the following section.

IX. RECOMMENDATIONS

A. Interim Recommendations:

These recommendations are intended for more immediate implementation. Due to the varying circumstances affecting worker exposures to grain fumigants, some situations do not lend themselves to a simple or expedient solution.

1. Workers should be provided respirators equipped with dust cartridges (in accordance with an established respiratory protection program - see OSHA General Industry Standard Section 1910.134) in place of the single-use disposable respirators currently used. Laborers involved in railcar dumping and filling, workers in the immediate areas, and dusty housekeeping tasks should be afforded this protection (unless other circumstances such as the presence of fumigants dictates a higher level of or additional protection).

2. Workers required to open fumigated railcars should be provided respiratory protection. The respirator could be donned once the worker is on top of the car and prior to opening it up (the car hatches) avoiding the necessity of climbing with a reduced field of vision due to the respirator facepiece. As a minimum, workers should be provided an approved gas mask to use during the opening of fumigated railcars.[19] More complete protection is provided by self-contained breathing apparatus (SCBA) to use during the initial opening of the shipments (s). This (SCBA use) would necessitate the accompanying training,

maintenance, and certification for SCBA users. Whichever equipment is used would require a respiratory protection program in compliance with CFR 1910.134 of the OSHA General Industry Standards.

3. The current 24 hour passive aeration of railcars appears adequate in maintaining exposures of railcar sampling workers at a low level, provided their breathing zone remains above the top of the railcar itself. Little exposure hazard is expected through skin contact with the grain provided it is not wet with the fumigant.

4. Fumigant placards should be placed on top of the cars by the hatch or doors in addition to being attached to the side of the car. (Sec. 174.208 para (b) of the Hazardous Material Transportation Act regulations state that a railcar with treated lading"... must be placarded on each door (or as close as possible to the door if it is not possible to placard the door) ...". An alternative could be the use of an additional metal tag denoting fumigation. This would be incorporated as part of the car seal and would alert the worker, prior to opening the car, that this shipment of grain has been fumigated. This latter method may have greater durability under a variety of environmental conditions and could not be as easily overlooked.

5. Workers need to be informed that the designated opening dates and times given on placards do not refer to the car's safety for entry or absence of fumigant vapors after that time period but that the time frame used is primarily to ensure effective insect kill.

6. Workers using indicator tubes to assess fumigant concentrations should be trained in the use of such equipment and also be made aware of its limitations.

7. Elevator managers and operators should routinely elicit information on fumigant treatment of incoming grain prior to its arrival at the elevator.

B. Long-Term Recommendations:

The following recommendations are considered appropriate in addressing the long-term solution of this problem.

1. Implementation of local exhaust ventilation at railcar dumping and loading points should be undertaken to reduce worker exposures to grain dust. A reduction in housekeeping

requirements and increased visibility in the area would be expected to accompany this change.

2. Institute a method of tracking grain fumigation during a shipment's passage through the grain handling system with the burden of assurance that a shipment does not exceed acceptable fumigant levels upon the shipper and/or owner.

3. Develop a uniform approach mutually agreed upon and honored by the elevators concerning how fumigated grain shipments should be handled. This could serve as a deterrent to shipping heavily fumigated grain or of shippers searching among elevators for those with the most lenient policies for incoming fumigated grain.

C. Long Term Needs for Protecting Workers from Fumigant Exposures:

Development of methods which assure quick, effective, and economical removal of fumigants from treated grain.

Determination of the best approach in evaluating fumigated grain, to insure that a health risk to workers handling the grain will not occur. An example of this is the question of sampling in-the-grain mass versus above-the-grain mass in deciding if fumigated grain presents a health hazard.

Development of both equipment and strategies for evaluating incoming suspect grain shipments for the identification and quantitation of fumigant content.

Substitution of fumigants having higher toxicity and significant residue potential with compounds having lower human toxicity. These substitutes should leave little if any residual fumigant concentrations in the grain.

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Local 118 American Federation of Grain Millers, Superior, WI.
2. Archer Daniel Midland Elevator, Superior, WI.

3. International Multifoods Elevator, Duluth, MN.
4. Congressman David Obey
5. NIOSH, Region V
6. OSHA, Region V

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I
Job Titles and General Job Description of Elevator Workers at Archer Daniel Midland
and International Multifoods
American Federation of Grain Millers, Local 118
Superior, Wisconsin
May 1984
HETA 84-311

Job Title	General Job Elements, Location	Elevator*
Annexman	Located in elevator annex, move or spot trippers, start belts, open bins, take samples. May have basement annex operators.	ADM, IMF
Cleaner Operator	Operates grain cleaners, at IMF assigned as Floorman, open slide gates on bins, work on main floor.	IMF
Inspectors	Railyard, grain inspection laboratories, car and truck dump areas - check for fumigants; carry samples to laboratory, inspect grain, check protein (IMF).	ADM, IMF
Laborer	Work on main floor area, railcar unloading, also referred to as Dumpmen at IMF in railcar dump area.	ADM, IMF
Leverman	Stationed on Mill (main) floor or Lever Operator.	IMF
Millwright	Maintenance activities throughout entire elevator.	ADM, IMF
Oiler	Works throughout elevator, oils bearings, starts legs, may be incorporated in Millwright tasks at IMF.	ADM

(continued)

Table I (continued)
Job Titles and General Job Description of Elevator Workers at Archer Daniel Midland and International Multifoods
American Federation of Grain Millers, Local 118
Superior, Wisconsin
May 1984
HETA 84-311

Job Title	General Job Elements, Location	Elevator*
Prober	Railyard, probes grain - collecting samples goes out on railcars.	IMF
Scalemen	Also called weighers, weighmen, on scale floor and set spouts on spouting floor (ADM); in weighing office (IMF)	ADM, IMF
Spouter	Set Spouts on spouting floor to direct grain to proper bin (IMF); job incorporated into scaleman tasks at ADM.	IMF
Sweeper	Bin floors, head house, areas throughout elevator - general cleaning in the form of dry sweeping.	ADM

Note: A worker with any one title is not limited exclusively to that job. Depending upon grain handling activities, shiploading, and season workers may take on other tasks. During this survey many workers were involved with sweeping or assisted in the dumping of railcars or trucks in addition to their regular duties.

* ADM: Archer Daniel Midland
IMF: International Multifoods

TABLE II
Contaminant Exposure Evaluation Criteria
American Federation of Grain Millers
Superior, Wisconsin
HETA 84-311

Contaminant	Formula	Recommended TWA Exposure Limit mg/m^3 (ppm)	Recommended Ceiling mg/m^3 (ppm)*	Source[a]	OSHA[b] 8 hour TWA PEL mg/m^3 (ppm)	OSHA Ceiling mg/m^3 (ppm)	Target Organs[d]
Carbon disulfide	CS_2	3 (1)	30 (10)	NIOSH	62 (20)	93 (30)	central nervous systems, peripheral nervous system, cardiovascular system
Carbon tetrachloride	CCl_4	-	12 (2)[c]	NIOSH	62 (10)	15 (25)	central nervous system, eyes, lungs, liver, kidneys
Ethylene dibromide	CH_2BrCH_2Br	0.34 (0.045)	1(0.13)	NIOSH	0.767 (0.1)	3.8 (0.5)	respiratory system, liver, kidneys, skin, eyes
Grain dust	-	4	-	ACGIH	-	-	respiratory system

*: Concentrations have been presented in milligrams per cubic meter (mg/m^3) and parts per million (ppm).

a: NIOSH sources cited are, in order of appearance, reference 6 & 7 - internal NIOSH memorandum. ACGIH criteria are taken from reference 8.

b: The OSHA standard for ethylene dibromide presented here is the proposed limit, 9. All other OSHA standards are from 29 CRF 1910 (reference 10).

c: Denotes compounds considered to have carcinogenic potential in man. NIOSH recommends these substances be treated as suspect occupational carcinogens. No recommended exposure limit, other than maintaining levels as low as feasible is given for ethylene dichloride.

d: See Toxicity Discussion. Information presented here from reference 11.

Table III
Personal Exposure Monitoring Results for Grain Dust
American Federation of Grain Millers, Local 118
Superior, Wisconsin
HETA 84-311
May 15 - 17, 1984

Date	Job Location	Job Title	Sample Duration (minutes)	Concentration in mg/m³*
	International Multifoods - Duluth, Minnesota			
5/15	Inspection Laboratory & outdoors	Sample Carrier	364	1.3
	Inspection Laboratory	Inspector	365	0.73
	Railcar Dump	Laborer	316	8.5
	Railcar Dump	Laborer	316	9.5
	Mill Floor	Cleaner Operator	339	2.5
	Spouting Floor	Cleaner Operator	314	2.3
	Bin Floor	Cleaner Operator	296	0.64
	Annex 1	Annexman	371	3.6
	Annex 2 & 3	Annexman	368	1.1
5/16	Inspection Laboratory & outdoors	Sample Carrier	320	0.34
	Inspection Laboratory	Inspector	255	0.57
	Railcar dump	Laborer	321	5.3
	Railcar dump	Laborer	294	6.8
	Mill Floor	Mill Floor Operator	358	1.6
	Mill Floor	Lever Operator	274	1.4
	Spouting Floor	Cleaner Operator	271	1.0
	Annex 1	Annexman	377	1.9
	Annex 2 & 3	Annexman	375	0.28
5/17	Inspection Laboratory & Outside	Sample Carrier	360	1.1
	Laboratory	Inspector	305	0.74
	Mill Floor	Floorman	212	1.6
	Spouting Floor	Spouter	212	1.1
	Annex 2 & 3	Annexman	174	0.52

continued

Table III (continued)
Personal Exposure Monitoring Results for Grain Dust
American Federation of Grain Millers, Local 118
Superior, Wisconsin
HETA 84-311
May 15 - 17, 1984

Sample Description				
Date	Job Location	Job Title	Sample Duration (minutes)	Concentration in mg/m^3*
Archer Daniel Midland - Superior, Wisconsin				
5/15	Elevator X	Sweeper	406	2.9
	Elevator X	Oiler	400	0.34
	Elevator S, Main Floor	Laborer	429	0.88
	Elevator S, Main Floor	Oiler	428	3.0
	Elevator S, Bin Floor	Sweeper	425	38
	Elevator S, Basement Annex 2	Annexman	420	1.3
	Elevator S, Basement Annex 3	Annexman	419	1.6
5/16	Elevator X	Grain Inspector	191	2.8
	Elevator X, Weigh Station	Sweeper	410	2.1
	Elevator X	Oiler	398	0.67
	Elevator S, Main Floor	Laborer	435	1.6
	Elevator S, Bin Floor	Sweeper	434	30
	Elevator S, Basement-Main Floor	Oiler	426	0.56
	Elevator S, Basement Annex 2	Annexman	416	13
	Elevator S, Basement Annex 3	Annexman	424	0.34
5/17	Elevator X	Sweeper	412	0.46
	Elevator X	Oiler	410	0.65
Evaluation Criteria: ACGIH				4mg/m^3

*: Dust concentrations are given in milligrams per meter cubed (mg/m^3).

Table IV
Personal Exposure Monitoring Results for Carbon Disulfide and Carbon Tetrachloride
American Federation of Grain Millers, Local 118
Superior, Wisconsin
HETA 84-311
May 15 - 17, 1984

Date	Sample Description: Job Location	Job Title	Duration (minutes)	Contaminant Concentration in mg/m^3*: CS_2	CCl_4
	International Multifoods - Duluth, Minnesota				
5/15	Inspection laboratory & outdoors	Sample Prober	450	ND	ND
	Inspection Laboratory & outdoors	Sample Carrier	452	ND	ND
	Inspection Laboratory	Inspector	436	ND	ND
	Railcar Dump	Laborer	422	ND	ND
	Railcar Dump	Laborer	422	ND	ND
	Mill Floor	Cleaner Operator	331	--	ND
	Scale Floor	Weigher	493	--	ND
	Spouting Floor	Spouter	483	ND	ND
	Spouting Floor	Cleaner Operator	419	ND	ND
	Bin Floor	Cleaner Operator	396	ND	ND
	Annex 1	Annexman	499	ND	ND
	Annex 2 & 3	Annexman	490	ND	ND
5/16	Inspection Laboratory & outdoors	Sample Carrier	424	ND	ND
	Inspection Laboratory	Inspector	377	ND	ND
	Railcar dump	Laborer	428	ND	ND
	Railcar dump	Laborer	390	ND	ND
	Mill Floor	Operator	477	--	ND
	Mill Floor	Lever Operator	374	--	ND
	Scale Floor	Weigher	504	--	ND
	Spouting Floor	Spouter	505	ND	ND
	Spouting Floor	Cleaner Operator	361	ND	ND
	Bin Floor	Cleaner Operator	395	--	ND
	Annex 1	Annexman	503	ND	ND
	Annex 2 & 3	Annexman	501	ND	ND

(continued)

Table IV (continued)
Personal Exposure Monitoring Results for Carbon Disulfide and Carbon Tetrachloride
American Federation of Grain Millers, Local 118
Superior, Wisconsin
HETA 84-311
May 15 - 17, 1984

Date	Sample Description: Job Location	Job Title	Duration (minutes)	Contaminant Concentration in mg/m³*: CS_2	CCl_4
5/17	Railroad Loading	Sample Carrier	480	ND	ND
	Mill Floor	Floorman	275	--	ND
	Scale Floor	Weigher	537	--	ND
	Spouting Floor	Spouter	461	ND	ND
	Bin Floor	Cleaner	387	--	ND
	Annex 2 & 3	Annexman	232	ND	ND
Archer Daniel Midland - Superior, Wisconsin					
5/15	Elevator X	Grain Inspector	480	ND	ND
	Elevator S, Basement Annex 2	Annexman	494	ND	ND
	Elevator S, Basement Annex 3	Annexman	493	ND	ND
5/16	Elevator X	Grain Inspector	487	ND	ND
	Elevator S, Basement Annex 2	Annexman	490	ND	ND
	Elevator S, Basement Annex 3	Annexman	498	ND	ND
5/17	Elevator X	Grain Inspector	479	ND	ND
Analytical Limit of Detection:				0.01 mg/sample	0.01 mg/sample
Evaluation Criteria: NIOSH				3mg/m³	12.6 mg/m³

*: Concentrations are given in milligrams per meter cubed (mg/m³), CS_2 = carbon disulfide; CCl_4 = carbon tetrachloride. ND = none detected.

Table V
Selected Fumigant Concentrations Associated with Treated Grain as Determined by Air Bag and Short - Term Sorbent Tube Sampling at International Multifoods
American Federation of Grain Millers, Local 118
Duluth, Minnesota
HETA 84-311
May 15 - 16, 1984

Sample Description			Fumigant Concentration in mg/m^3(ppm)**			
			Carbon Disulfide		Carbon Tetrachloride	
Date	Railcar #	Location, Specific Sampling Conditions	GC	CT	GC	CT
5/15	CRDX 8078	rail siding, barley, hatch open, in-the-mass, prior to dumping	ND	ND	145(23)	23 (3.7)
5/15	SSIX 20337	cedar track, spring wheat, hatch open, in-the-mass, prior to dumping	19(6)	ND	126(20)	4.0(0.64)
5/15	CXIW 170692	Soo Line Yard, barley, hatch closed, above grain, prior to opening hatches or dumping	31(10)	ND	101(16)	9.0(1.4)
5/15	CXIW 170692	Soo Line Yard, barley, hatch open, in-the-mass prior to dumping	84(27)	2.0(0.64)	19(3)	34 (5.4)
5/15	CRDX 8078	spouting floor, barley, grain during passage through elevator, personal exposure in spouting area	ND	ND+	25(4)	ND+
5/15	SSIX 20337	spouting floor, spring wheat, grain during passage through elevator, personal exposure in spouting area	78(25)	ND+	25(4)	ND+
5/16	BN 455705	barley, previously in car CRDX 8078 on 5/15, passed through elevator and placed in railcar, in-the-mass, hatch open	ND	2.2(0.72)	754(120)	25 (3.9)
5/16	CNW 170692	spring wheat, previously in car SSIX 20337 on 5/15, passed through elevator and placed in railcar, in-the-mass, hatch open	50(8)	1.3(0.40)	207(33)	49 (7.8)
Analytical Limit of Detection:			approx 6 mg/m^3 (2 ppm)	0.01 mg/sample	approx 13 mg/m^3 (2 ppm)	0.01 mg/sample

** mg/m^3 = milligrams per meter cubed; ppm = parts per million
ND = indicates contaminant of interest was not detected in the sample.
GC = values obtained from portable gas chromatographic analysis of bag samples.
CT = short term charcoal tube samples analyzed in the laboratory (See Section IV Methods and Materials).
\+ = These exposures were obtained as a single sample.

Appendix A
Analytical Methods and Modifications
American Federation of Grain Millers
Superior, Wisconsin
HETA 84-311

Carbon Tetrachloride: Modifications to NIOSH Method S-314

Desorption Process	:	30 minutes in 1.0 milliliter of carbon disulfide containing 1 microliter/milliliter of benzene as an internal standard
Gas Chromatograph	:	Hewlett-Packard Model 5711A equipped with a flame ionization detector
Column	:	6' x 1/4" (2 mm i.d.) glass packed with 60/80 Carbopack B
Oven Conditions	:	150°C isothermal

Carbon disulfide: Modifications to NIOSH Method S-248

Desorption Process	:	1 hour minimum in 1 ml of benzene
Gas Chromatograph	:	Tracor 220 equipped with a flame photometric detector
Column	:	28" x 1/4" glass packed with 2% OV-225 on 80/100 Supelcoport
Oven Conditions	:	Isothermal: 70°C

Ethlene Dibromide: Analytical Method

The following conditions were used on the gas chromotograph (GC) equipped with an electron capture detector (ECD) for the survey sample set:

Instrument:	Hewlett Packard 5840 with ECD
Column:	3% OV-17 on WHP (6 ft x 1/8 in. glass column)
Carrier Gas:	95% argon/5% methane - 28 mL/min
Column Temperature:	70°C isothermal (8 min)
Injector Temperature	200°C
Detector Temperature:	250°C
Injection Volume:	2 uL
Attenuation:	26

The front sections of the charcoal tubes were desorbed for at least 1 hour with 10 mL of 1% methanol in benzene.

Appendix B
Follow-up Laboratory Study
American Federation of Grain Millers
Superior, Wisconsin
HETA 84-311

I. BACKGROUND

Samples of workplace area and breathing zone atmospheres from grain elevator operations, believed to contain CS_2 and CCl_4, were sampled and analyzed by three methods. There was little correlation between the results obtained by the three methods in the field. Because of this, a laboratory experiment was designed to compare the response of these methods to know concentrations of CS_2 and CCl_4 sampled from an all glass generation system and from aluminized mylar bags (Calibrated Instruments, Inc., Ardsley, NY).

The sampling and analysis methods used were: 1) The photovac gas chromatograph (Model 10A10, Photovac, Inc., Ontario, Canada) equipped with photionization detector and a CSP-20M, 4', 80/100 mesh column operated at ambient temperature, 2) standard charcoal tubes (100-50 mg, SKC, Inc., Eighty four, PA) operated at a flow rate of 1 liter per minute with a calibrated sampling pump (P-2500, Dupont Co., Wilmington, DL) and 3) color change detector tubes (CH 27401, Carbon Tetrachloride 5 L and 6728351, Carbon Disulfide 5 a, National Drager, Inc., Pittsburgh, PA).

II. EXPERIMENTAL:

Atmospheres of the vapors were generated separately in the laboratory vapor presure generation system. Samples were collected for each of the three methods directly from the generation systems' sampling bulb and from aluminized mylar bags that had been filled with the generated atmosphere from the sampling bulb. Samples collected from the bags were completed in a timely manner, none more than 45 minutes after filling. A random sampling schedule was followed throughout the experiment.

Note: The laboratory vapor pressure generating system used is discussed in the NIOSH Technical Report Gas and Vapor Generating Systems for Laboratories, DHHS (NIOSH) Publication No. 84-113, Cincinnati, Ohio, August 1984.

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