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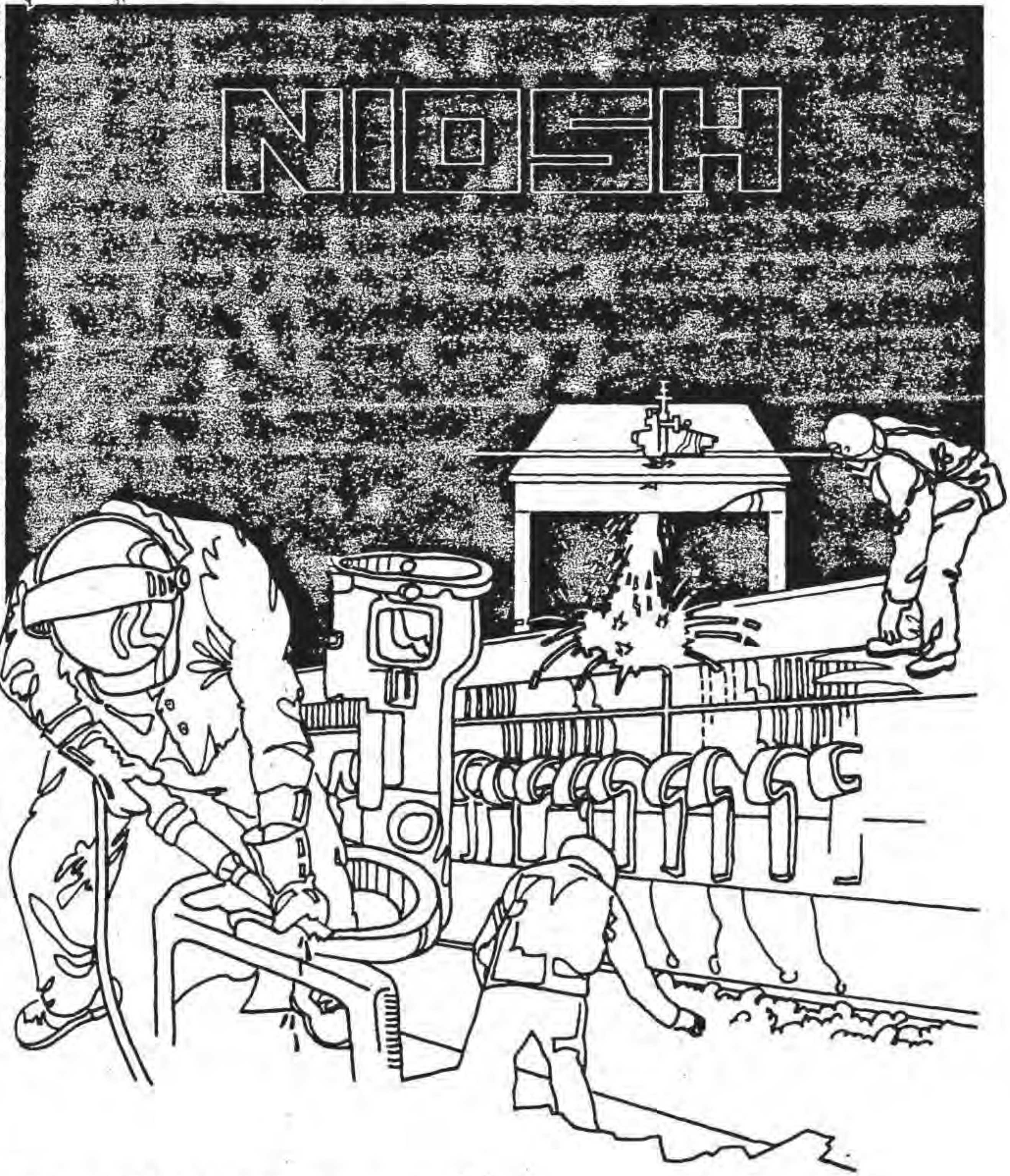

Health Hazard Evaluation Report

HETA 83-375-1521
FEDERAL GRAIN INSPECTION
SERVICE-USDA
PORTLAND, OREGON

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.

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I. SUMMARY

On July 27, 1983, the National Institute for Occupational Safety and Health (NIOSH) was requested by the United States Department of Agriculture (USDA) Federal Grain Inspection Service (FGIS) to evaluate grain fumigant exposures of grain samplers and inspectors in the Portland Oregon field office. A recent increase in movement of heavily treated grain and a subsequent increase in reports of health effects by workers prompted the request.

FGIS workers are required to manually collect representative grain samples from incoming grain shipments at the export elevators and to test and inspect the sample. These tests include a "sniff test" which requires an odor determination in which air in or directly above the grain is inhaled by the inspector.

NIOSH investigators conducted an initial survey November 14-18, 1983 with a follow-up April 8-14, 1984. Evaluation of worker exposures to fumigants and workplace contaminants was conducted primarily by personal exposure monitoring. Short-term sampling for grain fumigant concentrations in situations where higher levels were anticipated was also undertaken. Contaminants evaluated were: carbon disulfide, carbon monoxide, carbon tetrachloride, chloroform, 1,2-dichloroethylene, ethylene dibromide, ethylene dichloride, grain dust, methyl bromide, and noise.

Results from the initial survey found full shift exposures to ethylene dibromide (maximum 21 parts per billion or ppb), carbon disulfide (maximum 738 ppb), and carbon tetrachloride (maximum 1960 ppb). Respective NIOSH evaluation criteria are 45 ppb, ethylene dibromide; 1000 ppb, carbon disulfide; and 2000 ppb, carbon tetrachloride. No chloroform, ethylene dichloride, or 1,2-dichloroethylene were detected. Personal exposures (54 samples) to fumigants during the follow-up survey had a maximum of 0.49 ppb ethylene dibromide and 391 ppb of carbon tetrachloride. Carbon monoxide exposures of truck samplers were at trace levels (NIOSH criteria 35 ppm). No personal exposures to carbon disulfide or methyl bromide were documented. Area noise measurements were all below 90 decibels on the A weighted scale and did not indicate any excessive noise levels. Area concentrations of respirable dust were negligible (maximum concentration 0.37 milligrams per cubic meter (mg/m^3)) (OSHA standard - 5 mg/m^3). Short-term fumigant sampling associated with fumigated grain in railcars indicated extremely high short-term fumigant concentrations. Carbon disulfide concentrations in short-term samples ranged up to

levels in excess of 327,000 ppb. Carbon tetrachloride samples went up to a level in excess of 1,136,000 ppb. NIOSH ceiling concentrations for both carbon disulfide (10,000 ppb) and carbon tetrachloride (2,000 ppb) were exceeded - although comparison of all short-term samples obtained to these criteria may not be appropriate.

The results of this investigation indicate a serious potential health hazard due to high fumigant concentrations present in and immediately adjacent to incoming treated grain. Since workers often must rely on sensory perception of fumigants, whose odor thresholds can be above the level considered to cause adverse effects, overexposures may occur without their knowledge. Inspectors appear to be at risk from direct inhalation of low levels of fumigants, some of which are suspected carcinogens. Recommendations, both short-term and long term are offered concerning personal protective equipment, hazard communication, and treatment of fumigated grain. Long-term recommendations are coupled with Research Needs and include the aeration of fumigated grain to be inspected and modification or elimination of the sniff test as a routine procedure.

KEYWORDS: SIC 4782 (Inspection and Weighing Services Connected with Transportation), grain inspection, grain fumigants, sniff test, carbon disulfide - CAS # 75-15-0, carbon tetrachloride - CAS # 56-23-5, ethylene dibromide - CAS # 106-93-4, grain elevators - export.

II. INTRODUCTION

On July 27, 1983 the National Institute for Occupational Safety and Health (NIOSH) received a request from the United States Department of Agriculture (USDA) Federal Grain Inspection Service (FGIS) to evaluate exposure to fumigants at grain sampling and inspection stations operated by the Portland, Oregon Field Office.

Subsequent to the initial survey, conducted November 14-18, 1983, the request was expanded by USDA to include railcar samples and inspectors. An interim report issued in February 1984, presented exposure data obtained during the initial survey. Workers were found to be exposed to ethylene dibromide, carbon disulfide, and carbon tetrachloride.

A follow-up survey was conducted April 8-14, 1984. Additionally, short-term sampling for fumigants was undertaken.

III. BACKGROUND

A. Federal Grain Inspection Service

The U. S. Grain Standards Act requires that, with some exceptions, all U. S. export grain undergo inspection as it is loaded on board the vessel that will carry it overseas. The inspection is performed by FGIS or by state agencies that have been delegated export inspection authority. The state of Oregon operated its own grain inspection service until early 1978 when the service became federally operated. The Federal Grain Inspection Service currently performs all grain inspections required under state law for grain moving into the state for export. Additionally, Oregon state law requires grain shipments to be inspected by an official agency if U. S. grade standards are used for price determination.

FGIS grain samplers and inspectors are represented by Local 3781 of the American Federation of Government Employees.

B. Process Description

The sampling and inspection process consists of two stages. Grain samplers assigned to truck inspections will collect a 2500 gram (g) grain sample from each truck. This is done with the use of a 6 to 12 foot (1.8 to 3.7 meter) grain trier. The grain sampler must either enter the truck (in the case of semi-trailer vans) or walk out on the top of open top trailers (flat bottom and hopper bottom trailers) and, following a predetermined sampling pattern, insert the probe into the grain, rotate the hollow trier to obtain samples at all levels, remove the trier and empty it on a sample canvas. This process is repeated until the required number of probes have been made. This composite sample is put into a sampling bag and delivered to the on-site laboratory for inspection.

The sample, upon delivery to the laboratory, is weighed and then split down into various fractions for inspection. A divider is used to separate the sample into a 1000 g work sample and a 1000 g file sample. A 250 g sample used for moisture determination is also obtained. Inspectors have reported experiencing fumigant odors during sample division on the Boerner® divider. The 1000 g working sample is then run through a dockage tester which removes the trash (chaff, weed seeds, stones, etc.) from the grain. The weight of grain per bushel is determined from this sample.

The subsamples obtained from the dockage tester are used in the percentage analysis where total defects, heat damage, and odor are determined. Odor is determined by conducting a "sniff test" which requires the inspector to place his/her nose immediately above the grain sample and check for a sour or musty grain odor. This procedure results in direct inhalation exposure of the inspector to residual fumigants present in the grain. The remaining 250 g sample is placed on a grain sizer which separates out broken and shrunken kernels. Grain perceived as fumigated is permitted to sit for four hours prior to inspection and the sniff test, but after it has passed through the splitter and dockage tester, to allow for offgassing of fumigants. The sample is placed off to the side or on an unused work bench area during this time. No local exhaust ventilation is present.

In the case of railroad hopper car sampling the sampler must obtain a sample by probing the grain through the hatch covers (or lids) on top of the car. Depending upon the level of grain in the compartments of the car, the sampler may or may not have to get down into the car itself.

In the past cars that had not been (placarded, indicating that no fumigants were applied to the grain during or after the present load was placed in the car for shipment), had been opened by the samplers while cars that were placarded were opened by elevator personnel and allowed to aerate passively for 24 hours outdoors with the top of the car open. Currently, elevator personnel open all railcars. The grain is probed in a manner similar to that for truck shipments. The samples are handled in an identical manner to truck samples once in the lab.

An additional method of sampling grain, used primarily for railcars during inclement weather and for grain coming from barges or going onto ships, is the use of diverter samples. This is a mechanical sampling device that periodically passes through the grain flow on its way into the elevator and directs it through a series of tubes to a collection point in the FGIS lab.

The number of grain shipments officially inspected in the Portland FGIS District can exceed 100,000 per year.

Grain traffic was not considered by workers or supervisory staff to be moving at maximal levels during either of NIOSH's surveys in Portland. The variability in grain movement activity from day-to-day can be appreciated by the fact that during our follow-up survey among three major export elevators, incoming truck shipments ranged from 0 to about 60 and railcar shipments from 16 to about 80 cars. During the NIOSH surveys there were reports of occasional fumigant odors associated with grain being processed, however all workers displayed a degree of wariness when handling any grain perceived or reported as having a fumigant odor. The general consenus among workers was that the number of grossly fumigated shipments coming into the elevators was down during our surveys.

C. Problem Description

Management at both the Field Inspection Office and national level have expressed concern over the increase in incidence in workers experiencing ill effects associated with fumigated grain. Reported symptoms include loss of coordination, mental confusion, dizziness, lightheadedness, headache, fatigue and drowsiness, burning or watery eyes, and nausea. Individuals reporting these symptoms are the samplers - especially when opening unplacarded fumigated railcars or upon entering trucks having fumigated grain, and the on-site lab personnel involved with preparing and grading samples. Perception of the grain as having been treated is primarily sensory in the absence of placarding. Additionally, the inspectors are concerned about potential chronic health effects associated with long term inhalation of fumigant mixtures.

Numerous difficulties and unknowns are encountered in both evaluating the problem and in taking corrective action. The identification of treated, unplacarded grain shipments before an overexposure has occurred in 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 placarding 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 make determinations of where the grain was treaded 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. Multiple fumigation of grain during storage and shipment 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 making it "safe" for conducting a sniff test remain speculative and unproven as to their efficacy. The question of what constitutes sufficient aeration of grain in order to conduct a sniff test is still unanswered. 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 controversy, 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 another issue. Do 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.

D. Current Approach to Evaluating Fumigant Levels

The method of assessing fumigant levels of grain shipments by the elevators is done exclusively with direct reading indicator tubes. Although this is one of the most expedient methods in attempting to evaluate a rather elusive fumigant exposure situation, this system is subject to all of the previously discussed (see Background) shortcomings in addition to the inherent limitations of indicator tube systems. The significance attached to what may be a cursory and/or improperly obtained fumigant concentration determination appears at times to be inappropriate.

Additionally, any evaluation of a fumigated grain incident, after it has been accidentally 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.

E. 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 has 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)][1] 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)].[1] 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).[1] 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.[2] 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.

E. Surveys Conducted by NIOSH Investigators

A NIOSH investigator conducted an initial survey at three of the Portland FGIS inspection sites during the week of November 14, 1983. He conducted monitoring of truck samplers and truck inspectors to fumigants during their work shift. Fumigants sampled were ethylene dibromide, carbon disulfide, carbon tetrachloride, trichloromethane or chloroform, 1,2-dichloroethane, and 1,2-dichloroethylene. The three-truck sampling stations were located at Bunge Grain Corporation, Cargill Terminal, and Columbia Grain Terminal. The sampling was conducted November 15-18, 1983.

April 8-14, 1984 NIOSH investigators conducted a follow-up survey which included personal exposure monitoring for ethylene dibromide, carbon disulfide, carbon tetrachloride, methylbromide, and carbon monoxide. Area samples for measurement of airborne concentrations of respirable dust in the lab and at truck sampling locations were also obtained. Short-term sampling in an effort to define higher level exposures associated with incoming fumigated grain was also undertaken. The follow-up survey involved monitoring of both railroad car (track) samplers and truck samplers as well as the inspectors grading grain from these two incoming modes of transportation. FGIS inspection locations at the three elevators involved in the November 1983, survey were again the sites of the follow-up survey. Investigators also took general noise level measurements in work areas and by equipment used by FGIS employees.

IV. METHODS AND MATERIALS

A. Initial Survey

During the initial survey exposure monitoring was conducted with portable, battery-operated sampling pumps each equipped with a manifold permitting the collection of four simultaneous samples per worker. Standard 150 milligram charcoal tubes were used for the collection media and the approximate flow rate through each sorbent tube was 100 cubic centimeters per minute for near full-shift sampling. Three of the four tubes were analyzed from each sample set. The fourth tube was retained until after laboratory analyses were completed, allowing an extra sample from each set in the event that additional compounds of interest requiring further analyses were identified.

B. Follow-up Survey

Sampling during the follow-up survey included both personal exposure monitoring and short-term source and exposure sampling. The following types of samples were collected:

Personal Exposures

- Carbon disulfide at 100 cc/min on charcoal
- Carbon tetrachloride at 100 cc/min on charcoal
- Ethylene dibromide at 200 cc/min on charcoal
- Methyl bromide at 50 cc/min on 2 Qazi and Ketchum tubes in series
- Carbon monoxide using Draeger long-term detector tubes (at 20cc/min)

Area and Short-Term Samples

- Carbon tetrachloride and carbon disulfide on standard charcoal tubes - 2 in series at 1 liter per minute (Lpm);

- Area respirable dust samples using a 10 mm nylon cyclone at 1.7 Lpm;

- Area noise levels using a grazing incidence Type II sound level meter; and

- Bag sampling for carbon tetrachloride and carbon disulfide using 5 L aluminized mylar bags, filling them at a rate of about 1 Lpm, and analyzing the sample on site with the use of a portable gas chromatograph

Personal exposure monitoring was to determine worker exposure to the different contaminants encountered over several work days. Most workers for which exposure monitoring was done wore a three tube sampling manifold for fumigants (the first three compounds listed under Personal Exposures). Grain inspectors were asked to move the sorbent tube holders towards their nose during the time they conducted the sniff test. Additionally, railcar samplers were monitored for methyl bromide. Truck samplers were monitored for carbon monoxide from truck exhaust. All sorbent tube samples were stored and shipped cold using blue ice.

Short-term fumigant samples (on charcoal tubes) and bag samples were obtained by sampling in the grain mass in railcars, above the grain mass in railcars, the head space in railcars prior to fully opening the lids, in and above the laboratory grain sample, and at several other locations such as at the grain stream while dumping hopper cars, during the probing of grain in a railcar, and during the conduct of a sniff test. The short-term sorbent tubes required different analytical procedures for carbon disulfide and carbon tetrachloride and therefore the samples were split by the laboratory upon receipt. Confirmation of the presence of carbon disulfide and carbon tetrachloride on the short-term sorbent tubes by gas chromatography-mass spectroscopy was also requested.

Carbon disulfide was analyzed by gas chromatography using NIOSH Method S-248[3] with modifications. Benzene was used for desorption and the gas chromatograph was equipped with a flame photometric detector, operated in the sulfur mode. The limit of detection for carbon disulfide was 3 micrograms per sample for the initial survey sample set, 10 micrograms per sample on the follow-up survey sample set.

Carbon tetrachloride, chloroform, 1,2-dichloroethane, and 1,2-dichloroethylene were analyzed by gas chromatography according to NIOSH Method P&CAM 127[4]. The desorption solvent was carbon disulfide and the gas chromatograph was equipped with a flame ionization detector. The following limits of detection were attained for the initial survey set (given in micrograms per sample): carbon tetrachloride, 10; chloroform, 10; 1,2-dichloroethane, 10; and 1,2-dichloroethylene 10. The follow-up survey sample set was analyzed for carbon tetrachloride according to NIOSH Method S-314[3] with modifications. The analytical limit of detection for this sample set was 10 ug per sample.

Ethylene dibromide samples were analyzed by gas chromatography/electron capture detection (GC/ECD). The analyte was desorbed using a solution of 1% methanol in benzene. The analytical limit of quantitation was 50 nanograms per sample with a limit of detection of 10 nanograms per sample in the initial survey set. Samples collected during the follow-up survey had a limit of quantitation of 23 nanograms per sample and a limit of detection of 5 nanograms per sample.

Methyl bromide samples were analyzed by GC/ECD. The analyte was desorbed using a 2 mL solution of 1% methanol in benzene for at least 1 hour. The analytical limit of quantitation was 0.44 ug/sample and the limit of detection was 0.40 ug/sample.

Carbon monoxide exposures were evaluated using Draeger long-term carbon monoxide tubes (Cat #CH28121) and a low flow sampling pump calibrated at a flow rate of 20 cc per minute. Tubes were read at the termination of the sample.

Respirable dust sampling used a preweighed polyvinyl chloride filter in a 10 millimeter (mm) nylon cyclone, respirable dust sampling train. The flow rate of 1.7 Lpm was established using a Kurz® Mass Flow Meter and a representative sampling train. Sampling trains were pre- and post-shift calibrated. Total weights were determined by weighing the samples plus the filters on an electrobalance and subtracting the previously determined tare weight of the filters. The tare and gross weighings were done in duplicate. The instrumental precision of weighings done at one sitting was 0.01 milligrams. Due to variable factors such as overloading, hygroscopicity of sample, humidity, and the physical integrity of the filter itself, the actual precision can be considerably poorer and occasional slight net negative particulate weights can be expected.

Short-term bag samples were collected using aluminized mylar bags and an SKC Universal Pump®. Samples were taken to the field lab where they were analyzed for carbon tetrachloride and carbon disulfide. Samples were analyzed using a Photovac Model 10A10 gas chromatograph equipped with a photoionization detector.

Short-term sorbent tubes for carbon disulfide and carbon tetrachloride were analyzed as two sample sets submitted sequentially. An initial subset of the tubes collected was analyzed by gas chromatography using Method S-248[3] with modifications to determine the value of submitting the remaining samples for analysis. The limits of detection were 0.01 mg/sample

for both carbon disulfide and carbon tetrachloride.

The identities of carbon disulfide and carbon tetrachloride were confirmed on several of the short-term sorbent tube samples. These samples were reanalyzed on a HP 5992 gas chromatograph/mass spectrometer.

Noise measurements were obtained using a General Radio Type II sound level meter, Model 1565B. The unit was calibrated before and after each day's use. Sound pressure level readings were obtained on both the A-weighted scale and also on the C-weighted scale. Slow meter response was used.

Modifications used with the different analyses, as well as a further description of the bag sampling and portable chromatographic sample analyses, are presented in Appendix A. Table I presents information on the effect sample duration and volume have on the environmental limits of detection for the primary fumigants of interest.

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 occur, 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, diminshed 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.[6]

Dermatitis and vesiculation may result from skin contact with the vapor or liquid.[14] Exposure by inhalation of vapor may be compounded by percutaneous absorption of liquid or vapor.[15] Cutaneous exposure of rabbits to carbon disulfide vapor resulted in measureable 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.[16] A study done by Cesaro[17] 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 measurement 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 for an eight-hour TWA and has an acceptable ceiling concentration of 30 ppm. The acceptable maximum peak above the acceptable ceiling concentration for an eight hour shift is 100 ppm for 30 minutes and this maximum peak must be included in the eight-hour TWA calculation.[12]

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[5].

Carbon disulfide is not known to be an eye irritant and since the odor threshold (7.7 ppm or less) is below the PEL it has good warning properties.[6]

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. 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; 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. Hepatomas have been reported in several animal species exposed to carbon tetrachloride; human exposure has also been associated with hepatomas.[6] Liquid CCl_4 can be absorbed through the skin.[18]

The current OSHA PEL for CCl_4 is 10 ppm over an eight-hour TWA with an acceptable ceiling concentration of 25 ppm and a maximum acceptable peak of 200 ppm for five minutes occurring only once in any four hours and included in the overall TWA calculation.[12]

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, 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.[6]

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 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).[6]

OSHA has proposed a reduction in the EDB PEL from an eight-hour TWA of 20 ppm to 0.10 ppm. 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 over a 15-minute period from the current five minute acceptable maximum peak of 50 ppm.[11]

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) 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) 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, well above occupational exposure limits and therefore is considered to have poor warning properties. Ethylene dibromide is also reported to be an eye irritant.[6]

4. Chloroform

Acute health effects associated with short-term exposures to chloroform or trichloromethane are headache, drowsiness, vomiting, dizziness, unconsciousness, irregular heartbeat, and death. Liver and kidney damage may also result from exposure to chloroform vapor. Prolonged exposure to chloroform may cause liver and kidney damage. A potentiating effect of ethyl alcohol ingestion on the toxicity of chloroform vapor in the occupational setting is suspected, but has not been proven in industrial practice. Liver tumors have been reported in animals and the International Agency for Research on Cancer after evaluating the data on this chemical has concluded that chloroform is a carcinogen.[6]

The current OSHA standard for chloroform is a ceiling level of 50 ppm (240 mg/m^3).[12] NIOSH has recommended that the permissible exposure limit be reduced to ceiling level of 2 ppm averaged over a one hour period and that chloroform be regulated as an occupational carcinogen.[6]

5. 1,2-Dichloroethane

1,2-dichloroethane or ethylene dichloride produces similar acute exposure health effects for all routes of entry: ingestion, inhalation, and skin absorption. Acute exposures result in nausea, vomiting, dizziness, internal bleeding, bluish-purple discoloration of the mucous membranes and skin (cyanosis), rapid but weak pulse, and unconsciousness. Acute exposures can lead to death from respiratory and circulatory failure. Autopsies in such situations have revealed widespread bleeding and damage in most internal organs. Repeated long-term exposures to ethylene dichloride have resulted in neurologic changes, loss of appetite and other gastrointestinal problems, irritation of mucous membranes, liver and kidney impairment, and death. A National Cancer Institute study indicates that ethylene dichloride fed to laboratory rats and mice results in a statistically significant excess of malignant and benign tumors, as compared to controls.[8] Since ethylene dichloride causes progressive, malignant disease of various organs in two species of animals, NIOSH recommends that ethylene dichloride be considered carcinogenic in man. NIOSH recommends that exposure to ethylene dichloride be kept as low as feasible.

The current OSHA PEL for ethylene dichloride is 50 ppm over an eight-hour TWA with an acceptable ceiling concentration of 100 ppm. The acceptable maximum peak above the ceiling concentration is 200 ppm for five minutes during any three-hour period.[12] All peak and ceiling concentrations must be included in the eight-hour TWA calculation.

6. 1,2-Dichloroethylene

1,2-dichloroethylene vapor is a narcotic and a mucous membrane irritant. A concentration of 39,000 ppm was lethal to guinea pigs, and narcosis was produced at 18,000 ppm. Dogs exposed to high concentrations of vapor developed superficial corneal turbidity which was reversible. No effects were observed in several species with repeated exposure for up to six months at 1000 ppm. It has been used as a general anesthetic in man; one industrial fatality was due to very high vapor inhalation in a small enclosure. Exposure to 1,2-dichloroethylene may cause dizziness, drowsiness, and unconsciousness.[6]

The current OSHA PEL for 1,2-dichloroethylene is 200 ppm over a eight-hour TWA. 1,2-dichloroethylene is an eye irritant and with an odor threshold of 0.85 ppm is regarded as having adequate warning properties.

7. Methyl Bromide

Methyl bromide is a severe pulmonary irritant and neurotoxin. It is also narcotic at high concentrations. The onset of toxic symptoms is usually delayed, and the latent period may be from 30 minutes to several days. Early symptoms include headache, visual disturbances, nausea, vomiting, and malaise. In some cases eye irritation, vertigo, and tremors of the hands have occurred; the tremors may progress to twitchings and finally to convulsions. The onset of dyspnea may herald the development of pulmonary edema. Tubular damage of the kidneys has been observed in fatal cases. Victims who recovered from severe intoxication have had persistent central nervous system effects including vertigo, depression, hallucinations, anxiety and inability to concentrate.[6]

The current OSHA PEL for methyl bromide is 20 ppm over an eight-hour TWA. The ACGIH recommends an eight-hour exposure limit of 5 ppm.[9] Since methyl bromide has virtually no odor and no immediately irritating effects, it is considered to have poor warning properties.

8. 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.[19]

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.[19]

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.[19]

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.[19] This is the basis of the recommended time-weighted TLV of 4 mg/m^3 for total dust.

9. Carbon Monoxide

Carbon monoxide (CO) gas causes tissue hypoxia by preventing the blood from carrying sufficient oxygen. CO combines reversibly with the oxygen-carrying sites on the hemoglobin molecule with an affinity ranging from 210 to 240 times greater than that of oxygen. In addition, carboxyhemoglobin (COHB) interferes with the release of oxygen carried by unaltered hemoglobin. Exposure to high concentrations such as 4000 ppm and above may have only transient weakness and dizziness as the premonitory warnings before the individual goes into a coma. Cerebral edema is the most common early aftermath of severe intoxication. Exposure to concentrations of 500 to 1000 ppm causes the development of headache, tachypnea (rapid breathing), nausea, weakness, dizziness, mental confusion, and in some instances, hallucinations, and may result in brain damage. The affected person is commonly cyanotic (blue). Concentrations as low as 50 ppm result in blood COHb levels of up to 10% in an 8-hour day. This greatly increases the risk of angina pectoris and coronary infarctions by decreasing the oxygen supply in the blood and also in the myoglobin of the heart muscle. These effects are aggravated by heavy work, high ambient temperatures, and high altitudes. Pregnant women are especially susceptible to the effects of increased CO levels. Smoking also increases the risk: cigarette smoke contains 4% CO (40000 ppm), which results in 5.9% COHb if a pack a day is smoked. The diagnosis of CO intoxication depends primarily on the demonstration of significantly increased carboxyhemoglobin in the blood.[6]

The current OSHA PEL for carbon monoxide is 50 ppm (55 mg/m^3) averaged over an eight-hour work shift. NIOSH recommends that the PEL be reduced to 35 ppm (40 mg/m^3) with a ceiling of 200 ppm (230 mg/m^3).[6]

Carbon monoxide is an odorless, colorless, non-irritating gas and therefore has no warning properties.

10. Noise

Exposure to intense noise causes hearing losses which may be temporary, permanent, or a combination of the two. These impairments are reflected by elevated thresholds of audibility for discrete frequency sounds, with the increase in decibels (dB) required to hear such sounds being used as a measure of the loss. Temporary hearing losses, also called auditory fatigue, represent threshold losses which are recoverable after a period of time away from the noise. Such losses may occur after only a few minutes of exposure to intense noise. With prolonged and repeated exposures (months or years) to the same noise level, there may be only partial recovery of the threshold losses, the residual loss being indicative of a developing permanent hearing impairment.

The losses in hearing due to exposure to intense occupational noise (105 dB(A) or above) tend to reach a plateau at certain frequencies (most notably 4000 Hertz) after about 10 years of exposure. The hearing loss for such frequencies, which result from a 10-year exposure to noise, appears to approximate the temporary hearing loss resulting from a single days exposure.[15]

The OSHA PEL for continuous noise exposure is 90 dB(A) for a duration of eight hours per day. NIOSH and the ACGIH recommend that the daily noise exposure or dose not exceed 85 dB(A) over an eight-hour work shift. The ACGIH also recommends the inclusion of all on-the-job noise exposures of 80 dB(A) or greater in calculating daily noise exposure.[9]

VI. RESULTS

A. Initial Environmental Survey

Personal exposure monitoring results for fumigants conducted November 14-18, 1983, are presented in Table III. A total of 24 personal exposure samples for ethylene dibromide, carbon disulfide, and other chlorinated fumigant compounds were collected over the workers' full work-shift (13 inspectors, 11 samplers).

Ethylene dibromide full-shift TWA exposures ranged from non-detectable to 160 ug/m^3 (21 ppb). Twelve samples (50%) had concentrations above the analytical limit of quantitation, eight samples (33%) were identified as having EDB present, but below quantifiable levels (trace quantities); and four samples (16%) had no detectable EDB. The geometric mean (GM) concentrations for all samples in which EDB was present is 2.46 ug/m^3 (0.32 ppb) with a geometric standard deviation (GSD) of 4.81. For grain samplers, EDB exposures had a GM of 1.74 ug/m^3 (0.23 ppb) with a GSD of 2.50 and for grain inspectors the GM EDB exposure value was 1.19 ug/m^3 (0.16 ppb) with a GSD of 7.04. (All means are calculated from quantifiable and trace exposures, non- detectables have been omitted). The EDB recommended exposure limit is 345 ug/m^3 (45 ppb).

Carbon disulfide TWA exposures ranged from nondetectable up to 2280 ug/m^3 (738 ppb). Eleven of 24 CS_2 samples (46%) were above the analytical limit of quantitation. The remaining 13 (54%) were non-detectable. The GM exposure was 208.2 ug/m^3 (67 ppb) with a GM of 2.64 for all samples-excluding nondetectables. Grain samplers had exposures with a GM of 303.5 ug/m^3 (98 ppb) and GSD of 4.19 and grain inspectors had a GM exposure of 167.9 ug/m^3 (54 ppb) with a GSD of 1.87. The recommended CS_2 exposure limit is 3000 ug/m^3 (1000 ppb).

Eleven of the 24 CCl_4 samples (46%) were above the analytical limit of quantitation. The remaining 13 (54%) were non-detectable. Carbon tetrachloride TWA exposure ranged from non-detectable up to 12350 ug/m^3 (1960 ppb). The GM for all samples is 775 ug/m^3 (123 ppb) with a GSD of 2.82. The mean exposure for grain samplers was 1856 ug/m^3 (295 ppb), GSD of 6.15; and for grain inspectors was 558 ug/m^3 (89 ppb), GSD of 1.46. The recommended exposure limit for CCl_4 is 12,600 ug/m^3 (2,000 ppb).

Samples for chloroform, ethylene dichloride, and 1,2-dichloroethylene were all below detectable levels.

One short-term sample taken in a railcar containing fumigated grain demonstrated a CS_2 concentration of 8800 ug/m^3 (28000 ppb) and a CCl_4 concentration of 32500 ug/m^3 (5167 ppb).

B. Follow-up Environmental Survey:

The follow-up survey included personal exposure monitoring for fumigants and carbon monoxide, short-term source monitoring for fumigants, area respirable dust samples, and area sound level measurements.

1. Fumigant Exposures

A total of 54 personal exposure samples were obtained for EDB, CS_2, and CCl_4. Twelve of the 54 EDB samples (22%) were above detectable limits. Six of the 54 samples (11%) fell between the analytical limits of detection and quantitation. Six (11%) were quantifiable. The GM concentration for all EDB samples is 0.48 ug/m^3 (0.06 ppb), GSD 2.6. Ten grain samplers had EDB exposures with a mean of 0.54 ug/m^3 (0.07 ppb), 2.4 GSD; and two grain inspectors had trace exposures. Recommended exposure limit to EDB is 345 ug/m^3 (45 ppb).

Of the 54 samples obtained for CS_2, none were determined to have a detectable concentration of CS_2.

Ten of the 54 (18%) samples taken for determining CCl_4 exposures were quantifiable. The remaining 44 (81%) were below analytical limits of detection. The GM concentration of all ten samples was 480 ug/m^3 (76 ppb) with a GSD of 2.3. Five grain samplers and five grain inspectors monitored for CCl_4 exposure composed this group of samples, with the GM exposure for grain samplers of 755 ug/m^3 (120 ppb) - GSD 1.8. The recommended exposure limit for CCl_4 is 12,600 ug/m^3 (2,000 ppb).

Nine personal exposure samples for methyl bromide were obtained for railcar samplers. None of these samples documented the presence of any methyl bromide during the follow-up survey.

Results of the monitoring for grain fumigant exposure during the April, 1984 survey are presented in Table IV.

2. Carbon Monoxide

Six truck samplers were monitored for carbon monoxide (CO) exposures associated with idling truck engines in the truck sampling area. Full shift sampling indicated that the workers did not encounter any significant exposures due to the idling of truck engines in these sampling areas. The two samples indicating trace concentrations had a small amount of color change in the indicating layer but produced an insufficient stain length to obtain any estimate of concentration. The minimum quantifiable CO concentration was about 10 ppm (10000 ppb) for a 10 liter air sample. Table V presents carbon monoxide exposure monitoring data.

3. Short-Term Fumigant Sampling

The results of short-term fumigant sampling for carbon disulfide and carbon tetrachloride are presented in Tables VI and VII and Figures I and II. Short-term bag sampling data obtained with the use of a portable gas chromatograph is presented in Table VI along with the corresponding sorbent tube samples. The sampling and analytical methods used to assess these transient circumstances presented limitations which restricted our ability to evaluate this type of situation. Analytical limits of detection, sample volume, and sample duration all influence the ability to evaluate fumigant concentration. One of the difficulties encountered with our portable gas chromatograph appears to be the vast range of unknown fumigant concentrations seen in grab samples. Concentrations ranged from below the instruments capabilities of detection up to a level which resulted in overloading of the unit to the point where it was rendered nonfunctional for prolonged periods of time (loss of sensitivity due to "swamping the column"). Due to problems encountered with the unit no further presentation of the bag sampling data is given other than in this section. All conclusions will be drawn from sorbent tube sampling data.

Short-term fumigant data were extremely eratic, with concentrations varying widely among different samples obtained for any one car of grain, in addition to the variation in fumigant concentrations between different railcars. The highest fumigant concentrations for both CS_2 and CCl_4 were seen in the samples of railcar head spaces and samples obtained in the grain mass itself. Overall fumigant concentrations among all samples taken spanned three to four orders of magnitude. A total of 47 sorbent tube samples were taken along with 33 bag samples.

Eleven of the 29 bag samples having detectable quantities of CS_2 exceeded the respective sorbent tube sample quantities. The mean concentration of CS_2 among these samples was 4.7 ppm (GSD 11.7) compared to 3.8 ppm (GSD 16.2) for the sorbent tubes. Note that in Table VI the environmental limits of detection for different samples varies. This is influenced by sample volume and duration (See Table I).

Confirmation of the presence of CS_2 and CCl_4 on the short-term sorbent tube samples was done on selected samples. Both CS_2 and CCl_4 were confirmed to be present on samples in which these compounds had already been identified with the gas chromotographic analyses.

4. Area Respirable Dust Sampling

A total of eighteen area respirable dust samples were obtained with seventeen having a measurable weight gain. The GM dust level was 0.09 mg/m^3 (GSD 2.1). Table VIII presents the respirable dust sampling results.

5. Area Sound Level Measurements

Noise level measurements obtained on both the A- and C-weighted scale are presented in Table IX along with the maximum recommended exposure time (in hours) to a continuous noise of the intensity measured. No A-weighted levels above 90dB(A) were measured. A total of 23 different measurements were obtained.

6. Review of Fumigant Exposure Incident Reports

A review of the OSHA Log of Federal Occupational Injuries and Illnesses for 1982 and 1983 indicated that there were two fumigant exposure incidents in 1982 for the Federal Grain Inspection Service, Portland Oregon Field Office and 12 in 1983. The occupation of workers involved were Agricultural Commodity Grader and Agricultural Commodity Technician.

Incident reports concerning fumigant exposures were examined for the time period of February through July, 1983. During this period nine fumigant exposures were reported. Thirty three percent (3/9) involved grading or inspecting grain, 56% (5/9) involved truck sampling, and 11% (1/9) involved railcar grain sampling. Symptoms reported by workers were as follows:

loss of coordination, mental confusion, dizziness,lightheadness	89% (8/9)
headache	33% (3/9)
fatigue, drowisness	33% (3/9)
burning or watery eyes	33% (3/9)
nausea	11% (1/9)

Eight of the reported instances identified the fumigant as an "80/20" fumigant. One involved phostoxin. The age range of the affected workers was 27 to 34.

VII. DISCUSSION

A. Personal Exposure Monitoring Results:

Personal exposure monitoring for fumigants conducted during both the initial and follow-up surveys demonstrated the occurrence of measurable worker exposures to the fumigants. While no personal exposures exceeded recommended or permissible exposure limits the extreme variability and uncertainty associated with fumigant levels in grain shipments received at the elevators makes the assumption that over exposure will not occur improper.

Almost all ethylene dibromide exposures occurred among truck grain samplers and truck grain inspectors. A decrease in ethylene dibromide exposures between the initial and follow-up survey is considered attributable to the recent banning of ethylene dibromide as a grain fumigant. Exposures to ethylene dibromide occurring during the follow-up survey may most likely represent exposure to residual levels present in older grain. The absence of any CS_2 exposures during the follow-up survey (for truck grain shipments) as compared to the initial survey may indicate that grain moving last November had been fumigated more recently than that brought in in April, that application rates were heavier, or possibly grain moved in April had been handled more after treatment allowing for greater aeration of the grain. Other confounding factors previously mentioned in the Background section may also contribute to this observed decrease in fumigant levels.

Compounds with lower vapor pressures, such as EDB and CCl_4, appear to remain in grain for a longer period of time possibly contributing to low level worker exposures. This appears desirable from the standpoint of insect eradication (as in the case of EDB) for grain stored in non-airtight facilities.

Methyl bromide exposures, suspected as possibly occurring due to use of the compound as an EDB substitute, were not observed for railcar samplers. Due to the extremely high vapor pressure of methyl bromide, concentrations of this compound at any work location after the opening of a more airtight enclosure (such as a railcar) is considered to be very low. Therefore sampling for methyle bromide was limited to situations where detectable concentrations were considered to be most likely to occur.

B. Short-term Sampling Results from Fumingated Grain Shipments:

Evaluation of fumigant concentrations in incoming railcars demonstrated the presence of a potentially serious health hazard. Railcar head space concentrations were well in excess of recommended ceiling limits for CS_2 and CCl_4. Consideration of the head space fumigant concentrations when reviewing reported acute health effects and comparing them to the toxicology of these compounds suggests that short-term high level acute exposures to CS_2 and $CCl4$ can occur. The initial disruption of a high level head space concentration during the opening of railcar lids by unprotected personnel may result in a significant exposure falling between the reported full-shift trace exposures reported for personal exposures and the high concentrations seen in the head spaces. Since fumigated and nonfumigated railcar shipments are indentical in appearance except for placarding, workers opening unplacarded fumigated grain shipments probably will not realize the grain has been treated until after the exposure has occurred. Loss of placards in transit and failure to remove placards from nonfumigated grain shipments were also mentioned as contributing to the confusion in identifying fumigated shipments. During the NIOSH surveys, elevator personnel were required to open up all placarded railcars.

C. Fumigant Sampling Results from In-the Mass Versus Above-the Mass:

Samples obtained in the grain mass in the railcars, while not comparable to any breathing zone or ambient air exposure limit, demonstrate a reservoir of fumigant vapor which can become airborne as the shipment is processed through the grain handling system enroute to its final destination.

Comparison of in-the-mass with above-the-mass air samples shows that sampling done in-the-mass is not comparable to above-the-mass airborne fumigant concentrations. The two railcars with the highest head space fumigant concentrations could not be sampled in-the-mass since this grain was dumped by the elevator and brought into the house without an on site grade determination. All in-the-mass samples were obtained after passively aerating the railcars for a period of 24 hours. One must also realize that the question of uniformity of distribution of fumigants throughout the shipment has not been determined.

NIOSH investigators have also observed the discrepancy between fumigant concentrations above a grain mass versus in the grain mass in another instance involving fumigated grain (Interim letter report, HETA 84-194, American Federation of Grain Millers, Superior, Wisconsin, March 1984). Concentrations of fumigants in that situation were not observed to be as high as in this present evaluation. One reason for this may have been the fact that in HETA 84-194 some efforts to aerate the grain had been ongoing for a week prior to sample collection.

The debate over using fumigant levels obtained in-the-grain mass versus above the grain mass also remains. Both approaches present some problems. Sampling above the grain mass, especially in more open or outdoor areas, will provide a substantial amount of dilution ventilation which, when combined with a relatively small sample volume may produce an artificially low estimation of exposure risk. Not all locations or procedures through which this grain may pass at the elevator will always have this same amount of ventilation. Conversely, sampling directly in the grain mass may also over- or underestimate the potential exposure hazard.

Non-uniformity of fumigant concentrations in the mass may produce artificially high or low levels compared to the total shipment. Additionally, these fumigant concentrations do not represent actual breathing zone exposures (with the possible exception of workers required to do sniff tests). More likely these in-the-mass concentrations reflect a level of fumigant which will decrease over time as it is released into the surrounding atmosphere during handling, down to some residual level influenced by the grain kernels ability to absorb and hold fumigant under the influence of a myriad of envrionmental conditions.

D. Handling of Fumigated Grain at the FGIS Inspection Laboratories:

Problems have also been expressed concerning the bringing of fumigant laden samples into the FGIS lab for inspection. Current practice in handling fumigated grain samples is to split down the sample and allow the grain to air out in an open metal pan or container for four hours. Presence of fumigants (i.e., whether the sample has sufficiently aired out) is determined largely by the presence or absence of fumigant odor. Since not all fumigants used on grain have odor thresholds below hazardous exposure levels, a negative odor determination alone does not insure the absence of higher fumigant levels. Additionally, the practice of using inspectors to evaluate grain odors influential in grade determination while also inhaling low or unknown concentrations of fumigants, some suspect carcinogens, is a highly questionable practice having substantial impact on the grain industry.

The primary route of exposure of FGIS workers to fumigants is considered to be inhalation. Skin absorption of fumigant vapors, such as carbon disulfide,[16] may be possible at high concentrations, however the contact time FGIS workers have with large quantities of heavily treated grain is considered to be minimal.

Basically, evaluating fumigant grain shipments coming into the elevators requires being prepared for unanticipated occurrences and then having the circumstances work out in such a way that fumigant monitoring is in progress or can be done while the event takes place. Additionally, the heightened level of concern among workers about fumigants and their cautious approach and/or refusal to process treated grain most likely contributes to a reduction in the overall number of acute fumigant exposures. Due to the number of parties involved with a grain shipment, from the time it is initially stored after harvest through to its final destination, solution of the problem requires involvement of all concerned.

E. Dust, Carbon Monoxide, and Noise Levels:

Exposures of FGIS workers to respirable dust, carbon monoxide, and noise does not appear to be a problem, although in the case of noise, conducting personal noise dosimetry during periods of peak truck and lab activity would provide a better picture of noise exposure. Depending upon duration some noise overexposures may occur on a sporadic basis, since some levels were in the upper 80 dBA range.

VIII. CONCLUSION

Although no personal overexposure of workers to fumigant vapors was documented during this investigation, the results of this investigation indicate a serious potential health hazard associated with incoming fumigated grain shipments. Due to the myriad of variables influencing these situations, documentation of actual worker overexposures will probably only happen through a fortuitous sequence of events. The evaluation process for sour or musty grain which requires inspectors to directly inhale air from grain which may have been treated with fumigants, including those considered to have carcinogenic potential, places these workers at an increased risk. The effect of chronic low level inhalation of fumigants such as CS_2 and CCl_4, singly or in combination with other fumigants is unknown.

VII. RECOMMENDATIONS

A. Interim Recommendations

These recommendations are intended to be amenable to 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 required to open fumigated railcars should have self-contained breathing appratus to use during the initial opening of the shipment(s).

2. 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.

3. 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) ...".

4. 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.

5. 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.

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

7. Utilizing information available from placards and shipper reporting of fumigant usage, samples to be sniff tested should be evaluated at the grain sample surface after having been split and run through the dockage tester. Levels of CS_2 at or exceeding 10 ppm or CCl_4 at or above 2 ppm should be used as criteria in deciding whether to grade the sample or allow it to stand in an open area (preferably well ventilated away from the main area of activity) following the current four hour wait before conducting the sniff test. Fumigant level determination should be repeated before conducting the sniff test.

8. The current policy of requiring truck drivers bringing in recently fumigated grain to park for 24 hours or refusing to sample if the fumigant is still present in the grain should be publicized. Especially in the case of trailer vans, the sampler may not perceive the presence of fumigant until he/she is inside, making a cautious approach difficult unless self-contained or air-line respiratory protection is provided.

9. All FGIS inspection labs should be evaluated concerning the general make-up air systems in order to insure sufficient air exchanges capable of removing low level airborne contaminants (vapors). Inspection laboratories having local exhaust hoods should insure sufficient make-up air to replace what is being exhausted.

10. Enclosure of the Boerner® Divider below the drop at the location where grain cascades over the internal cone should be provided to reduce dust and fumigant release into the operators breathing zone. Depending upon the materials used to achieve this, the amount of noise generated may also be reduced slightly.

B. Long-Term Recommendations

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

1. 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.

2. 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.

3. An alternative method of evaluating grain for sourness or mustiness should be implemented, (See Research Needs) phasing out the conventional sniff test, or at least reserving the sniff test for contested or non-routine grading procedures. Changes in fumigant usage (i.e., elimination of fumigants associated with residual levels in grain) may alter this recommendation.

4. Development of a registry of grain handlers and inspectors along with descriptive job elements which will permit long term surveillance of the group tied in with occupational history.

C. Research Needs

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.

Identification of other compounds or properties of sour or musty grain which can be used as a replacement for the sniff test. A quantitative, fast, reproducible method is highly desirable.

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

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

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1. U.S. Federal Grain Inspection Service
2. USDA Federal Grain Inspection Service - Portland Field Office
3. American Federation of Government Employees - Local 3781
4. American Federation of Government Employees - Washington D.C.
5. NIOSH, Region X
6. OSHA, Region X

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

Affect of Sample Duration and Volume on Environmental Limits of Detection
Portland Field Office Inspection Sites

Portland, Oregon
HETA 83-375

Compound	Analytical LOD in ug per sample	Sampling Rate (LPM)	Sampling Volume (L)	Minimum Duration (min)	Environmental Limit of Detection in ug/m^3 (ppb)*
Carbon disulfide	10	0.1	1	10	10000 (3200)
			5	50	2000 (640)
			10	100	1000 (320)
			48	480	200 (70)
Carbon tetrachloride	10	0.1	1	10	10000 (1600)
			5	50	2000 (320)
			10	100	1000 (160)
			48	480	200 (30)
Ethylene dibromide	0.005	0.2	1	5	5 (0.6)
			5	25	1 (0.1)
			10	50	0.5 (0.06)
			48	240	0.1 (0.01)
Methyl bromide	0.40	0.05	1	20	400 (100)
			5	100	80 (20)
			10	200	40 (10)
			24	480	20 (4)

*Concentrations are given in micrograms per cubic meter (ug/m^3) with parts per billion (ppb) in parentheses.

TABLE II

Contaminant Exposure Evaluation Criteria

Federal Grain Inspection Service
Portland, Oregon
HETA 83-375

Contaminant	Formula	Recommended TWA Exposure Limit ug/m3 (ppb)*	Recommended Ceiling ug/m3 (ppb)*	Source[a]	OSHA[b] 8 hour TWA PEL ug/m3 (ppb)	OSHA Ceiling ug/m3 (ppb)	Target Organs[d]
1 Carbon disulfide	CS_2	3000 (1000)	30000(10000)	NIOSH	62040 (20000)	93061 (30000)	central nervous systems, peripheral nervous system, cardiovascular system
2 Carbon monoxide	C O	40000 (35000)	228570 (200000)	NIOSH	55000 (50000)	-	cardiovascular system, lungs, blood, central nervous system
3 Carbon tetrachloride	CCl_4	-	12600 (2000)[c]	NIOSH	62857 (10000)	157143 (25000)	central nervous system, eyes, lungs, liver, kidneys
4 Chloroform	$CHCl_3$	-	9714 (2000)[c]	NIOSH	-	240000 (50000)	liver, kidneys, heart, eyes, skin
5 1,2-Dichloroethylene	ClCH=CHCl	-	-	-	790000 (2000000)	-	respiratory system, eyes, central nervous system
6 Ethylene dibromide	CH_2BrCH_2Br	345 (45)[c]	1000 (130)	NIOSH	767 (100)	3838 (500)	respiratory system, liver, kidneys, skin, eyes
7 Ethylene dichloride	$ClCH_2CH_2Cl$	c	-	NIOSH	202000 (50000)	404082 (100000)	kidneys, liver, eyes, skin, central nervous system
Grain dust	-	4000	-	ACGIH	-	-	respiratory system
Methylbromide	CH_3Br	20000 (5000)	-	ACGIH	-	80000 (20000)	central nervous system, respiratory system, lungs, skin, eyes
Noise+	-	85dBA/8 hrs	115dBA/.12hr.	ACGIH	90dBA/8 hrs	115dBA/.25hr	auditory system

*: Concentrations have been presented in micrograms per cubic meter (ug/m^3) and parts per billion (ppb) in parentheses. To convert to milligrams per cubic meter (mg/m^3) or parts per million (ppm) divide listed value by 1000.

a: NIOSH sources cited are, in order of appearance, references 5, 6, 7, 6, - internal NIOSH memorandum, 8, 10. ACGIH criteria are taken from reference 29.

b: The OSHA standard for ethylene dibromide presented here is the proposed limit, 11. See Appendix B. All other OSHA standards are from 29 CFR 1910 (reference 12).

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 13.

+: Noise evaluation criteria is given for a continuous sound level.

Table III

Fumigant Exposures of Federal Grain Inspection Service Workers

Portland Field Office Inspection Site
Portland, Oregon
HETA 83-375
November 15-18, 1983

Date	Elevator	Job	Duration(min)	Concentration in ug/m³(ppb)+		
				$C_2H_4Br_2$	CS_2	CCl_4
11/15	Columbia Grain	Truck Sampler	320	trace	ND	ND
11/15	Columbia Grain	Truck Sampler	293	trace	ND	ND
11/15	Columbia Grain	Truck Inspector	319	10 (1.3)	130 (41)	430 (68)
11/15	Columbia Grain	Truck Inspector	295	trace	130 (41)	ND
11/15	Bunge Elevator	Truck Sampler	388	12 (0.16)	ND	ND
11/15	Bunge Elevator	Truck Inspector	366	43 (0.56)	ND	570 (90)
11/15	Bunge Elevator	Truck Inspector	365	160 (21)	90 (29)	590 (94)
11/16	Columbia Grain	Truck Sampler	387	ND	310 (101)	1570 (250)
11/16	Columbia Grain	Truck Sampler	373	trace	100 (32)	330 (53)
11/16	Columbia Grain	Track Sampler	340	ND	2280 (736)	12350 (1960)
11/16	Columbia Grain	Truck Inspector	389	trace	260 (85)	660 (105)
11/16	Columbia Grain	Truck inspector	402	trace	410 (131)	1020 (161)
11/16	Bunge Elevator	Truck Sampler	386	1.8 (0.23)	ND	ND
11/16	Bunge Elevator	Truck Inspector	395	2.5 (0.32)	ND	560 (88)
11/16	Bunge Elevator	Truck Inspector	400	1.7 (0.22)	80 (26)	270 (43)
11/16	Cargill Elevator	Truck Inspector	392	ND	ND	ND
11/16	Cargill Elevator	Track Inspector	464	trace	ND	ND
11/17	Columbia Grain	Truck Sampler	376	2.6 (0.34)	ND	ND
11/17	Columbia Grain	Truck Sampler	374	2.3 (0.29)	120 (38)	ND
11/17	Columbia Grain	Truck Inspector	365	2.7 (0.36)	290 (93)	640 (102)
11/17	Bunge Elevator	Truck Sampler	442	2.8 (0.36)	ND	ND
11/17	Bunge Elevator	Truck Inspector	435	6.0 (0.76)	ND	ND
11/18	Cargill Elevator	Truck Sampler	233	trace	ND	ND
11/18	Cargill Elevator	Truck Inspector	244	ND	ND	ND
11/18	Columbia Grain - Rail Car Headspace*		15	ND	8800 (2836)	32500 (5167)
OSHA 8 hour TWA PEL ** in ug/m³(ppb)				767 (100)	62040(20000)	62857(10000)
Analytical Limit of Detection in ug per sample				0.01	3	10

+Concentrations are given in micrograms per cubic meter (ug/m³) with parts per billion (ppb) given in parentheses.
ND indicates sample concentration was below the given limit of detection for that substance.
Trace denotes ethylene dibromide samples in which the compound was identified as being present but was below a concentration which could be analytically quantified or less than 50 nanograms but greater than 10 nanograms per sample
Fumigants sampled were:

$C_2H_4Br_2$ = ethylene dibromide
CS_2 = carbon disulfide
CCl_4 = carbon tetrachloride

*The rail car in which this sample was taken was known to contain fumigated grain. The top hatches had been propped open for approximately 70 to 90 minutes prior to sampling

** Values are the 8 hour time weighted average (TWA) permissible exposure limit (PEL) Reference 12
The ethylene dibromide value is taken from OSHA's proposed rule.

Table IV

Exposure of Federal Grain Inspection Service Workers to Ethylene Dibromide, Carbon Disulfide, and Carbon Tetrachloride

Portland Field Office Inspection Site
Portland, Oregon
HETA 83-375

April 9-13, 1984

Date	Elevator	Job	Duration (min)	Concentration in ug/m^3 (ppb)+ $C_2H_4Br_2$	CS_2	CCl_4	CH_3Br
4/09	Columbia Grain	Truck Sampler	433	0.85 (0.11)	ND	ND	-
		Truck Sampler	410	0.92 (0.12)	ND	ND	-
		Truck Inspector	426	Trace	ND	ND	-
		Truck Inspector	413	ND	ND	ND	-
		Track Sampler	136	ND	ND	ND	ND
		Track Inspector	245	ND	ND	ND	-
		Track Inspector	243	ND	ND	ND	-
4/09	Cargill Elevator	Truck Sampler	417	0.62 (0.08)	ND	ND	-
		Truck Inspector	431	ND	ND	ND	-
		Track Sampler	342	0.56 (0.07)	ND	585 (93)	ND
		Track Inspector	427	ND	ND	ND	-
		Track Inspector	453	ND	ND	ND	-
		Ship Inspector	412	ND	ND	ND	-
4/10	Columbia Grain	Truck Sampler	399	ND	ND	ND	-
		Truck Sampler	422	Trace	ND	ND	-
		Truck Inspector	400	ND	ND	ND	-
				ND	ND	ND	-
		Track Sampler	210	ND	ND	ND	ND
		Track Sampler	222	ND	ND	ND	ND
		Track Inspector	273	ND	ND	ND	-
		Track Inspector	274	ND	ND	ND	-
		Track Inspector	260	ND	ND	ND	-

Continued

Table IV
Continued

Date	Elevator	Job	Duration (min)	Concentration in ug/m^3 (ppb)$^+$ $C_2H_4Br_2$	CS_2	CCl_4	CH_3Br
4/10	Bunge Elevator	Truck Sampler	376	Trace	ND	ND	-
		Truck Inspector	384	ND	ND	ND	-
		Track Sampler	422	ND	ND	ND	ND
		Track Inspector	424	ND	ND	ND	-
		Track Inspector	414	ND	ND	ND	-
4/11	Bunge Elevator	Truck Sampler	425	ND	ND	ND	-
		Truck Inspector	457	ND	ND	184 (29)	-
		Track Sampler	390	ND	ND	ND	ND
		Track Inspector	484	ND	ND	ND	-
		Track Inspector	454	ND	ND	ND	-
4/11	Cargill Elevator	Truck Sampler	407	Trace	ND	2457 (391)	-
		Truck Inspector	432	ND	ND	694 (110)	-
		Truck Inspector	386	ND	ND	ND	-
		Track Sampler	351	ND	ND	ND	ND
		Track Inspector	406	ND	ND	ND	-
		Track Inspector	410	ND	ND	ND	-
4/12	Columbia Grain	Truck Sampler	411	3.8 (0.49)	ND	ND	-
		Truck Sampler	377	ND	ND	292 (46)	-
		Truck Inspector	414	ND	ND	ND	-
		Truck Inspector	392	ND	ND	ND	-
		Track Sampler	363	ND	ND	ND	ND
		Track Inspector	417	ND	ND	ND	-
		Track Inspector	389	Trace	ND	ND	-
4/12	Cargill Elevator	Truck Sampler	409	0.60 (0.08)	ND	499 (79)	-
		Truck Inspector	444	ND	ND	ND	-
		Truck Inspector	435	ND	ND	ND	-

Continued

Table IV
Continued

Date	Elevator	Job	Duration (min)	Concentration in ug/m³ (ppb)+ $C_2H_4Br_2$	CS_2	CCl_4	CH_3Br
		Track Sampler	261	Trace	ND	1172 (186)	ND
		Track Inspector	411	ND	ND	487 (77)	-
		Track Inspector	409	ND	ND	ND	-
4/13	Bunge Elevator	Truck Sampler	499	ND	ND	ND	-
		Truck Inspector	511	ND	ND	230 (37)	-
		Truck Inspector	526	ND	ND	184 (29)	-
OSHA 8 hour TWA PEL* in ug/m³ (ppb)				767 (100)	62040 (20000)	62857 (10000)	80000 (20000)
Analytical Limit of Detection in ug per sample				.005	10	10	0.4

\+ Concentrations are given in micrograms per cubic meter (ug/m^3) with parts per billion (ppb) in parentheses

ND indicates sample concentration was below the given analytical limit of detection for that substance

Trace denotes ethylene dibromide samples in which the compound was identified as being present but was below a concentration which could be analytically quantified or less than 0.023 ug per sample but greater than 0.005 ug per sample.

\- indicates worker exposure to methyl bromide wasn't determined.

Fumigants sampled were:
$C_2H_4Br_2$ = ethylene dibromide
CS_2 = Carbon disulfide
CCl_4 = Carbon tetrachloride
CH_3Br = methyl bromide

* Values are the 8 hour time weighted average (TWA) permissible exposure limits (PEL) (reference 12). The value for ethylene dibromide is taken from OSHA's proposed rule. (See Ref 11.)

Table V

Truck Samplers Carbon Monoxide Exposures
Portland Field Office Inspection Sites

HETA 83-375
April 9-11, 1984

Date	Work Location*	# of trucks+	Duration** (min)	Concentration***
4/9	Columbia Elevator, truck sampling platform	47	431	Negligible
4/9	Columbia Elevator, truck sampling platform		412	Negligible
4/9	Cargill Elevator, truck sampling platform	30	512	Trace
4/10	Columbia Elevator, truck sampling platform	29	400	Negligible
4/10	Bunge Elevator, truck sampling platform	54	437	Trace
4/11	Bunge Elevator, truck sampling platform	54	428	Negligible

* All samples are personal breathing zone exposures for truck samplers doing grain sampling at the truck sampling platform

** Duration is given in minutes. Pumps were collected (with the exception of the third value), during the worker's lunch period.

***Drager® long term carbon monoxide tubes were used, CH28121, lot #0524199, expiration date March 1986.
Sample volumes were between 5 and 8 liters, providing a lower environmental detection limit of 5 to 10 parts per million. Trace denotes a minor brownish discoloration at the beginning of the indicating layer but no concentration could be obtained from the tube.

\+ Number of trucks is a total for the day, as reported by the worker.

Table VI

Short-Term Fumigant Samples for Carbon Disulfide and Carbon Tetrachloride

Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375

April 11-13, 1984

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m³ (ppm) Carbon Disulfide	Carbon Tetrachloride
UP 73909	3/30/84	4/11/84	Bunge, above grain, in car	X	CT BG	15 5	1.3 (0.43) 0.90 (0.29)	4.7 (0.74)
			Bunge, in-the-mass, in car	X	CT BG	12 5	683 (220)* 198 (63.9)	1750 (278)
UP 73909	3/30/84	4/11/84	Bunge, in-the-mass, in car, back-up sample	X	CT	12	7.5 (2.4)	<0.83 (<0.13)
			Bunge, grain surface, after dockage tester	X	CT BG	5 5	4.0 (1.3) 1.9 (0.61)	10 (1.6)
UP 73909	3/30/84	4/11/84	Bunge, BZ sample, track sampler, top of car	X	CT BG	7 5	<1.4 (<0.46) (4.9)	<1.4 (<0.23)
UP 73909	3/30/84	4/11/84	Bunge, grain surface, lab sample prior to being split	X	CT BG	10 5	1.0 (0.32) (0.58)	5.0 (0.80)
UP 73909	3/30/84	4/11/84	Bunge, BZ, personal exposure during grain inspection. Grain inspector.	X	CT	8	<1.2 (<0.40)	<1.2 (<0.20)
UP 73909	3/30/84	4/12/84	Bunge, dumping grain, at grain stream	X	CT BG	5 5	<2.0 (<0.64) (<1)	<2.0 (<0.32)
UP 73909	3/30/84	4/12/84	Bunge, grain surface, grain sample from auto-sampler	X	CT BG	6 5	1.7 (0.54) (0.3)	10 (1.6)

(Continued)

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m³ (ppm) Carbon Disulfide	Carbon Tetrachloride
UP 73735	4/ 2/84	4/11/84	Bunge, above grain, in car	X	CT BG	14 5	1.4 (0.46) 6.8 (2.2)	5.7 (0.91)
			Bunge, in-the-mass, in car	X	CT BG	16 5	412 (133)* 68 (22)	1562 (249)
UP 73735	4/ 2/84	4/11/84	Bunge, in-the-mass, in car, back-up sample	X	CT	16	0.63 (0.20)	<0.63 (<0.10)
			Bunge, grain surface, after dockage tester	X	CT BG	5 5	2.0 (0.64) 1.2 (0.4)	4.0 (0.64)
UP 73735	4/ 2/84	4/11/84	Bunge, BZ, track sampler, top of car	X	CT BG	6 6	<1.67 (<0.54) (0.21)	<1.67 (<0.27)
UP 73735	4/ 2/84	4/11/84	Bunge, grain surface lab sample prior to being split	X	CT BG	10 5	1.0 (0.32) (0.35)	5.0 (0.80)
UP 73735	4/ 2/84	4/11/84	Bunge, BZ, personal exposure during grain inspection, grain inspector	X	CT	7	1.4 (0.46)	<1.4 (<0.23)
UP 73735	4/ 2/84	4/12/84	Bunge, dumping grain, at grain stream	X	CT BG	5 5	<2.0 (<0.64) (<1)	<2.0 (<0.32)
UP 73735	4/ 2/84	4/12/84	Bunge, grain surface, grain sample from auto-sampler	X	CT BG	8 5	<1.2 (<0.40) (<1)	2.5 (0.40)

(Continued)

(Continued)

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m³ (ppm) Carbon Disulfide	Carbon Tetrachloride
UP 22293	4/ 1/84	4/12/84	Bunge, head space prior to fully opening car lid		CT BG	6 5	137 (44) 1.0 (0.34)	233 (37)
UP 22293	4/ 1/84	4/13/84	Bunge, above grain, in car	X	CT	15	<0.67 (<0.22)	1.3 (0.21)
UP 22293	4/ 1/84	4/13/84	Bunge, in-the-mass, in car	X	CT	16	481 (155)*	1250 (199)
UP 22293	4/ 1/84	4/13/84	Bunge, in-the-mass, in car, back-up sample	X	CT	16	<0.63 (<0.20)	<0.63 (<0.10)
UP 22293	4/ 1/84	4/13/84	Bunge, dumping grain, at grain stream	X	CT BG	6 5	<1.7 (<0.54) (0.50)	<1.7 (<0.27)
UP 22293	4/ 1/84	4/13/84	Bunge, unsplit initial grain sample in lab	X	CT BG	15 5	0.7 (0.21) 6.2 (2)	2.0 (0.32)
UP 22293	4/ 1/84	4/13/84	Bunge, splitting of grain sample, in lab, personal sample	X	CT	1	<10 (<3.2)	<10 (<1.6)
UP 22293	4/ 1/84	4/13/84	Bunge, BZ, grain inspector, sniff test during inspection	X	CT	1	<10 (<3.2)	<10 (<1.6)

(Continued)

(Continued)

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m³ (ppm) Carbon Disulfide	Carbon Tetrachloride
UP 14546	4/ 1/84	4/12/84	Bunge, head space prior to fully opening car lid		CT BG	6** 5	233 (75) 22 (7.2)	400 (64)
UP 14546	4/ 1/84	4/13/84	Bunge, above grain, in car	X	CT BG	15 5	173 (56)* (3)	2667 (424)*
UP 14546	4/ 1/84	4/13/84	Bunge, in-the-mass, in car	X	CT BG	15 5	413 (133)* 65 (21)	1533 (244)
UP 14546	4/ 1/84	4/13/84	Bunge, in-the-mass in car, back-up sample	X	CT	15	<0.67 (<0.22)	<0.67 (<0.11)
UP 14546	4/ 1/84	4/13/84	Bunge, dumping grain, at grain stream	X	CT BG	6 5	1.7 (0.54) (5)	5.0 (0.80)
UP 14546	4/ 1/84	4/13/84	Bunge, unsplit initial grain sample in lab	X	CT BG	18 5	1.1 (0.36) 9.3 (3)	3.3 (0.53)
UP 14546	4/ 1/84	4/13/84	Bunge, splitting of grain sample, in lab, personal exposure	X	CT	2	<5.0 (<1.6)	<5.0 (<0.80)
UP 14546	4/ 1/84	4/13/84	Bunge, BZ, grain inspector, sniff test, during inspection	X	CT	1	<10 (<3.2)	<10 (<1.6)

(Continued)

(Continued)

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m^3 (ppm) Carbon Disulfide	Carbon Tetrachloride
UP 76314	4/ 5/84	4/12/84	Bunge, head space prior to fully opening car lid		CT BG	7 5	214 (69)* 17 (5.4)	1157 (184)*
UP 76314	4/ 5/84	4/12/84	Bunge, headspace prior to fully opening car lid, back-up sample		CT	7	<1.4 (<0.46)	<1.4 (<0.23)
UP 76314	4/ 5/84	4/13/84	Bunge, above grain, in car	X	CT BG	15 5	1.3 (0.43) (<1)	8.7 (1.4)
UP 76314	4/ 5/84	4/13/84	Bunge, in-the-mass, in car	X	CT BG	15 5	353 (114)* 776 (250)	4333 (689)*
UP 76314	4/ 5/84	4/13/84	Bunge, in-the-mass, in car, back-up sample	X	CT	15	800 (258)*	2200 (350)
UP 76314	4/ 5/84	4/13/84	Bunge, dumping grain, at grain station	X	CT BG	6 5	<1.7 (<0.54) (<1)	5.0 (0.80)
UP 76314	4/ 5/84	4/13/84	Bunge, unsplit initial grain sample in lab	X	CT BG	18 5	47 (15) (N.D.)	52 (8.2)
UP 76314	4/ 5/84	4/13/84	Bunge, BZ, splitting of grain sample, in lab, personal sample	X	CT	2	<5.0 (<1.6)	<5.0 (<0.80)
UP 76314	4/ 5/84	4/13/84	Bunge, BZ, grain inspector, sniff test during inspection,	X	CT	1	<10 (<3.2)	<10 (<1.6)

(Continued)

(Continued)

Railroad Car ID Number	Date Fumigated	Date Sampled	Sample Location	Grain "Aerated"	Sample Type	Sample Duration	Fumigant Concentration in mg/m^3 (ppm) Carbon Disulfide	Carbon Tetrachloride
BN 452278	4/ 5/84	4/12/84	Cargill, head space prior to fully opening car lid		CT BG	7 5	1014 (327)* 354 (114)	2857 (455)
BN 452278	4/ 5/84	4/12/84	Cargill, headspace prior to fully opening car lid, back-up sample		CT	7	13 (4.2)	1.4 (0.23)
UTCX 44256	4/ 5/84	4/12/84	Cargill, head space prior to fully opening car lid		CT BG	7 5	871 (281)* 695 (224) 310 (100)	7143 (1136)*
UTCX 44256	4/ 5/84	4/12/84	Cargill, headspace prior to fully opening car lid, back-up sample		CT	7	771 (249)	400 (64)
PLCX 22916	Unknown	4/13/84	Cargill, in-the-mass, in car		CT BG	9 5	<1.1 (<0.36) (470) (385)	<1.1 (<0.18)
PLCX 22916	Unknown	4/13/84	Cargill, grain surface, file sample (?)		CT BG	20 5	6.0 (1.9) 9.3 (3)	26 (4.1)
SLSF 86565	Unknown	4/13/84	Cargill, above grain in car		CT BG	12 5	5.0 (1.6) (0.75)	27 (4.1)
SLSF 86565	Unknown	4/13/84	Cargill, above grain, file sample in lab split once		CT BG	12 5	7.0 (2.3) 2.3 (0.75)	24 (3.8)

(Continued)

Explanatory Notes: Sample Descriptors

Date Fumigated obtained from placard.

Sample Locations are defined as follows:
above grain: samples obtained about 6 inches to 1 foot about the grain surface
in-the-mass: sampling train inlet submerged in the grain
grain surface: sampling train opening located at the grain surface to slightly above (approx. 1/2 - 2 inches).
head space: sample of space above grain prior to fully opening lids on car. See Methods and Materials Section.
back-up sample: sorbent tube sampling done with two tubes in series. These samples designate the second tube of samples demonstrating break-through on the first tube. (See Methods and Materials Section).

Grain Type: Soft White Wheat

Grain "Aerated" denotes grain held in the railroad car and standing for 24 hours with the hatch doors (lid) open.

Sample Type denotes whether the sample was a bag sample (BG) analyzed in the field using a portable gas chromatograph or a charcoal tube (CT) sample analyzed in the laboratory. BZ denotes a breathing zone sample obtained for a worker.

Sample Duration for CT samples is given in minutes, bag samples were run until mylar bag was filled, or about 5 minutes (See Methods and Material Section).

Explanatory Notes: Fumigant Concentrations

Fumigant Concentrations are given in milligrams per meter cubed (mg/m^3) with the parts per million value (ppm) in parentheses.

< Indicates concentrations were below the analytical limit of detection. The value given in these instances is the calculated environmental limit of detection for that sample.

* Breakthrough occurred on tube - more than 30% of the analyte was found on the back-up section of the charcoal tube.
** approximate sample duration
*** back-up section lost in analysis.

Table VII

Sample Break-down and Statistics for Short-term Fumigant Sampling

Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375
April 11-13, 1984

Railroad Car	Elevator	Sample Description Codes (see key below) A	B	C	D	E	F	G	H	I	J
UP 73909	Bunge		X	X̲	X	X	X	X	X		X
UP 73735	Bunge		X	X̲	X	X	X	X	X		X
UP 22293	Bunge	X	X	X̲	X	X				X	X
UP 14546	Bunge	X	X̲	X̲	X	X				X	X
UP 76314	Bunge	X̲	X	X̲	X	X				X	X
BN 452278	Cargill	X̲									
UTCX 44256	Cargill	X̲									
PLCX 22916	Cargill			X							
SLSF 86565	Cargill		X								
Number of samples (n)		5	5(6)*	5(6)*	5**	5	2**	2**	2**	3**	5**
Geometric mean (ppm)	CS_2	116	1.5	147	-	0.65	-	-	-	-	-
	CCl_4	186	2.4	297	-	0.98	-	-	-	-	-
Geomet. Std. Deviation	CS_2	2.5	8.2	1.3	-	5.8	-	-	-	-	-
	CCl_4	4.0	19	1.6	-	3.5	-	-	-	-	-
Range (ppm)	CS_2	44-327	ND-56	ND-155	ND-0.54	0.21-15	ND-0.54	0.64-1.3	ND	ND	ND-0.46
	CCl_4	37-1136	0.21-424	ND-689	ND-0.80	0.32-8.2	0.40-1.6	0.64-1.6	ND	ND	ND

Key to Sample Location and Identity:
A: Rail car head space
B: Above the grain in the rail car
C: In-the-mass, in the rail car
D: At the grain stream during dumping
E: At the grain surface, in the lab, for the unsplit sample.
F: Grain surface of a lab sample obtained from the automatic sampler.
G: At the grain surface after the grain has run through the dockage tester.
H: Breathing zone sample for a track sampler while on top of the rail car.
I: Breathing zone sample for a worker splitting a grain sample in the lab.
J: Breathing zone sample for a grain inspector during the grain inspection (i.e., sniff test).

Note: See Table VI for data on individual samples.
X̲ - Means that sample had break-through, values presented are lower than the actual concentrations.
* - Calculation of statistical values excluded non-detected to remain consistent with the way other statistical values were obtained elsewhere in this report. Numbers in parenthesis is the total number of samples taken, first number is the points used in calculating the statistics.
** - Means were not calculated if over 50% of the samples were non-detectable or due to small sample size.

Table VIII

Results of Area Respirable Dust Sampling

Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375

April 9-12, 1984

Date	Elevator	Sample Location	Duration (min)	Vol (L)	Dust Concentration in mg/m^3
4/9	Columbia	Side of Boerner® divider (splitter), truck grain inspection lab	495	792	0.37
4/9	Columbia	Side of Boerner® divider, track (railroad car) grain inspection lab	425	680	0.09
4/9	Cargill	Sample preparation room, grain inspection lab	524	865	0.05
4/9	Cargill	Technician preparation room, grain inspection lab	486	802	0.05
4/10	Columbia	Truck grain inspection lab	502	874	0.20
4/10	Columbia	Track grain inspection	519	895	0.08
4/10	Bunge	Truck sampling catwalk	485	829	0.02
4/10	Bunge	Side of Boerner® divider, grain inspection lab	487	816	0.18
4/11	Bunge	Truck sampling catwalk	514	874	0.05
4/11	Bunge	Side of Boerner® divider, grain inspection lab	535	904	0.29

Continued

Table VIII
Continued

Date	Elevator	Sample Location	Duration (min)	Vol (L)	Dust Concentration in mg/m^3
4/11	Cargill	Side of Boerner® divider, grain inspection lab	510	867	++
4/11	Cargill	Grading Lab	513	872	0.06
4/12	Columbia	Track grain inspection lab	495	842	0.06
4/12	Columbia	Truck grain inspection lab	480	816	0.10
4/12	Cargill	Grain inspection Lab	511	884	0.05
4/12	Cargill	Side of Boerner® divider, grain inspection lab	510	880	0.06
4/13	Bunge	Truck sampling catwalk	542	921	0.07
4/13	Bunge	Grain inspection	551	937	0.14

Evaluation Criteria: OSHA Nuisance Dust - Respirable Fraction* 5.00 mg/m^3

++No weight grain recorded for this sample.

* Respirable nuisance dust evaluation criteria given. No silica determination was made on these samples. ACGIH recommends a total grain dust exposure limit of 4 mg/m^3, however their limit is not applicable to this data since it represents only the respirable fraction of the grain dust.

Table IX

Noise Level Measurements
Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375
April 9-13, 1984

Date	Noise Source Description	Location	Sound Level Measurement* A scale	Sound Level Measurement* C scale	A scale Allowed Time (hrs)**
4/9	Truck sampling area, truck engines	Cargill	87	90	6.1
	Grading Area	Cargill Lab	83	83	10.6
	Sample Preparation Area	Cargill Lab	76	80	27.8
	Track sampling, rail yard	Cargill	76	88	27.8
4/10	Near Boerner Divider® in track inspection lab+	Columbia Lab	85	85	8
	Between divider and dockage tester in track inspection lab+	Columbia Lab	81	81	13.9
4/10	Inspection lab equipment operating, general area	Bunge Lab	80	85	16
	Truck sampling area, two trucks pulling in	Bunge	83	88	10.6
	Track sampler, out on cars in rail yard	Bunge	65	74	128

(Continued)

Table IX

(Continued)

Date	Noise Source Description	Location	Sound Level Measurement* A scale	C scale	A scale Allowed Time (hrs)**
4/11	Near first divider in lab+	Bunge	86	86	7.0
	Near second divider in lab+	Bunge	82	82	12.1
	Back of dockage tester	Bunge	80	84	16
	Railyard, railcar sampling area	Bunge	72	76	48.5
	Truck sampling area	Bunge	76	84	27.8
4/11	Sample Preparation Area (during full operation)	Cargill Lab	74	76	36.8
	Grading Area (during full operation)	Cargill Lab	66	73	11.4
	Truck sampling platform (while sampling truck)	Cargill	77	87	24.2
	Railyard, railcar sampling area	Cargill	75	84	32
4/12	Truck sampling platform, trucks idling	Columbia	76-78	82-84	27.8-21.1

(Continued)

Table IX
(Continued)

Date	Noise Source Description	Location	Sound Level Measurement* A scale	Sound Level Measurement* C scale	A scale Allowed Time (hrs)**
4/12	Inspection lab (general)	Cargill Lab	75	85	32
	Railyard, railcar sampling area	Cargill	70	88	64
	Truck sampling platform area	Cargill	75	83	32
4/13	Truck sampling platform, trucks idling	Bunge	76	85	27.8

Evaluation Criteria: See Table I - ACGIH 85dBA - 8 hour workshift, continuous noise.

Measurements obtained with a General Radio Type II sound level meter, Model 1565B, Serial No. 4308. Unit was calibrated daily.

*Sound level meausurements were obtained on both the A scale, representing the noise level as perceived by the human ear, and the C scale which does not apply any weighting factor to the different frequencies.

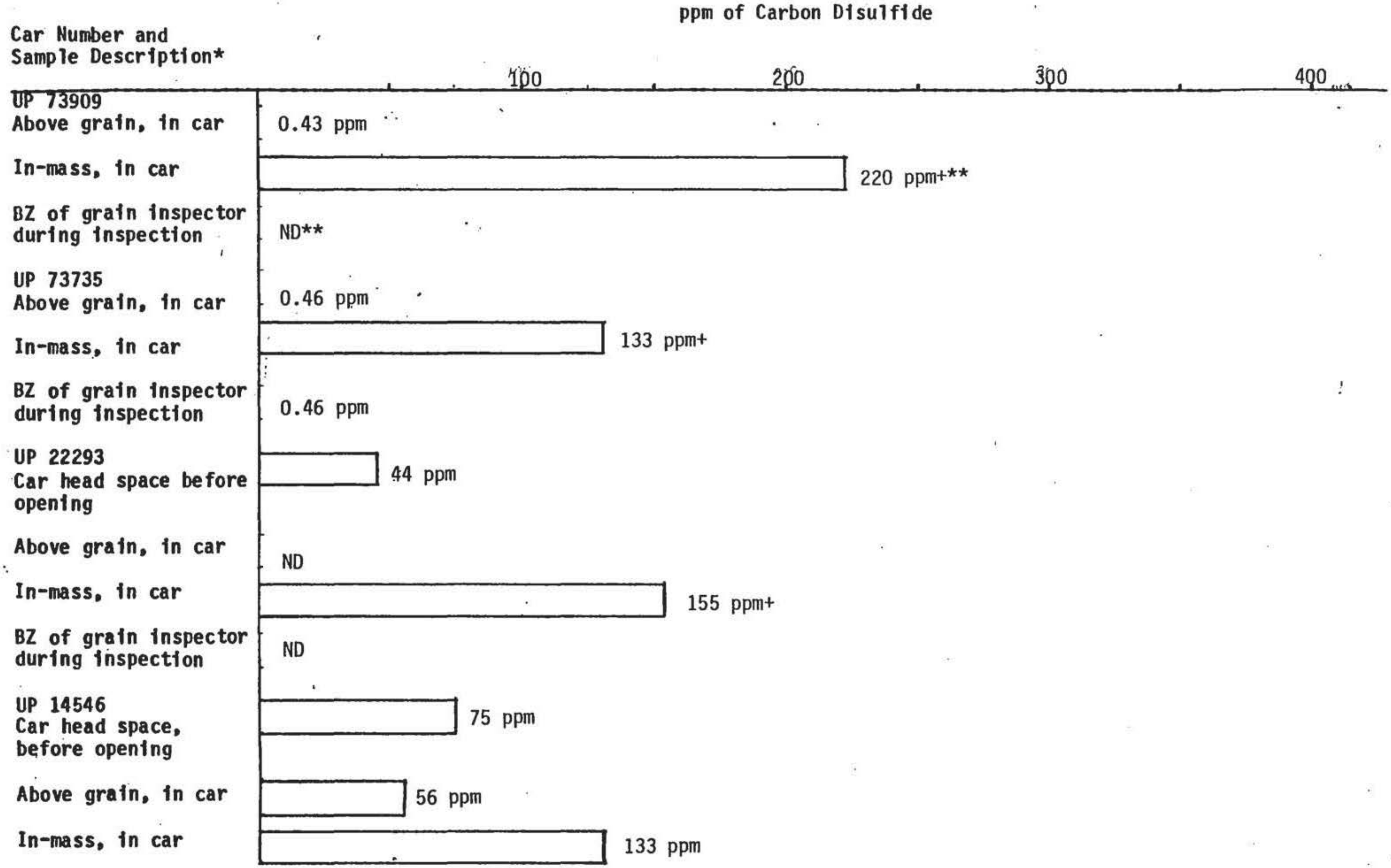
+Noise levels are influenced by the grain being run through the dividers.

**This column presents the allowed duration (in hours) of exposure to this noise level assuming the noise is continuous and that an exposure limit of 85dBA over an eight-hour workshift is applied. The formula used is: allowed time = $\frac{480 \text{ min}}{2^{0.2\,(LA-N)}}$

LA = measured noise level in dBA
N = 8-hour noise limit
This value is divided by 60 to obtain hours.
Source: NIOSH Industrial Noise Control Manual, Revised Edition, reference 20.

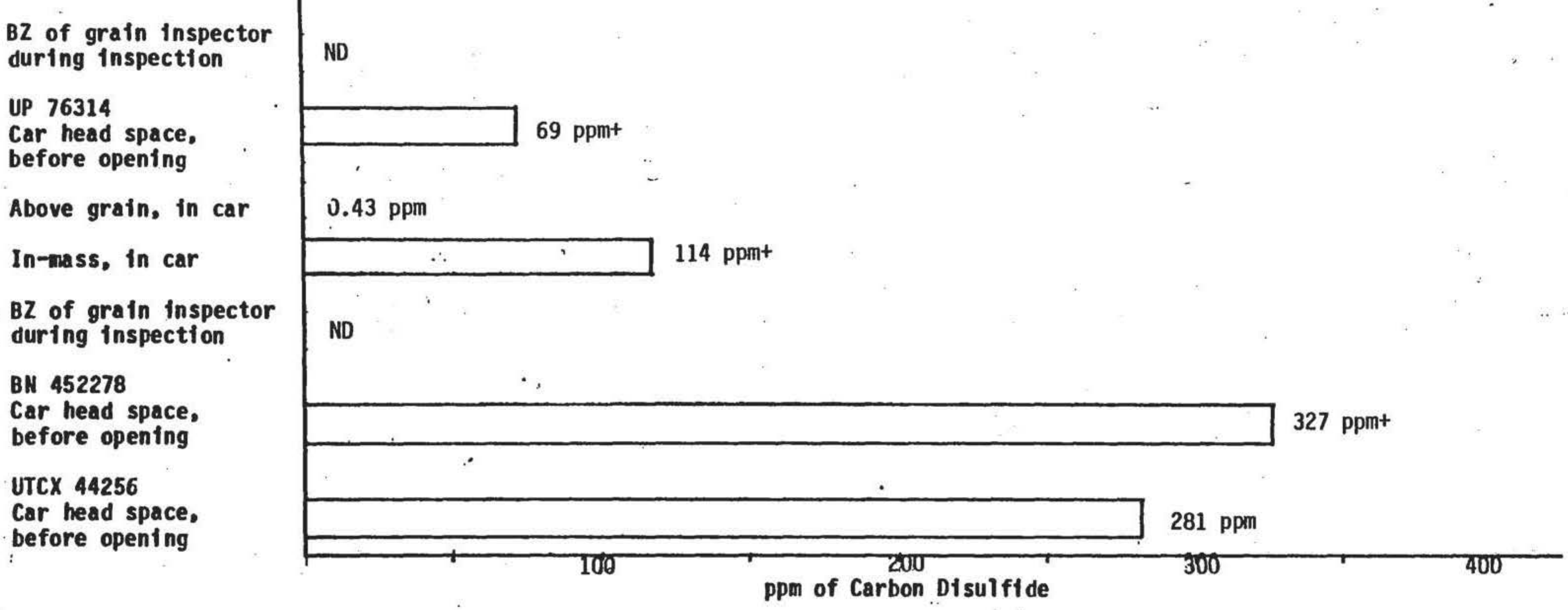
Figure I

Carbon Disulfide Fumigant Levels Obtained From Rail Car Grain Shipments
Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375



Continued

Figure 1 Continued

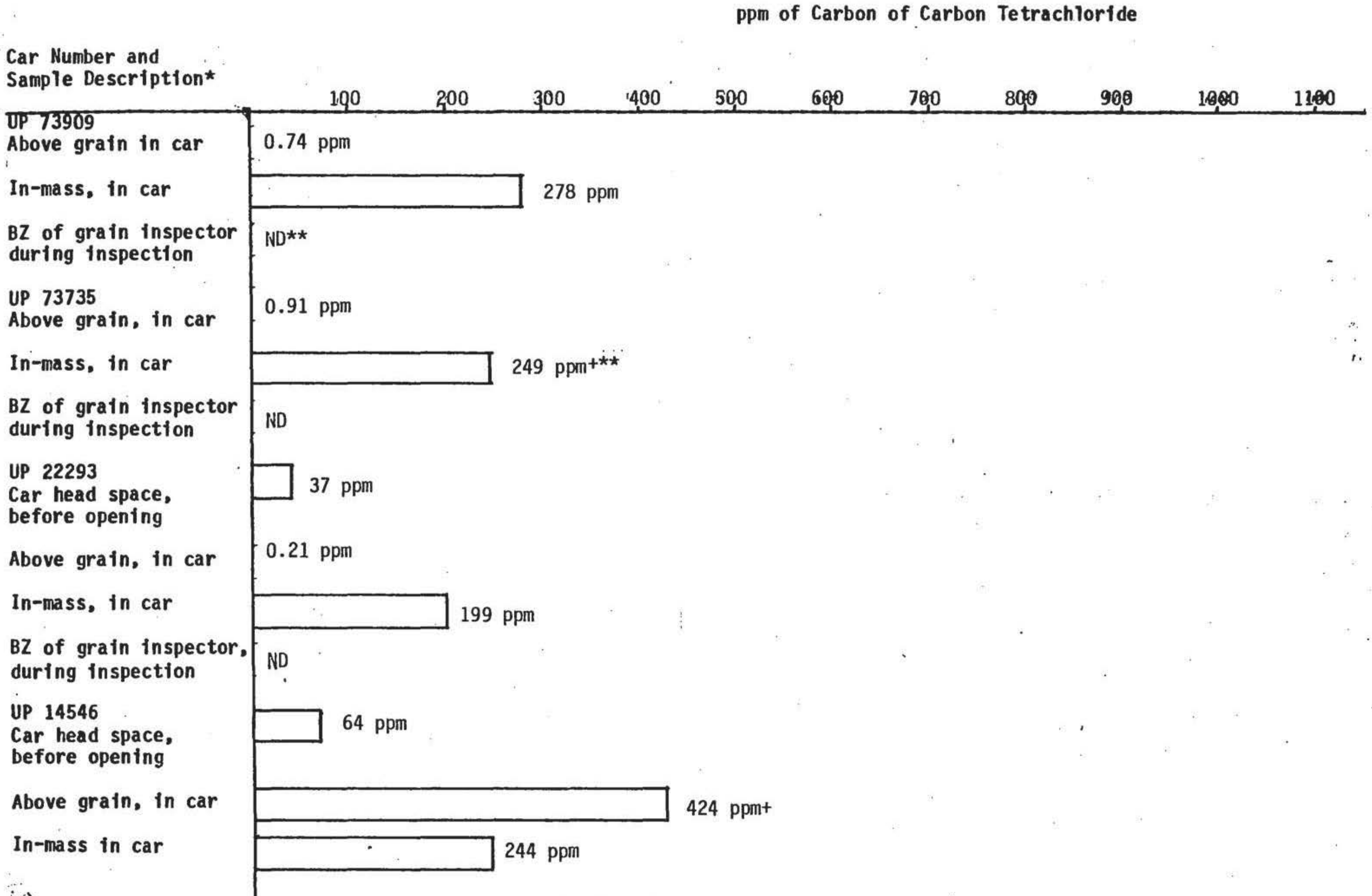


* See Table VI for more detailed sample description and additional short-term samples for carbon disulfide. BZ denotes breathing zone sample.

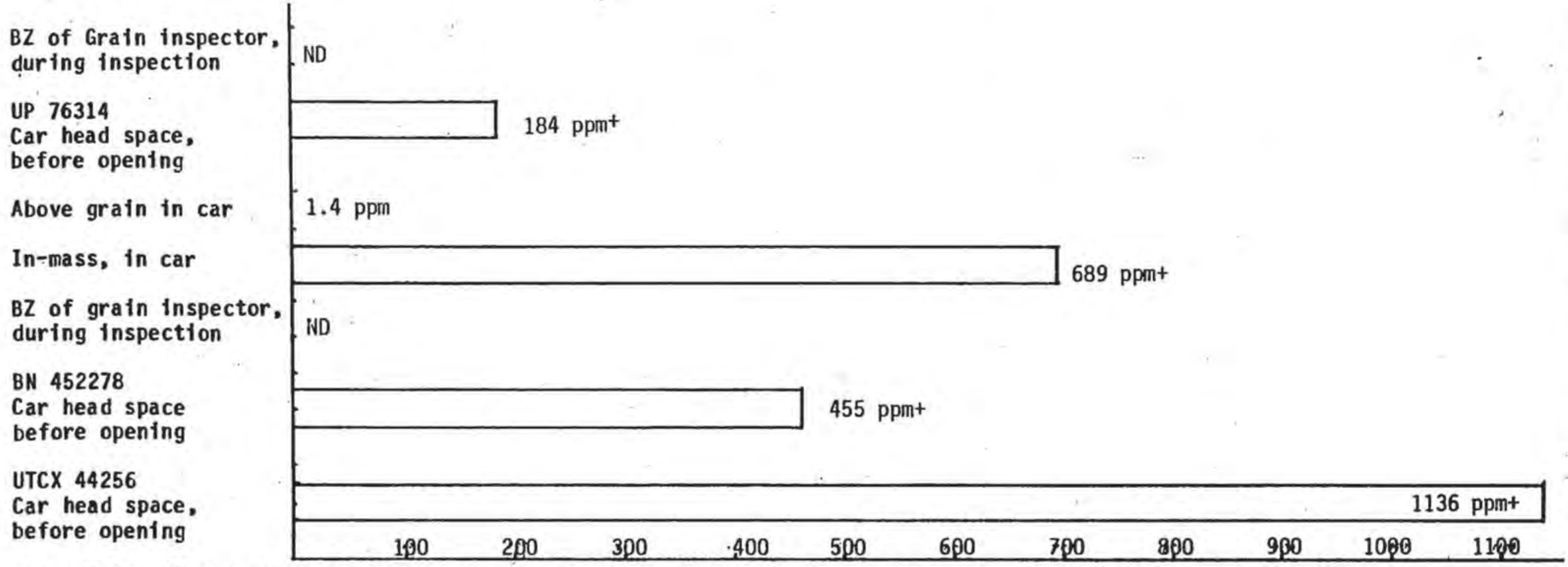
** Concentrations are given in parts per million (ppm) and breakthrough of the sample (i.e., loss from overloading) is designated with a +; ND denotes sample was below the limits of detection.

Figure II

Carbon Tetrachloride Fumigant Levels Obtained From Rail Car Grain Shipments
Portland Field Office Inspection Sites
Portland, Oregon
HETA 83-375



Continued



*See Table VI for more detailed sample description and additional short-term samples for carbon tetrachloride. BZ denotes breathing zone sample.

**Concentrations are given in parts per million (ppm) and break through (i.e., loss from overloading) is designated with a +; ND denotes sample was below the limits of detection.

Appendix A
Analytical Methods and Modifications
Federal Grain Inspection Service
Portland, Oregon
HETA 83-375

Ethylene Dibromide: Analytical Method

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

Instrument:	Hewlett Packard 5840 with ECD
Column:	3% OV-17 on WHP (6 ft x 1/8 inch OD glass column)
Carrier Gas:	95% argon/5% methane - 28 mL/min
Column Temperature:	75°C isothermal (4 min)
Injector Temperature:	250°C
Detector Temperature:	300°C
Injection Volume:	1 uL
Attenuation:	2 8

The front sections of the charcoal tubes were desorbed for at least 1 hour with 10 mL of 1% methanol in benzene. The back sections were desorbed in 1 mL of this solution. Tetrachloroethane was added as an internal standard at 200 ng/mL.

For the follow-up survey sample set these GC/ECD conditions were used for ethylene dibromide:

Instrument:	Varian Vista 6000 CC with ECD
Column:	DB-5 fused silica capillary column, 30 M x 0.32 mm ID
Carrier Gas:	2 mL/min Helium
Make-up Gas:	28 mL/min Nitrogen
Column Temperature:	40°C
Injector Temperature:	200°C
Detector Temperature:	285°C
Injection Volume:	1 uL
Range:	1
Attenuation:	16
Chart Speed:	1.0 cm/min

The charcoal tubes were desorbed in the same manner as the previous set. No internal standard is indicated.

(Continued)

Carbon Disulfide: Modifications to NIOSH Method S-248

Desorption Process:	1 hour in 1 mL benzene
Gas Chromatograph:	Tracor Model MT-220 equipped with a flame photometric detector, operated in the sulfur mode
Column:	3' x 2 mm ID glass column packed with 3% OV-17 and 3% OF-1 on 100/120 mesh chromosorb G
Oven Conditions:	50°C isothermal
Other:	Nitrogen was used as the carrier gas

The following conditions were changed for the analysis of the follow-up survey carbon disulfide sample set:

Column:	28" x 1/4" glass packed with 2% OV-225 on 80/100 Supelcoport
Oven Conditions:	70°C Isothermal

Carbon Tetrachloride, Chloroform, 1,2-Dichloroethane, 1,2-Dichloroethylene: Modification to NIOSH Method P&CAM 127

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:	60 m x 0.32 mm ID fused silica capillary coated internally with 0.25 um of OV-351
Oven Conditions:	Temperature programming from 55°C (held for 8 min) to 100°C at a rate of 8°C/minute

The following modifications were made in NIOSH Method S-314 during analysis of the follow-up survey carbon tetrachloride sample set:

Desorption Process:	30 minutes in 1.0 milliliter of carbon disulfide containing 1 microliter per milliliter of toluene as an internal standard

(Continued)

Column:	20' x 1/8" OD stainless steel packed with 20% SP 2100, 0.1% CW 1500 on 100/120 Supelcoport
Oven Conditions:	120°C isothermal

Methyl Bromide: Analytical Method

The following GC/ECD conditions were used in the methyl bromide analysis:

Instrument:	Hewlett Packard 5840 GC with ECD
Column:	1% SP-1000 on 60/80 Carbopack B (6 ft x 2 mm ID glass column)
Carrier Gas:	5% Methane/95% Argon at 30mL/min
Column Temperature:	45°C isothermal (30 min)
Injector Temperature:	200°C
Detector Temperature:	250°C
Injection Volume:	1 uL
Attenuation:	2^4
Retention Time:	3.70 min

The front sections of the charcoal tubes were desorbed for at least 1 hour with 2 mL of 1% methanol in benzene.

Short-Term Air Bag Sampling: Carbon Tetrachloride and Carbon Disulfide

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 lab 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, carbon tetrachloride, and ethylene dibromide) by adding microliter quantities to metered volumes of air in aluminized mylar bags.

Carbon Disulfide, Carbon Tetrachloride Short-Term Sorbent Samples: Modification to NIOSH Method S-248

The samples were desorbed for a minimum of 30 minutes in 1.0 milliliter benzene.

The analysis of carbon disulfide was performed on a Tracor 220 gas chromatograph equipped with a flame photometric detector in the sulfur mode. A 28" x 1/4" glass column packed with 2% OV-225 on 80/100 Suplecoport was used at an isothermal temperature of 70°C.

The analysis of carbon tetrachloride was performed on a Hewlett Packard Model 5711A gas chromatograph equipped with a flame ionization detector. A 12' x 1/8" stainless steel column packed with 10% TCEP on 80/100 mesh chromosorb PAW was used at an oven temperature of 100°C.

Carbon Disulfide and Carbon Tetrachloride Confirmation

Samples previously prepared for analysis by desorption in benzene, analyzed and found to contain both CS_2 and CCl_4 by standard chromatographic methods were reanalyzed on a Hewlett Packard 5992 gas chromatograph/mass spectrometer to confirm the presence of CS_2 and CCl_4. A 30 m wide-bore fused silica capillary column was used isothermally at 22°C with a split injection ratio of 20:1.