COMPOSITE REPORT

INDUSTRIAL HYGIENE CHARACTERIZATION OF GRAIN ELEVATOR WORKERS' EXPOSURES TO PHOSPHINE DURING BULK GRAIN FUMIGATION WITH ALUMINUM PHOSPHIDE

Dennis D. Zaebst
Leo M. Blade
Paula Morelli-Schroth

Division of Surveillance, Hazard Evaluations, and Field Studies

William J. Woodfin
G.E. Burroughs

Division of Physical Sciences and Engineering

May, 1987

U.S. Department of Health and Human Services
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226

DISCLAIMER

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

Authors:

Dennis D. Zaebst A
Leo M. Blade A
James Woodfin B
Guy E. Burroughs B
Paula Morelli-Schroth C

Affiliation:

A Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations, and Field Studies (DSHEFS), National Institute for Occupational Safety and Health (NIOSH), Cincinnati, Ohio 45226

B Monitoring Control Research Branch, Division of Physical Sciences and Engineering, NIOSH

C PEI-IT, Inc., 11499 Chester Rd., Cincinnati, Ohio, 45246; formerly with the Industrywide Studies Branch, DSHEFS, NIOSH

ACKNOWLEDGEMENTS

The authors wish to thank Dan Molina, who ably contributed to the field work and analysis of the data, Dave Smith and Peter Eller, who offered valuable guidance in quality control of field samples, Barry Belinki, Don Dollberg (at NIOSH), and the many chemists at Arthur D. Little, Inc., and UBTL, Inc., where analyses of field samples were carried out. Sincere appreciation is extended to Marianne Fleckinger and Pat Lovell for their assistance in typing and editing this manuscript.

TABLE OF CONTENTS

ABSTRACT

The Industrywide Studies Branch of NIOSH conducted a series of industrial hygiene surveys in 1985 and 1986 to assess worker exposures to phosphine gas during the addition of aluminum phosphide pellets to wheat prior to, and during, long term storage. Full shift, breathing zone sampling to measure workers' exposures to phosphine, and area monitoring, were conducted using silica gel sorbent tubes impregnated with mercuric cyanide. In addition, a portable gas chromatograph, incorporating a photoionization detector, was used to evaluate very brief (2-5 minute) peak exposures during specific job tasks. Results indicate that the use of aluminum phosphide can result in demonstrable, and frequently excessive, exposures when compared to relevant criteria, even under very cold air temperatures ranging down to 18 degrees F. Full-shift, personal exposures to phosphine ranged from non-detectable (<0.01 ppm) to 1.6 ppm, which is more than five times the current OSHA-PEL and ACGIH TLV (both 0.3 ppm). Short-term, personal exposures during filling and emptying an automatic tablet dispenser averaged 2.5 ppm, and ranged from 0.1 to 52 ppm, over periods ranging from 2-5 minutes. Examination of the sampling data suggested that the exposures to phosphine were partly a result of uncontrolled point sources and lack of appropriate local exhaust ventilation, and seemed to depend on the general level of fumigation activity. Storage of increasing quantities of treated grain over a three week period at one elevator did not appear to result in a trend of increasing exposures. General recommendations for reducing exposures through improved local exhaust ventilation and work practices are made.

Introduction

Chemical treatment of grain, machinery or facilities to control insects is conducted in all segments of the grain industry, including farms, country elevators, regional/inland (subterminal) elevators, export terminals, flour and feed mills, and grain or food processing plants. Treatment may also occur during transportation by trucks, railcars, barges, and ships.(1) In the grain industry, different types of pesticides are used depending on the situation and the job at hand. The modes of pesticide use can generally be described as protectant, fumigant, or space treatment. The fumigants are perhaps the most important insecticides in the grain industry, both from an economic and occupational exposure standpoint.

Fumigants are insecticides which, in contrast to protectants, leave little or no residue, and are usually applied to eliminate existing infestation in grain. Fumigants kill by entering the insect through its respiratory organs. In order to work, therefore, the fumigant must produce a high airborne concentration of gas or vapor over a sufficient time period. Thus, fumigants are necessarily gaseous, (e.g. methyl bromide, infrequently used to treat grain, but often used in grain handling facilities), liquids which volatilize to form toxic vapors in the grain (e.g. carbon disulfide/carbon tetrachloride mixtures), or solids which react to release toxic gas (e.g. aluminum and magnesium phosphide, which generate phosphine). Because of their nature, these products are almost always applied to grain stored, or about to be stored, in confined-spaces (e.g. concrete storage bins, rail cars, etc.).

Until recently (1986), the most-used fumigants were products referred to generically as "80/20". These are liquid mixtures containing primarily carbon tetrachloride and carbon disulfide (in an 80/20 ratio), but which might also contain a number of other halogenated organics including ethylene dichloride, methylene chloride, and others.(1) Until 1984, another frequently used fumigant was ethylene dibromide.(1) Both of these pesticide products have been banned by the U.S. EPA, ethylene dibromide in 1984,(2) and liquid formulations containing carbon disulfide or carbon tetrachloride in 1986.(3) Occupational exposures to these and other fumigant compounds used in the grain industry have not been studied extensively, but a few historical reports exist indicating highly variable exposures to carbon disulfide, carbon tetrachloride, and a few other fumigants (4-5) and some health effects in grain industry workers.(4,6-9)

More recently, several NIOSH investigators have conducted a number of environmental assessments aimed at determining the current nature and extent of occupational exposures to grain fumigants. These studies have included three Health Hazard Evaluations, and two surveys (conducted under contract to NIOSH by the University of Utah) of exposures to carbon disulfide and carbon tetrachloride in elevators using liquid fumigants. In the Health Hazard Evaluations, exposure evaluations were conducted in the absence of active fumigation activities, since the concern at the time was principally the potential for workers' exposures resulting from receipt of previously fumigated grain. The exposures measured in each of these hazard evaluations were invariably extremely low or not detectable.(10-12) The University of

Utah studies, in contrast, found relatively high exposures to carbon disulfide and carbon tetrachloride during active fumigation activities at two elevators.(1)

As a result of changing regulations, the pattern of pesticide use in the United States in the last few years has changed drastically. A 1980 report indicated that the market shares for the three most regularly used fumigants were 45% liquid mixtures (such as 80/20), 50% aluminum phosphide, and 5% methyl bromide.(13) Since June 1986, liquid fumigants may no longer be used, and since there are currently few other viable substitutes, the market share for phosphide products (aluminum and magnesium) for fumigant purposes in the grain industry is much higher, essentially supplanting the use of the liquid formulations.

Phosphide products are classified by the EPA as restricted-use pesticides. Thus, they must be used by trained and certified applicators under controlled conditions. However, due partly to lack of data, and due to assumptions about the nature of the phosphide formulations available for use, it had been assumed that occupational exposures to phosphine during use of phosphide products were minimal. The Pesticide Registration Standard for aluminum phosphide, published in 1981, states that "if the label instructions are followed, applicators should not be exposed to measurable levels...".(14) This is somewhat surprising, since empirical data were available which indicated measureable, and excessive, exposures could occur.(14,15)

This paper presents the results of four surveys conducted in 1985 and 1986 to evaluate elevator employees' exposures to phosphine during the active application of aluminum phosphide in grain elevators. The results of the three Hazard Evaluations, and the University of Utah studies, have been presented elsewhere (1,10-12). These surveys were conducted in partial fulfillment of an industry wide study initiated in response to: 1) ongoing concerns that exposures to fumigants were a potential hazard to the health of grain industry workers;(6-8) and 2) the changing pattern of pesticide use due to increasing regulation, economic factors, and changing technology. The objectives of these studies were to provide exposure characterizations where newer types of pesticides were being used, and to provide a data base for use in any future health studies of this workforce.

Chemistry and Toxicity of Phosphide and Phosphine

Phosphide pellets (spherically shaped) or tablets (disk shaped), which are composed of aluminum phosphide (57%), urea, and ammonium carbamate (total 43%), decompose in the presence of moisture (in the air or in the grain) to yield phosphine gas, ammonia, and carbon dioxide.(16) The aluminum phosphide reacts with water as follows:

$$2AlP + 6H_2O ====> 2Al(OH)_3 + 2PH_3$$

Phosphide products have been reported to begin decomposing 1 to 4 hours after the original container is opened.(16) The reaction, which takes place largely in the grain mass (usually inside a confined space such as a storage bin), reportedly speeds up with increasing moisture content and increasing temperature. Thus, it is reasonable to assume that the higher the grain moisture and temperature, the shorter the time needed to evolve significant concentrations of phosphine. The residue (commonly referred to as "ash"), which remains largely in the grain after decomposition, is mainly aluminum hydroxide, a relatively inert and innocuous material which is a common constituent of clay. Other low-level residues may include aluminum oxide, oxidation products of phosphine (phosphorous oxy-acids and/or their salts), and a small amount of tightly bound aluminum phosphide (17).

Phosphine is an acutely toxic gas by inhalation.(18,19) An Australian report, by Jones et al. in 1964, reported breathing zone concentrations of up to 11 ppm (intermittently as high as 35 ppm) of phosphine during the addition of aluminum phosphide tablets to wheat prior to long term storage or loading out on ships. In this study, varying physiological responses were exhibited by phosphine-exposed workers, ranging from chest tightness to vomiting, diarrhea, and central nervous system effects.(15) Harger, et al. reported 59 cases of acute phosphine poisoning, including 26 deaths, between 1900 and 1958, including one death from pulmonary edema after 8-ppm exposures one or two hours per day.(20)

The U.S. EPA's Pesticide Incident Monitoring System (1981) reported 29 incidents of human exposure from 1966 to 1981, involving 80-90 people, including 71 who received medical treatment, 33 who were hospitalized, and two deaths.(14) In 22 of these incidents, pesticide exposure occurred when aluminum phosphide was used as a grain fumigant. The U.S. EPA reported that in all of these incidents, exposure to aluminum phosphide or phosphine occurred as a result of improper application procedures or improper handling of the pesticide. However, no details of these incidents were provided, nor were exposure concentrations or length of exposures reported.

Wilson, et al. in 1980 reported acute illnesses in 29 adults and two children (one of whom died) exposed to phosphine aboard a freighter carrying grain previously treated with a phosphide product.(21) Symptoms observed in the adults were predominantly headache, fatigue, nausea, vomiting, cough, and shortness of breath. Abnormal physical findings included jaundice, paresthesias (tingling of the skin), lack of motor coordination, tremors, and diplopia (double vision). The dead child showed evidence of myocardial infiltration, pulmonary edema, and widespread small vessel injury. The surviving child also showed myocardial injury. Although exposures were undoubtedly very high in this incident, no concentrations were reported, and the durations of exposures were uncertain.

The effects of chronic exposure in humans have apparently not been clearly defined. These effects have been stated to include anemia, bronchitis, gastrointestinal disturbances and nervous disorders including visual, speech, and motor disturbances.(22) Other authorities state that chronic phosphine poisoning is similar to that of phosphorous, including embrittlement of teeth and bones.(20,23) The Documentation of Threshold Limit Values, however, indicates that no such cases have been reported in the modern literature.(19)

In animals, phosphine exhibits acute inhalation toxicity in which concentration and time to mortality appear to be inversely related.(14) In general, the higher the concentration, the smaller the time interval to death. Waritz and Brown in 1975 determined a four-hour LC_{50} in rats of 11 ppm.(24) Klimmer in 1969 exposed a variety of animals to concentrations of phosphine ranging from 151 to 205 ppm in which the "time to death" was recorded as ranging from 50 to 93 minutes. At 25 ppm, the time to death was on the order of four to eight hours.(25)

Both Klimmer, in 1969 and Muller et al. in 1940 also conducted experiments at lower concentrations over longer time periods. Muller exposed rabbits and guinea pigs at concentrations ranging from 5 ppm to 20 ppm. In exposures of four hours per day, time to death was recorded as 6 days at 5 ppm, and 2 days at 20 ppm.(26) Klimmer maintained three species of test animals at 1 and 2.5 ppm for over 800 hours (six hours/day, five days/week, four hours on Saturday) without outward signs of toxicity. However, at 5 ppm, there were deaths in two of three species at approximately 30 hours. However, both of these studies would be considered inadequate in terms of evaluation of other than overt mortality. In neither of these studies were biological parameters, such as body weight changes, organ weights, hematology, behavioral effects, and histopathology, evaluated.

Muthu, et al. in 1980 exposed white albino rats to concentrations of approximately 22 to 65 ppm for 4, 6, and 8 hours.(27) In this study, symptoms and mortality were recorded, and histopathology and organ weight changes were studied. The median lethal dose per four hours (sic) of phosphine was stated to be 0.44 micromoles/L (approximately 10 ppm, which agrees with Waritz et al.). Symptoms observed during exposure included excessive urine secretion, difficulty in breathing, loss of muscular coordination, and paralysis. Most (75%) of the animals died during exposure, 20% within 2 hours of exposure. Lung weights increased slightly at higher concentrations, although no other organ weight changes were observed. Some lungs were edematous, with severe cellular infiltration around the bronchioles.

Exposure Criteria and Odor Threshold

The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV),(28) and the OSHA Permissible Exposure Limit (PEL)(29) for full-shift (8-hour) exposures to phosphine are both 0.3 ppm. In addition, the ACGIH has also established a Short-Term Exposure Limit (STEL) of 1 ppm for exposures time-weighted over any 15 minute period, with no more than four such exposures per day. NIOSH has not recommended an exposure limit.(18) Previous reports are contradictory regarding the odor threshold and warning properties of phosphine. Leonardos reports the odor threshold of phosphine at 0.02 ppm, well below the TLV of 0.3 ppm, suggesting that phosphine has adequate warning properties.(30) However, Patty states the limit of perceptibility as 1.5 to 3 ppm, and says that phosphine has a foul odor like fish but this gives no warning of its threshold concentration. Amoore, et al. places the odor threshold of phosphine in between these values at 0.5 ppm, and further states that it has a category D (unreliable) odor response.(31)

Methods

Long-term (full shift) exposures to airborne phosphine, both personal and area, were evaluated using battery operated, portable sampling pumps at a flowrate of 50 cc/min in conjunction with glass tubes containing mercuric cyanide-impregnated silica gel tubes as specified by NIOSH method S-332.(32) Frequently, dual-tube manifolds were used which allowed the collection of two simultaneous (replicate) samples. The phosphorous content was extracted and oxidized to phosphate with hot acidic permanganate, converted to phosphomolybdate, and reduced with stannous chloride to a chromagen for spectrophotometric analysis.

Full-shift samples were used to evaluate personal exposures relative to 8-hour, time-weighted average (TWA) exposure criteria, and to evaluate many area concentrations in terms of sources of exposure. However, short term samples of a few minutes duration were also collected as necessary to evaluate peak exposures during certain cycles of activity and to evaluate sources of potential exposure.

Peak exposures to phosphine, and sources of potential exposure, were evaluated by collecting air in inert gas sampling bags followed by analysis on-site using a portable gas chromatograph. After collection, a small aliquot of air was withdrawn from the bag with a syringe (through a septum), and injected into a Photovac Model 10A10 (R) portable gas chromatograph incorporating an 11-eV photoionization source and detector. All samples were analyzed two or more times. Sensitivity obtained varied somewhat during the survey, but was on the order of 0.06 ppm.

Ventilation characteristics at each facility (Table 1) were described in a general way during each survey by measuring the rates and directions of air movement in pertinent areas (e.g. bin decks, scale floor, distributor floor, etc.). Air flowrates were determined using a thermoanemometer, and directions and patterns of air movement were determined by observation using smoke tubes.

Plant Description and Fumigation Procedures

In order to identify potential study sites, federal and state departments of agriculture, the Federal Grain Inspection Service, leading fumigant manufacturers, and trade associations were contacted, and directories of grain warehouses were obtained from several of the major grain producing states. The information obtained was used in making an initial list of facilities. Sites were then contacted to determine whether grain fumigation was being conducted or was planned in the near future. Selection criteria included the size of the facility and workforce, type of terminal (elevator), and information obtained in initial contacts regarding the nature of the fumigation process and the type of fumigant used. From these initial contacts, it became clear that aluminum phosphide was almost universally used to fumigate grain in storage in most areas of the country. Many facilities indicated that they had switched in the last few years from liquid fumigants and other chemicals such as methyl bromide. In addition, although minor variations were described in the application techniques depending on factors such as the type and age of the grain storage structures, the fumigation procedures described in this report appear to be very representative of techniques used throughout the industry.

The surveys were conducted at four midwestern elevators of varying sizes and characteristics (Table 1). The first survey was conducted in July 1985 at a small inland elevator (elevator A) associated with a flour mill. During this survey, wheat was treated as it was received and put into long-term storage. The second, third, and fourth surveys were conducted in September 1985, November 1985, and November 1986, respectively, at three additional midwest elevators, of medium to large size (elevators B, C, and D). At these three facilities, phosphine exposures and sources of exposures were evaluated during the "turning" (movement of grain from one bin to another within the same elevator) of wheat during storage.

TABLE 1

Elevator Characteristics
Grain Fumigation Study

Inland Elevator	Capacity (MM bu)	Year(s) of Construction	No. of Workers	Date of Evaluation	Ventilation Characteristics Local*	General+
A	0.75	1942	3-5	7/85	BL	Minimal
B	2.2	1917-55	15	9/85	T,B,BL	Fair
C	4.4	1922-31	14	11/85	T,B,BL	Good
D	10	1954-62	19	11/86	BL	Minimal

* T = local exhaust hoods at tripper discharge chutes;
B = local exhaust at bin openings on bin deck;
BL= local exhaust at belt loaders for grain dust control.

\+ Dilution ventilation was entirely natural, and not mechanically assisted.
Minimal = little/no measureable general air movement in most areas measured;
Fair = Measureable general air movement averaging <50 fpm;
Good = Measureable general air movement averaging >50 fpm.

Almost all inland grain storage elevators have a common layout and construction (Figure 1a). These facilities normally consist of a main building consisting of 6 to 8 floors referred to as the headhouse. In the headhouse are located several levels which serve specific functions. The topmost occupied level is the scale floor. One person, the scale operator, or weighmaster, is stationed full-time on this floor. Below this level is the distributor floor, on which is located chutes and machinery to route the grain (dropped from the scales above) to the desired location in the elevator. A transfer floor may or may not be present in an elevator depending on the construction. If present, this floor may contain additional chutes (and perhaps another open belt conveyor and tripper car) designed to move grain to the proper location. A cleaner floor may also be present, on which are located grain cleaners, using screens and shakers, designed to remove dirt and undesired plant matter from bulk grain.

The headhouse also usually houses the grain legs (vertically oriented conveyor systems consisting of "bucket" conveyors running inside rectangular metal enclosures, and designed to move the grain upwards inside the elevator), a stairwell, and a "man-lifter" (a vertically oriented belt designed to carry personnel between floors).

The headhouse usually adjoins one or more "houses" or annexes, consisting of numerous upright concrete storage bins, with an enclosed work space at the top known as the bin deck. The distributor floor (or occasionally a "transfer" floor below) is level with the bin deck(s) at the tops of the storage bins. The bin decks are enclosed on all four sides with limited natural ventilation, consisting of openable windows at intervals along each of the two long walls.

On each bin deck, one or more horizontally-running open belt conveyors traverse the length of the floor. Each belt is fitted with a "tripper car", a device which can be moved on rails along the bin deck belt conveyor, and positioned over the designated receiving bin. The tripper removes the grain from the belt and directs it into the receiving bin through one of the two side-discharge chutes.

Underneath the storage bins in each house or annex is the "tunnel" area. The tunnel contains one or more open belt conveyors which carry grain, removed from the storage bins, to the boot in the basement of the headhouse, where it is carried upwards in one of the grain legs. The flow of incoming and outgoing grain through the elevator varies in minor details due to construction or functions (such as grain drying) which may or may not be done at a specific elevator. Incoming grain is unloaded either at a truck or rail receiving pit. At either, the grain is dropped by gravity into the pit where it is picked up by a conveyor running beneath the pit. From here, the grain is routed to the headhouse, where it is picked up by a grain leg and elevated to the scale floor. At the top of the elevator, the grain enters one of the scale garners (holding vessels) and is weighed. Typically, all grain received, shipped, or "turned" (moved within the elevator) is routed through the scale garners. Grain is turned for any one of several reasons, most frequently in order to clean it, blend it with other grain batches to bring it into specification for its intended use, or to fumigate it. Grain may also be moved within an elevator to cool or dry it in order to lengthen storage life.

From the scale floor, the grain is dropped by gravity through grain chutes to the distributor floor. At this point, the grain is routed either directly into a headhouse storage bin, or to one of the conveyors leading to one of the adjoining storage houses. On the appropriate bin deck, the grain is intercepted by a previously positioned tripper car, and directed into the designated receiving bin.

Grain to be turned or shipped out is unloaded from its storage bin by manually opening the hopper gate in the tunnel area (as previously described), conveyed by an open belt conveyor to a grain leg, and elevated to the scale floor, where it is subsequently directed as described above. Grain to be shipped is moved in a similar fashion to a hopper or temporary storage bin from which it is dumped into a rail car or truck.

All four of the elevators surveyed used similar procedures to treat the grain. In this procedure, the aluminum phosphide pellets or tablets are mixed with the grain as it is moved within the elevator ("turned"), or as the grain is received at the elevator. The pellets are dispensed one at a time into the grain stream as the grain is conveyed past the point of addition on an open belt, or as it falls directly into a bin opening, from an electrically operated, automatic dispenser. The dispenser (Figure 1b) is a portable device on wheels which can be positioned at an advantageous point, typically at the headhouse distributor floor, or on the bin deck upstream of the tripper car.

A variation of this procedure was used at Elevator B. At this facility, no automatic dispenser was used. Instead, the pellets were measured and manually poured from the original container into a vertical grain conveyor (grain leg) housing through an access door in the basement (Figure 1c), at which point it was mixed with the grain stream being carried within the leg, and subsequently routed to the bin deck.

At all of the elevators, the treated grain containing the tablets or pellets was then directed to a storage bin. Subsequently, during storage, the tablets/pellets decomposed in the presence of the moisture in the grain, releasing relatively large quantities of phosphine into the confined space in the bin.

Table 2 summarizes some information gathered regarding environmental conditions (air temperatures and relative humidity), and information regarding grain treated (when available) during each survey. Most of these factors would be expected to influence to some degree the exposure of workers to phosphine, since the rate of generation of phosphine from aluminum phosphide is temperature and moisture dependent.(17) However, many other factors, such as work practices used, and quality of general dilution and local exhaust ventilation at critical points (Table 1), would also undoubtedly influence exposures.

TABLE 2

Environmental and Treated Grain Conditions
at Four Elevators Surveyed
July 1985 to November 1986

Elevator	Date of Survey	Air Temp. Range (°F)	Relative Humidity (%)	Grain Type & Quantity (1000 bu)*	Grain Temp. (°F)	Grain Moisture (%)
A	7/85	82-95	40-60	Wheat (25-49)	NA**	NA**
B	9/85	82	72	Wheat (40)	NA**	NA**
C	11/85	43-46	74-86	Wheat (22-43)	75-85	11-13
D	11/86	18-34	--	Wheat (40-53)	62-71	11-12

* Quantity of grain treated per shift.
** Information unavailable during survey.

Results

The following paragraphs summarize and compare the most important data obtained during the four surveys. These data are summarized in Figures 2-6, and in Table 3 in the text following. Complete statistical summaries of the data obtained are contained in Tables A1-A3 in Appendix A. Detailed sampling results from the individual plant surveys are contained in tables B1-B7 in Appendix B.

During June-August 1985 at elevator A, wheat was received by truck from various other country and inland elevators in the area. The grain was elevated to the bin deck (enclosed space at the tops of the storage bins) and discharged directly onto a conveyor belt running the length of the deck. Aluminum phosphide tablets were added to the grain stream at a rate of 7 per minute at the point of discharge onto the belt. At the belt loader (point of grain discharge), the tablets were dispensed onto the grain stream from an automatic dispenser through a plastic hose. The treated grain was then conveyed to a tripper positioned to intercept and direct the grain into the designated storage bin.

Figure 2 presents pertinent exposures of elevator personnel to phosphine at elevator A, and concentrations measured in four areas on the bin deck. These exposure measurements were obtained over a three week period (i.e. one day during each of three consecutive weeks), and represent 8-hour, time-weighted average (TWA) exposures, and geometric means (GM) of concentrations over four areas during a full shift in the areas measured.

Exposures of the bin floorman, who spent nearly 100% of his time on the bin deck, and who conducted the fumigation operation, were 1.57 ppm, 1.63 ppm, and 0.48 ppm on the three sampling dates, respectively. The supervisor's respective exposures were 0.56 ppm, 0.29 ppm, and not detected (<0.14 ppm). The supervisor spent approximately 50% of his time in the elevator, and floated between the bin decks and tunnel areas. The geometric means of area concentrations on the bin deck on the three dates were 1.44 ppm, 0.94 ppm, and not detected (<0.06 ppm).

These exposures and concentrations compare with the ACGIH TLV (and OSHA PEL) of 0.3 ppm. Although no short term measurements of phosphine concentrations were obtained to compare with the ACGIH Short Term Exposure limit of 1 ppm, many of the full-shift TWA exposures also exceeded this recommendation. At the time of the survey, only single-use, disposable dust respirators were being worn by exposed personnel.

The most noticeable trend in the data is the substantial drop in concentrations (both personal and area) during the three-week period of the survey. Prior to the survey, it was expected that concentrations (and exposures) might rise gradually over time due to the increasing volume of treated grain stored in the bins, and to the general lack of room ventilation at the bin deck level. Examination of the data suggests instead that this trend did not occur, and that it is more likely that the exposures measured reflected more immediate factors such as the level of activity (volume of grain received, and thus the quantity of fumigant used). In fact, 36,000, 49,000, and 25,000 bushels of grain, respectively, were received on the three days sampled. These numbers appear to reflect a trend similar to the bin floorman's exposures.

Figure 3 summarizes the data from Elevator A in a different way. Each vertical bar represents the geometric mean of all samples obtained in each of several areas and in the two jobs (bin floorman and supervisor). The values shown for the center of the bin deck near the tripper (0.54 ppm), the frame of the west tripper (0.53 ppm), and the frame of east tripper (0.39

ppm) suggest that a major source of exposure to the bin floorman was phosphine-contaminated air being forced out of the head space of the bin as it was being filled with treated grain over a period of several hours. The tripper chutes at Elevator A were not equipped with mechanical local exhaust ventilation. In addition, ventilation measurements indicated generally very little air movement in most areas of the elevator during the survey. These factors would enhance the contribution of this source of exposure.

The results obtained by area measurements at the north end of the bin deck near the dispenser (0.31 ppm) also suggested (although not conclusively) that the dispenser was a potential source of exposure. Based on these unexpected results, it was hypothesized that either the dispenser, or the processes of filling, re-filling, and emptying the dispenser's holding vessel, or both, were substantial contributory sources of the bin floorman's personal exposures to phosphine. The dispenser's tablet holding vessel, which is not airtight, may become a potential source of exposure during a day's use, since the tablets typically remain inside it for several hours. In addition, the data raised the possibility that exposures to applicators could occur as soon as the original phosphide canisters were opened. This was a somewhat unexpected finding, since it was assumed, based on the nature of the chemical reaction, that aluminum phosphide tablets or pellets would begin reacting slowly, and that significant generation of phosphine would not occur for several hours.(14,17)

These hypotheses were more fully investigated on surveys conducted subsequently as a part of this project. This was done by more intensive collection of short-term bag samples and analysis of the samples on-site using the portable gas chromatograph. These data, collected primarily at elevators C and D, are discussed later in this paper.

The high concentrations found in the basement, near the east belt (0.90 ppm) reflect forced aeration of bins of recently treated grain. Fans located in this area draw air from the top of the storage bin, through the phosphide treated grain, and exhaust either into the basement area, or through ducts to the outside. The aeration is done primarily to cool and dry grain which contains excessive moisture. These high concentrations may also have influenced the exposures of the supervisor, but not the bin floorman, since he spent very little time in the basement.

Figure 4 presents similar phosphine data obtained at elevator C. The process of addition of aluminum phosphide to grain was similar in concept to elevator A, with a few differences. For example, elevator C was much larger in size, and the spouters (the same job as the bin floorman at elevator A, and labelled bin floorman in Figure 4) were required to roam over much larger areas during the course of a typical day than at elevator A. General room ventilation was much better, although much reliance was still placed on natural rather than mechanical ventilation. In addition, relatively efficient local exhaust ventilation was used at the tripper discharge chutes. However, the same type of aluminum phosphide product was used at both facilities, and the method of addition was identical, employing an automatic dispenser which added approximately 6-7 tablets per minute to the grain stream as it passed by on an open belt. During the course of a shift, this dispenser was manually refilled by the spouter/applicator four to six times.

The values shown in Figure 4 indicate that the exposures of the spouters exceeded that of the scale operator, and that the exposures of the spouter/applicator were far greater than those of the other spouter who did not fumigate or handle fumigant. Since the two spouters conducted similar work, other than the manual re-filling of the dispenser, it is likely that this specific task significantly contributed to the exposure of spouter/applicator (GM 0.77 ppm). This conclusion is further supported by the results of a short-term sample (discussed later in this report) obtained in the breathing zone of spouter/applicator during the 2 to 3-minute tablet dispenser refilling process.

In contrast to elevator A, the escape of phosphine contaminated air from bins being filled with grain at elevator C did not appear to be a significant contributor to personal exposures, based on both integrated area sampling and short-term sampling results. This was probably due to the relatively effective local exhaust ventilation at the tripper discharge chutes, as well as the rubber strips with which the junctions between the chutes and the bin openings are sealed. General dilution ventilation at elevator C was also much better than at elevators A or D, which also undoubtedly played a significant role in lowering ambient concentrations in the bin deck area at elevator C.

Figure 5 shows the geometric means of phosphine samples obtained at elevator D. Elevator D was in many respects (size and fumigation procedures) very similar to elevator C, except that neither local or general ventilation (Table 1) was as good. Other unique aspects of elevator D were that the fumigation was conducted entirely on the second shift (thus minimizing exposures of other elevator personnel), and that relatively low air temperatures (18-34 degrees F) were encountered during the survey.

At elevator D, the three highest average area concentrations were in samples obtained near the bin receiving the treated grain (GM 0.13 ppm), on the tripper car handling the treated grain (GM 0.12 ppm), and at the dispenser during the application of the phosphide pellets (GM 0.12 ppm). These results suggest again that the dispenser (i.e. the tablets held within), and contaminated air emanating from the partially filled receiving bin are significant potential sources of phosphine exposure. This is a real possibility since no local exhaust ventilation was used at any of these points, unlike elevator C.

As shown in Figure 5, the second-shift galley man (labelled bin floorman/applicator), who conducted the fumigation process at elevator D, was exposed to by far the highest average personal concentrations (GM 0.21 ppm, range 0.13 to 0.37 ppm). The exposures of the second-shift galley man greatly exceeded the exposures of the two other second-shift personnel whose exposures were measured during the survey, as well as those of the man doing the same job (but not conducting fumigation) on the first shift.

At elevator B, aluminum phosphide was added to wheat as it was being turned. However, at this facility, the pellets were measured and manually poured directly from the original container into a leg through an access door in the basement. This process was conducted by one employee, the blender, approximately 6-7 times during the shift measured. As shown in Figure 6, all area samples indicated non-detectable concentrations of phosphine (<0.04 ppm to <0.05 ppm, depending on the sampled volume). In addition, the blender's exposure was also below the limit of detection (<0.05 ppm). The low exposure may be due in part to the fact that the access door, when opened to dump the pellets into the leg, acted effectively as a local exhaust hood, since the leg was under negative pressure relative to the space in the basement. Also, since no dispenser was used, there was no continuing point source (i.e. the non-airtight holding vessel on the dispenser) of exposure to the applicator.

Short-term Sample Results

Short-term samples were obtained at Elevators B, C, and D, and analyzed on site by portable gas chromatography (Table 3). As listed, several locations or processes were identified as potential sources of worker exposure. These included the processes of filling and emptying the dispenser's holding

Table 3 Summary of Analyses of Phosphine by Portable Gas Chromatography Elevators B, C, and D.

Sample Type	Location	Description*	N	Min. (ppm)	Max. (ppm)	Geometric Mean (ppm)
Elevator B						
BZ	Bin Deck	Blender, manually adding phosphide pellets to grain leg in basement	2	0.2	0.6	0.4
Elevator C						
BZ	Bin Deck	Spouter #1, Refilling dispenser	1	12	--	--
Source	Bin Deck	Inside bin, filling with treated Grain	1	1.3	--	--
Source	Bin Deck	Vent Outlet, bin filling with treated grain	1	0.54	--	--
Source	Bin Deck	Inside just-emptied pellet can	1	110	--	--
Source	Bin Deck	Inside just-emptied pellet dispenser	1	3,000	--	--
Elevator D						
BZ	Bin Deck	Galley Man, refilling dispenser	6	0.1	52	2.7
BZ	Bin Deck	Galley Man, emptying dispenser	6	0.3	30	2.5
Source	Bin Deck	Near Dispenser, lid closed	8	<0.06	0.44	0.13
Source	Bin Deck	At tripper discharge, at bin opening, air escaping from bin	4	<0.06	4.2	0.57
Source	Bin deck	Inside bin opening (12-24 hrs. after bin filled and sealed)	5	2.3	100	33
Source	Bin Deck	Inside partially filled pellet dispenser	1	1000		
Control	Outside Elevator	Background samples, away from fumigation activity	2	<0.06	<0.06	--

* Bag samples of air were obtained typically over 2-3 minutes, ranging up to 5 minutes.

vessel (usually done four to six times during a typical fumigation run), phosphine-contaminated air escaping from a bin being filled with treated grain, and the tablets or pellets held within the dispenser's holding vessel.

During one two-minute cycle of filling the dispenser's holding vessel with aluminum phosphide pellets at Elevator C, a breathing-zone exposure of 12 ppm was recorded. The significance of the process of filling the dispenser (or emptying it at the end of the shift) is corroborated by additional sampling data obtained at elevator D. During these procedures at elevator D, exposures ranged from 0.1 ppm to 52 ppm, and averaged approximately 2.5 ppm during each 2-3 minute time period. At elevator B, two short-term samples obtained in the breathing zone of the blender, during the 1-minute process of addition of the phosphide tablets through the grain leg access door, indicated peak concentrations of 0.2 and 0.6 ppm, respectively. However, the cumulative effect of these short exposures were not reflected in the single full shift sample obtained from the breathing zone of this employee. These short-term, breathing zone sample results compare with the ACGIH TLV of 1 ppm (time weighted over 15 minutes, with no more than four such exposures per day). Although most of these samples were obtained over shorter periods (i.e. 2-5 minutes), the magnitude of some of the highest results (up to 52 ppm) were substantially in excess of the 1 ppm criteria level.

Source samples obtained at elevator C indicate that during filling of a storage bin with recently treated grain, a concentration of 0.54 ppm was measured at the unventilated bin vent outlet (on the floor of the bin deck). This contaminated air was being forced out of the bin's head space into the bin deck area, and undoubtedly constituted at least a minor source of phosphine exposure during the fumigation process. Similarly, a concentration of 1.3 ppm was measured inside the head space (just inside the bin opening at floor level, at the junction of the bin opening and the tripper's grain discharge chute) of a second bin being filled with recently treated grain. The air at this point was being removed by the tripper chute's exhaust hood, and thus very likely was less important as a source of exposure to phosphine.

At elevator D, concentrations inside a bin 12-24 hours after being filled with treated grain ranged from 2.3 to 100 ppm (averaging 33 ppm), which were far above those measured during the fumigation activity, (averaging 0.57 ppm). This suggests that without adequate sealing of the bin openings, phosphine infiltration can easily become an important source of exposure to personnel working in adjacent areas, such as the bin deck or tunnel. In fact, concentrations in the bin deck areas on the shifts following fumigation averaged 0.05 ppm, and ranged up to 0.2 ppm (refer to Table A3 in Appendix A).

Finally, two short-term samples obtained inside the pellet dispensers' holding vessels at elevators C and D indicated concentrations of 3000 and 1000 ppm, respectively. Although short-term concentrations measured at elevator D near the dispenser (with the lid closed) averaged only 0.13 ppm, this indicates a potentially serious hazard, especially to the bin floorman during the process of filling and emptying the dispenser, since the lid must be opened at these times.

Discussion

Figure 6 presents the results of phosphine monitoring at all four sites, for selected areas and jobs which were considered to be generally comparable based on the process and activities. In general, it appears that area concentrations of phosphine, and consequently personal exposures, are substantially higher at Elevator A than at Elevators B, C or D. This is very likely due to a variety of factors, such as the lack of adequate general ventilation and specific local exhaust ventilation at the tripper in elevator A compared with elevator C. However, many other factors also appear to play a significant role in controlling exposures and general ambient levels of phosphine in the elevators.

It appears that, at all three elevators at which an automatic dispenser was used (A, C, and D), the process of manual addition of tablets to the dispenser, and the tablets held in the dispenser itself over the workshift, contributed to the bin floorman's (spouter's, galley man's) exposures to phosphine. At elevator B, perhaps due to the difference in technique in adding phosphide to the grain, and to the absence of the dispenser as an ongoing source of exposure, area concentrations, as well as most personal exposures, were below the limit of detection.

The contributions of other parameters such as ambient temperatures, relative humidity, and grain temperature and moisture cannot be fully assessed based on the limited data collected, although some trends are evident. Comparison of Figure 6 with Table 2 suggests that overall environmental temperatures play a role in determining exposures, which is not an unreasonable assumption, since the rate of reaction of aluminum phosphide is temperature dependent. Elevators A, C, and D appear to show a rough trend of increasing exposure to the applicator with increasing environmental temperature. Elevator B does not appear to follow this pattern, perhaps due to the substantially different method of fumigation (manual addition vs. automatic dispenser).

The effects of changes in grain temperatures cannot be assessed since grain temperatures varied only slightly between elevators (Table 2). Grain temperatures may play a more important role in concentrations developed inside the storage bin, both during the treatment process, and during subsequent storage. On the other hand, environmental temperatures probably play a more important role in concentrations developed at the pellet dispenser, or inside the original containers before and after they are opened.

However, it is also clear that other factors, most notably the volume of grain treated (and thus the quantity of phosphide fumigant used per shift), and of course the extent and effectiveness of local and general ventilation, also substantially influence exposures. This trend was evident at elevator

A, in which the exposures over a three week period seemed to follow the quantity of grain treated on a given shift. In addition, at elevator D, exposures were higher on the last of three days of sampling, despite a drop in environmental temperature from the mid-30's to 18 degrees F. At the same time, the volume of grain treated rose substantially on the last of the three days (approximately 53,000 bu) compared with the first two days (approximately 40,000 bu).

Previous reports variously indicate that phosphine has good or poor warning properties. In this study, employees were observed working without concern at concentrations in excess of 50 ppm for several minutes. Although the odor of phosphine was frequently detectable during these procedures (e.g., filling and emptying pellet dispensers), the presence of these very high concentrations did not make working conditions unacceptable to the employee such that the employee was compelled to leave the area or don an appropriate respirator.

Conclusions

The phosphine data obtained during these surveys appear to demonstrate that substantial exposures to phosphine can and do occur as soon as the original containers of aluminum phosphide are opened. This exposure may be due in part to the fact that aluminum phosphide begins immediately to react and produce phosphine, or more likely, that the aluminum phosphide has reacted with moisture sealed inside the container, in which case the phosphine would be released (under pressure) when the canister is opened. In either case, this can lead to demonstrable exposures (and frequently excessive exposures when compared to relevant exposure criteria) during the course of a typical 8-hour shift. Specifically, the task of repeatedly refilling and/or emptying the automatic tablet dispensers leads to a series of short, peak exposures which significantly contribute to TWA exposures over a work shift.

In addition, the temporary storage of the phosphide in the dispenser's holding vessel appears to be an important source of ambient concentrations of phosphine in the adjacent areas. These conclusions are based on area and source samples obtained at Elevators A, C, and D, which indicated high ambient concentrations near the dispenser, and extremely high peak and full-shift personal exposures in those employees required to refill the dispenser. Furthermore, at Elevator B, where no dispenser was used - i.e. the phosphide was dumped directly into a leg through an access door - the peak and full-shift personal exposures of the operator conducting this task were much lower or not detected.

In Elevators A and D, the escape of phosphine contaminated air from the head space of the storage bins being filled with phosphide treated grain appears to be an additional important source of exposure to personnel working in the bin deck area. Area samples obtained on the bin decks at Elevators A and D indicated that ambient concentrations of phosphine were highest at the tripper, where contaminated air was forced out of the head space of the storage bin. The lack of local exhaust at the tripper chute, and the general lack of general dilution ventilation, undoubtedly contributed to the significance of this source.

Phosphine sampling data obtained over a three week period at elevator A, and similar data obtained over a three day period at elevator D, suggested that the levels of exposure were in part a function of the amount of grain being treated, and thus the amount of phosphide used, on a given day. An upward trend in ambient levels of phosphine was not seen at elevator A as more and more treated grain was stored over a period of weeks at the elevator. This is undoubtedly a function of the tightness of the seal at the bin floor openings of filled bins, and the quality of bin construction. In older elevators, where construction is looser or the seals are inadequate, the stored, treated grain may indeed become a source of ambient phosphine concentrations and exposures.

The contributions of environmental parameters such as grain temperatures, moisture, ambient temperatures and relative humidity cannot be properly assessed based on the data obtained. Although these factors do in fact influence the rate of generation of phosphine from phosphide, it is not clear to what extent they influence levels of exposure in elevators using the phosphide products. The limited data obtained thus far suggest that a gross rise in environmental temperatures will result in a corresponding rise in phosphine exposures during fumigation activities. However, it is also clear that many other factors, as such as those discussed above, also substantially influence exposure levels, apparently to a much greater extent.

Recommendations

Compared with many other fumigants (such as the liquid, "80/20" types), or gases such as methyl bromide, aluminum phosphide products should be relatively easy to handle. However, in contrast with previous suppositions, the exposures found during these surveys indicate that the use of phosphide products can lead to excessive exposures if they are used without proper engineering controls and work practices, as documented in this report. Applicators should not, therefore, become complacent because of the seemingly innocuous nature of the solid tablets or pellets used.

Although demonstrable and sometimes excessive exposures to phosphine were measured during these surveys, control of exposures during active fumigation activities should be a relatively simple matter. Installation of local exhaust ventilation systems at the phosphide tablet/pellet dispenser, and at the tripper car discharge chute, would undoubtedly reduce exposures. The ventilation should evacuate the dispenser's holding vessel, and should have a hood over the cover to provide control during filling and emptying, as well as a location to store partially used or recently emptied phosphide canisters. For the most part, such ventilation devices could easily be integrated into the elevator's existing dust-control ventilation systems. For the portable dispensers, this could be accomplished by installing flexible ducts with quick-connect fittings at the locations where the dispensers are normally positioned. Work practices should then be implemented which would require the opening and re-use of phosphide canisters only under this local exhaust system.

References

1. MARANO, D.E., K.L. WHITE, H. DEER, and G. ALEXANDER. Carbon Tetrachloride/Carbon Disulfide Exposures in Grain Fumigation. CDC-NIOSH Contract No. 210-83-6002, Final Report (unpublished). 1985.

2. ENVIRONMENTAL PROTECTION AGENCY. Decision and Emergency Order Suspending Registrations of Pesticide Products Containing Ethylene Dibromide. 49 FR 4452, February 6, 1984.

3. CHEMICAL MARKETING REPORTER. 228(13):4. September 23, 1985.

4. PAULUS, H.J., M. LIPPMAN, and A. COHEN. Fumigation of Shelled Corn with a Mixture of Carbon Disulfide and Carbon Tetrachloride. Industrial Hyg. Quart. 18:345-350, 1957.

5. DEER, H.M., C.E. MCJILTON, P.K. HAREIN, and WW. SUMNER. Inhalation Exposure of Grain Samplers and Grain Inspectors to Carbon Tetrachloride. IN: ACS Symposium Series, Dermal Exposure Related to Pesticide Use, No. 273, pp. 221-241, 1985.

6. SMITH, A.R., L. GREENBURG, and W. SIEGEL. Respiratory Disease Among Grain Handlers. Industrial Bulletin 20:1, 1941.

7. PETERS, H.A., R. LEVINE, C. MATTHEWS, S. SAUTER, and J. RANKIN. Carbon Disulfide - Induced Neuropsychiatric Changes in Grain Storage Workers. American Journal of Industrial Medicine 3:373-391, 1982.

8. HEALTH HAZARD EVALUATION - Port of Duluth-Superior Grain Elevators: Report No. 75-11-403. National Institute for Occupational Safety and Health. Cincinnati, Ohio, 1977.

9. HEALTH HAZARD EVALUATION - Elevator, Terminal 4, Portland, Oregon: Report No. 76-13-316. National Institute for Occupational Safety and Health. Cincinnati, Ohio, 1976.

10. AHRENHOLZ, S.H. Health Hazard Evaluation - Federal Grain Inspection Service - Portland, Oregon: Report No. 83-375-1521. National Institute for Occupational Safety and Health. Cincinnati, Ohio, 1984.

11. AHRENHOLZ, S.H. Health Hazard Evaluation - Superior, Wisconsin: Report No. 84-194-1549. National Institute for Occupational Safety and Health. Cincinnati, Ohio, 1985.

12. RUHE, R. Health Hazard Evaluation - Federal Grain Inspection Service-USDA - New Orleans, Louisiana: Report No. 84-281-1607. National Institute for Occupational Safety and Health. Cincinnati, Ohio, 1985.

13. CHEMICAL ECONOMICS HANDBOOK. SRI International (201.2501-.2522), 1980.

14. U.S. ENVIRONMENTAL PROTECTION AGENCY. Pesticide Registration Standard: Aluminum Phosphide. Office of Pesticides and Toxic Substances, Washington, D.C., 20460, 1981.

15. JONES, A.T., R.C. JONES, and E.O. LONGLEY. Environmental and Clinical Aspects of Bulk Wheat Fumigation with Aluminum Phosphide. American Ind. Hyg. Assoc. J. 25:376-379, 1964.

16. FOOD AND ALLIED SERVICE TRADES DEPARTMENT, American Federation of Labor and Congress of Industrial Organizations: Health and Safety Fact Sheet - Phostoxin (Aluminum Phosphide). 815 Sixteenth St., N.W., Suite 408, Washington, D.C. 20006, 1984.

17. RESEARCH PRODUCTS COMPANY. Application Procedures for Detia Pellets and Detia Tablets (Current Labeling Information). Salina, Kansas, 1986.

18. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. DHHS (NIOSH) Publication No. 81-123, 1981.

19. DOCUMENTATION OF THRESHOLD LIMIT VALUES. Fourth Ed., with Supplements. American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio, 1980-1984.

20. HARGER, P.N., and L.W. SPOLYAR. Toxicity of Phosphine, with a Possible Fatality from this Poison. A.M.A. Archives Ind. Health 18:497-504, 1958.

21. WILSON, R., F.H. LOVEJOY, JR., R.J. JAEGER, P.L. LANDRIGAN. Acute Phosphine Poisoning Aboard a Grain Freighter. Epidemiologic, Clinical, and Pathological Findings. J. Am. Med Assoc; 244(2):148-150, 1980.

22. SAX, N.I. (ed.) Dangerous Properties of Industrial Materials (Sixth Ed.), p. 2212. Van Nostrand Reinhold, New York, 1984.

23. PATTY, F.A. (ed.) Toxicology, Vol. IIA of Industrial Hygiene and Toxicology (3rd ed. rev.), p. 2129. John Wiley and Sons, New York, 1981.

24. WARITZ, R.S., and R.M. BROWN. Acute and Subacute Inhalation Toxicities of Phosphine, Phenylphosphine, and Triphenylphosphine. American Ind. Hyg. Assoc. J. 36:452-458, 1975.

25. KLIMMER, O.R. [Study of the Action of Phosphide (PH3). Chronic Phosphine Poisoning.] Arch. Toxikol.; 224:164-187, 1969.

26. MULLER, W. [The Hydrogen Phosphide Intoxication (Animal Experiments). Report I. Acute and Subacute Intoxication.] Naunyn- Schmiederberg's. Archiv. fur Experimentelle Pathologie und Pharmakologie, 95:184-193, 1940.

27. MUTHU, M., M.K. KRISHNAUMARI, MURALIDHARA, S.K. MAJUMDER. A Study on the Acute Inhalation Toxicity of Phosphine to Albino Rats. Bull. Environ. Contam. Toxicol.; 24(3):404-410, 1980.

28. AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS. Threshold Limit Values and Biological Exposure Indices for 1986-87. Cincinnati, Ohio, 1986.

29. OCCUPATIONAL SAFETY AND HEALTH STANDARDS. Subpart Z - Toxic and Hazardous Substances. 40 FR 23072, Section 1910.1000, May 28, 1975.

30. LEONARDOS, G., D. KENDALL, and N. BARNARD. Odor Threshold Determinations of 53 Odorant Chemicals. J. Air Poll. Cont. Assoc. 19:91-95, 1969.

31. AMOORE, J., And E. HAUTALA. Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution. J. Applied Toxicol.; 3(6), 272-290, 1983.

32. NIOSH Manual of Analytical Methods, Second Ed., Vol. 5. DHHS (NIOSH) Publication No. 79-141. National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1979.

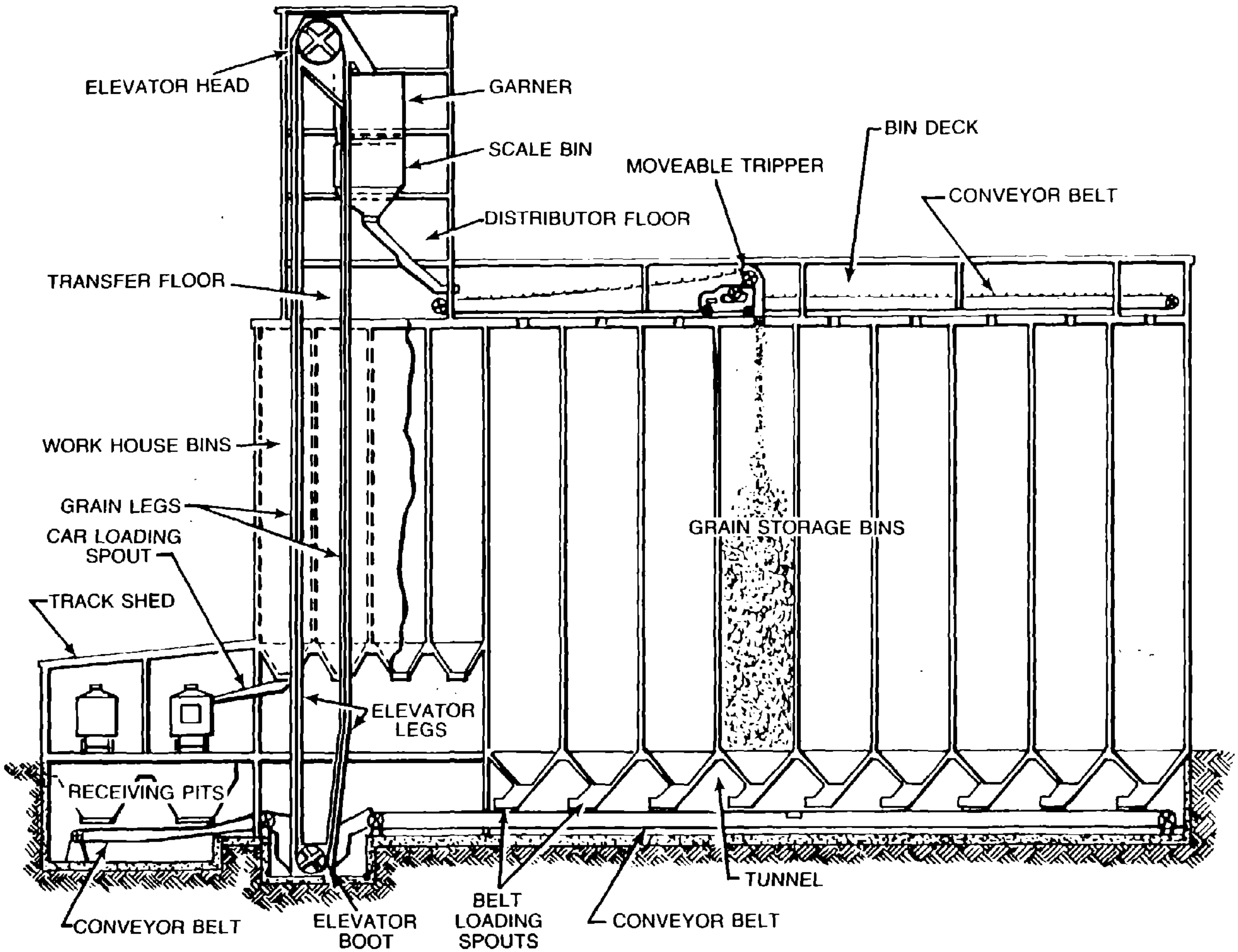


Figure 1a. Typical Elevator Construction; Cutaway View

(adapted from DHHS (NIOSH) Publication No. 83-126: Occupational Safety in Grain Elevators and Feed Mills)

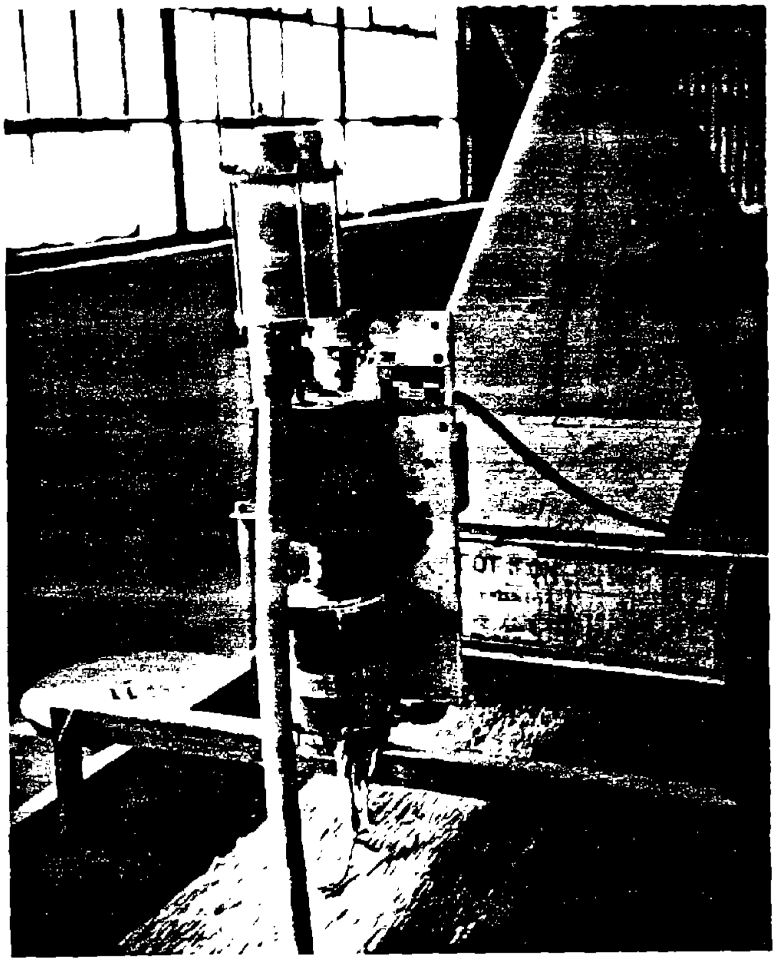


Figure 1b. Aluminum Phosphide tablet dispenser, permanently mounted over an open-belt conveyor.

Figure 1c. Manual Addition of phosphide to a grain-leg access door in headhouse basement.

Figure 2. Phosphine Concentrations over

a Three Week Period, Elevator A

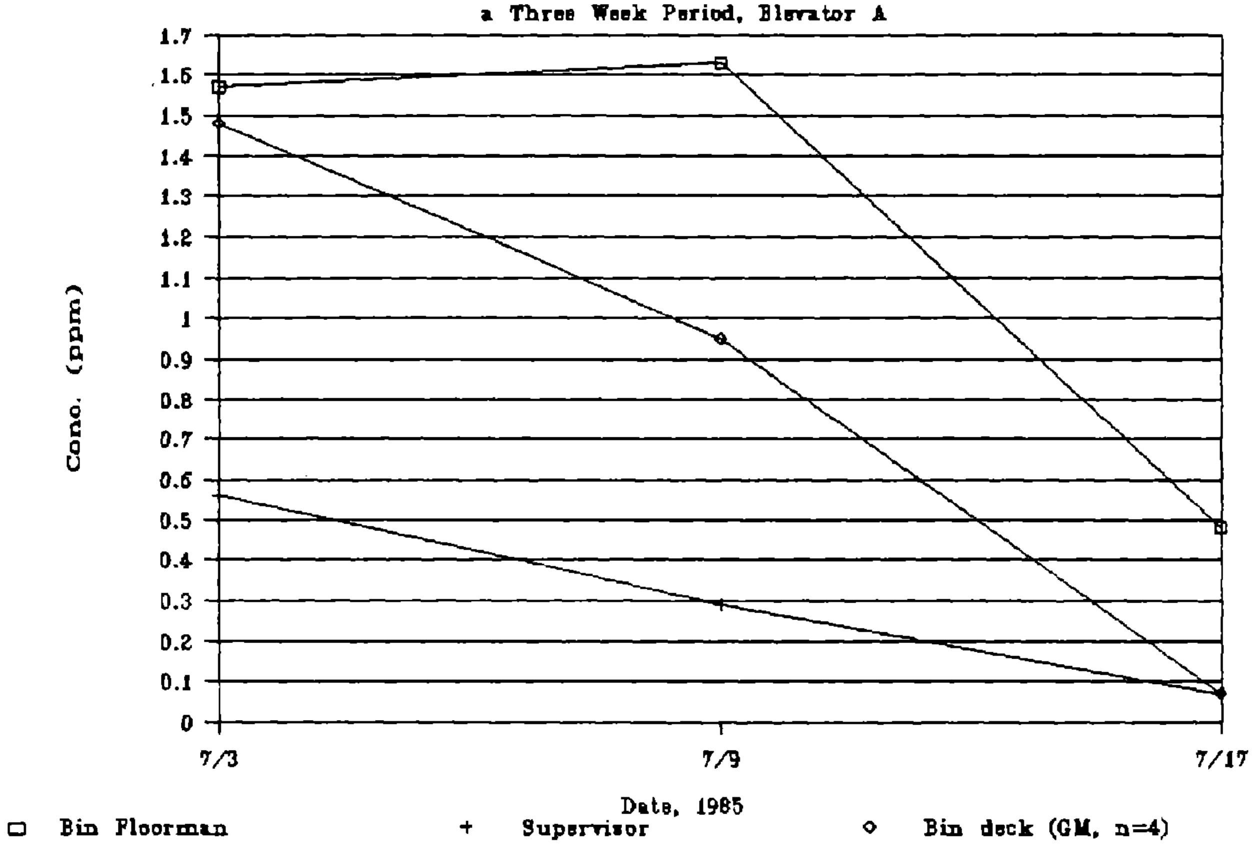
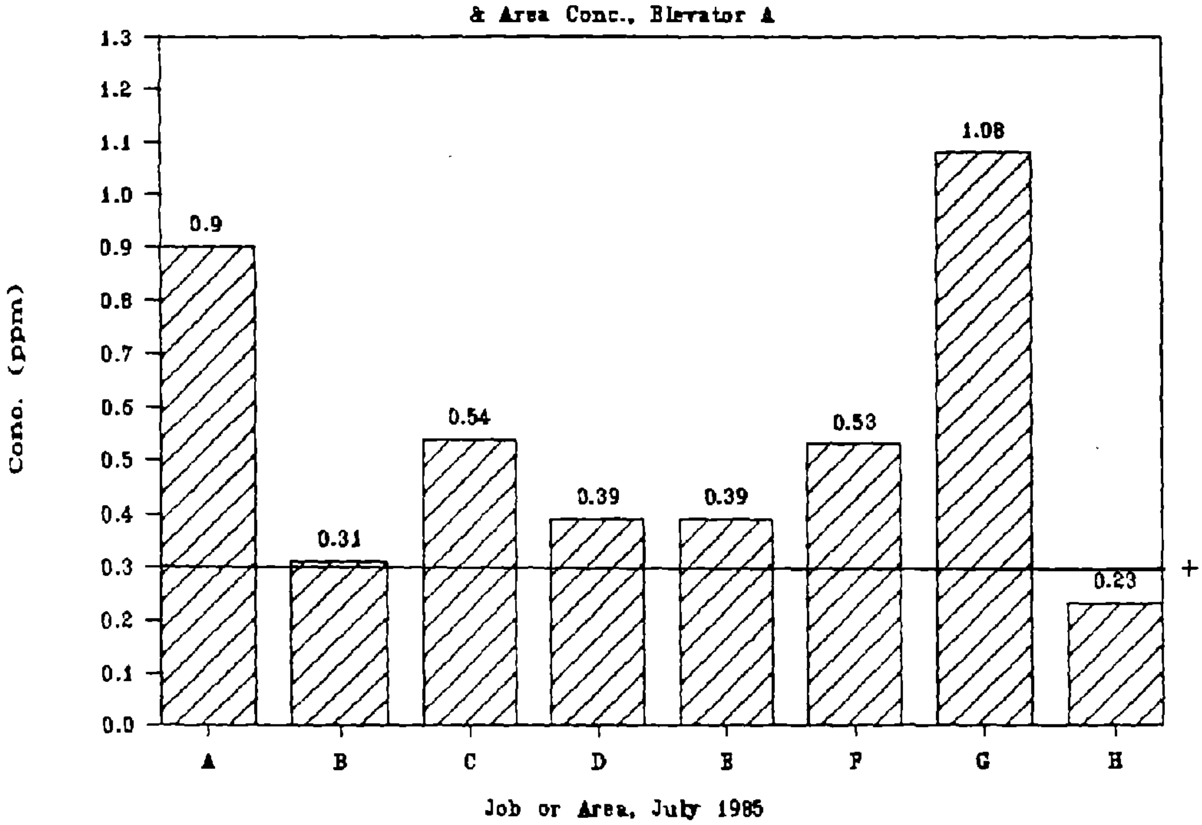


Figure 3. Geometric Mean PH_3 Exposures



+ OSHA PEL/ACGIH TLV

Area Samples:

A= tunnel, E. Belt (N=2)

B= At dispenser (N=3)

C= Near Tripper/bin (N=3)

D= Tunnel, bugroom (N=2)

E= At E. tripper (N=3)

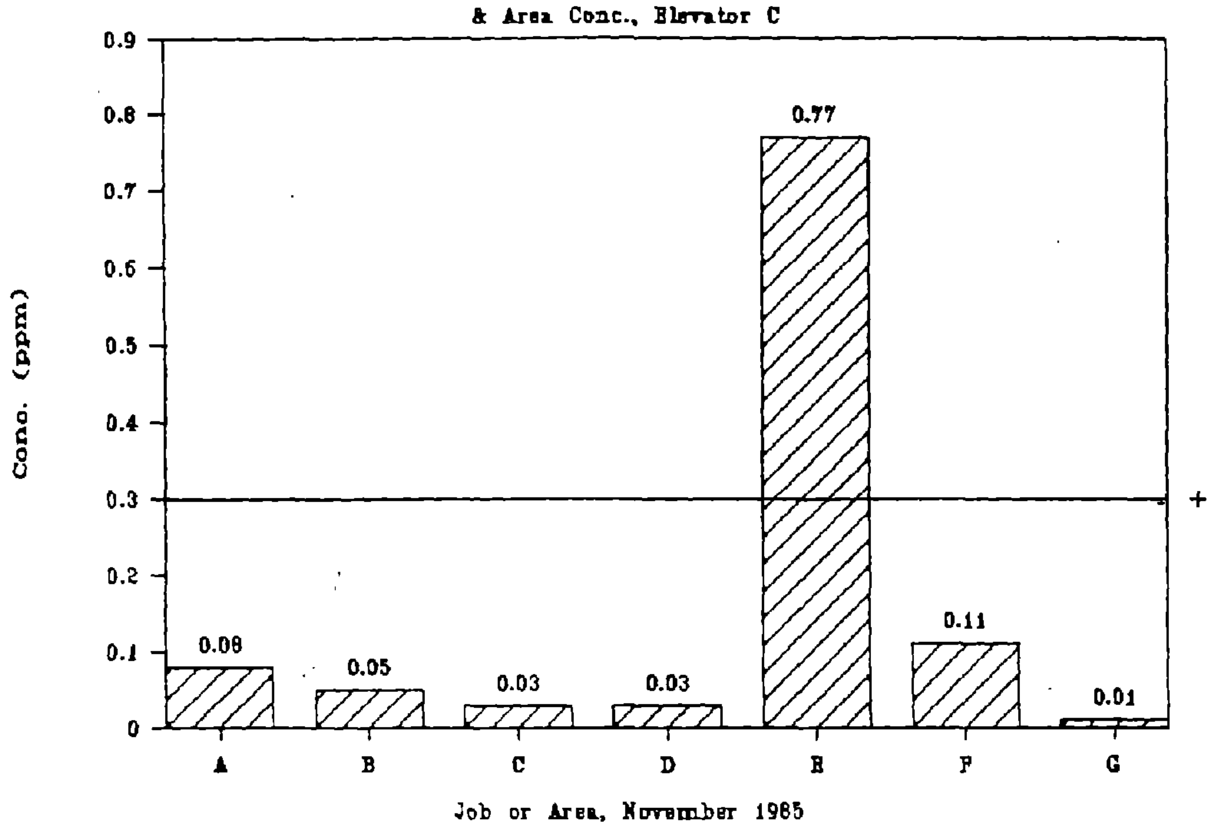
F= At W. tripper (N=3)

Personal Samples:

G= Bin floorman/Applicator (N=3)

H= Supervisor (N=3)

Figure 4. Geometric Mean PH3 Exposures



+ OSHA PEL/ACGIH TLV

Area Samples:

A= At dispenser, bin deck (N=8)

B= Along belt, bin deck (N=2)

C= At tripper/bin (N=6)

D= Near tripper (N=2)

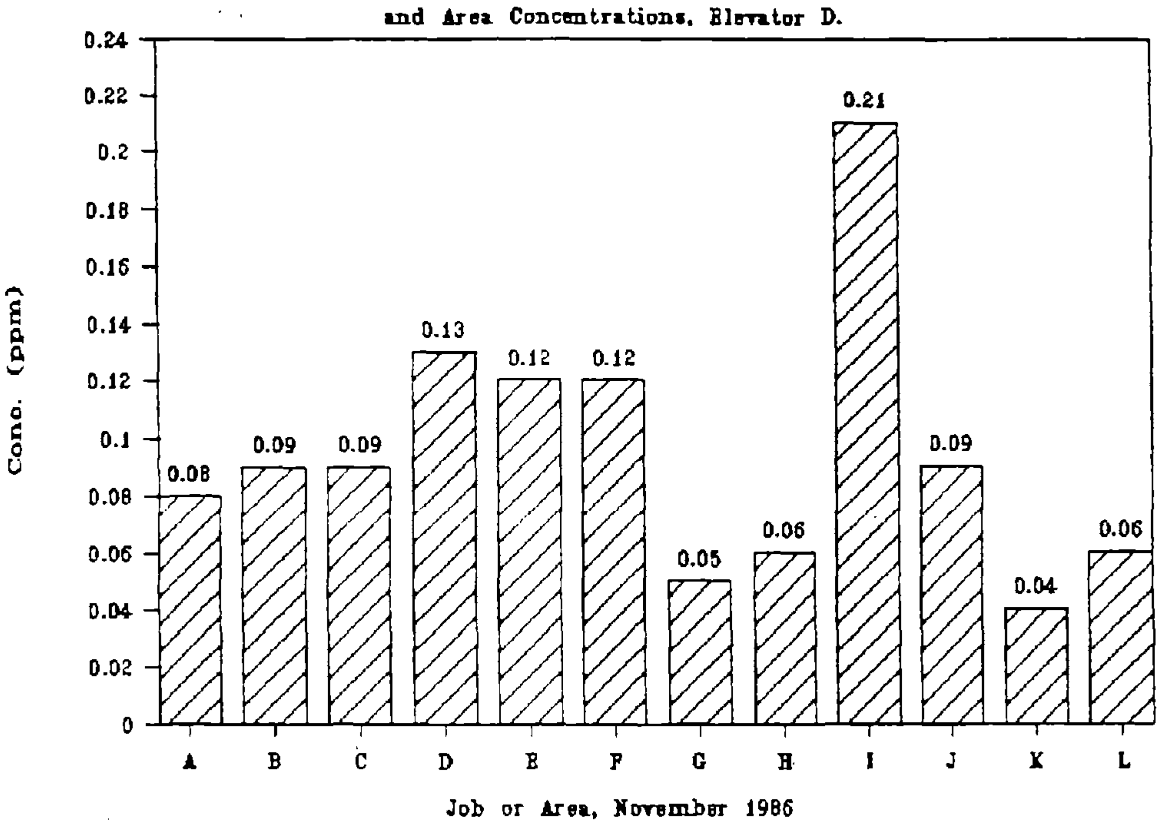
Personal Samples:

E= Bin floorman/applicator (N=4)

F= Bin floorman (no fumigation activity) (N=4)

G= Scale operator (N=4)

Figure 5. Geometric Mean PH3 Exposures



Area Samples:

A= Scale Floor, at controls (N=4)

B= Scale Floor, in office (N=3)

C= Scale floor, all areas (N=7)

D= Near receiving bin, bin deck (N=3)

E= At tripper/bin, bin deck (N=5)

F= At dispenser, bin deck (N=5)

G= Bin deck area, shift following fumigation (N=4)

H= Tunnel areas (N=9)

Personal Samples:

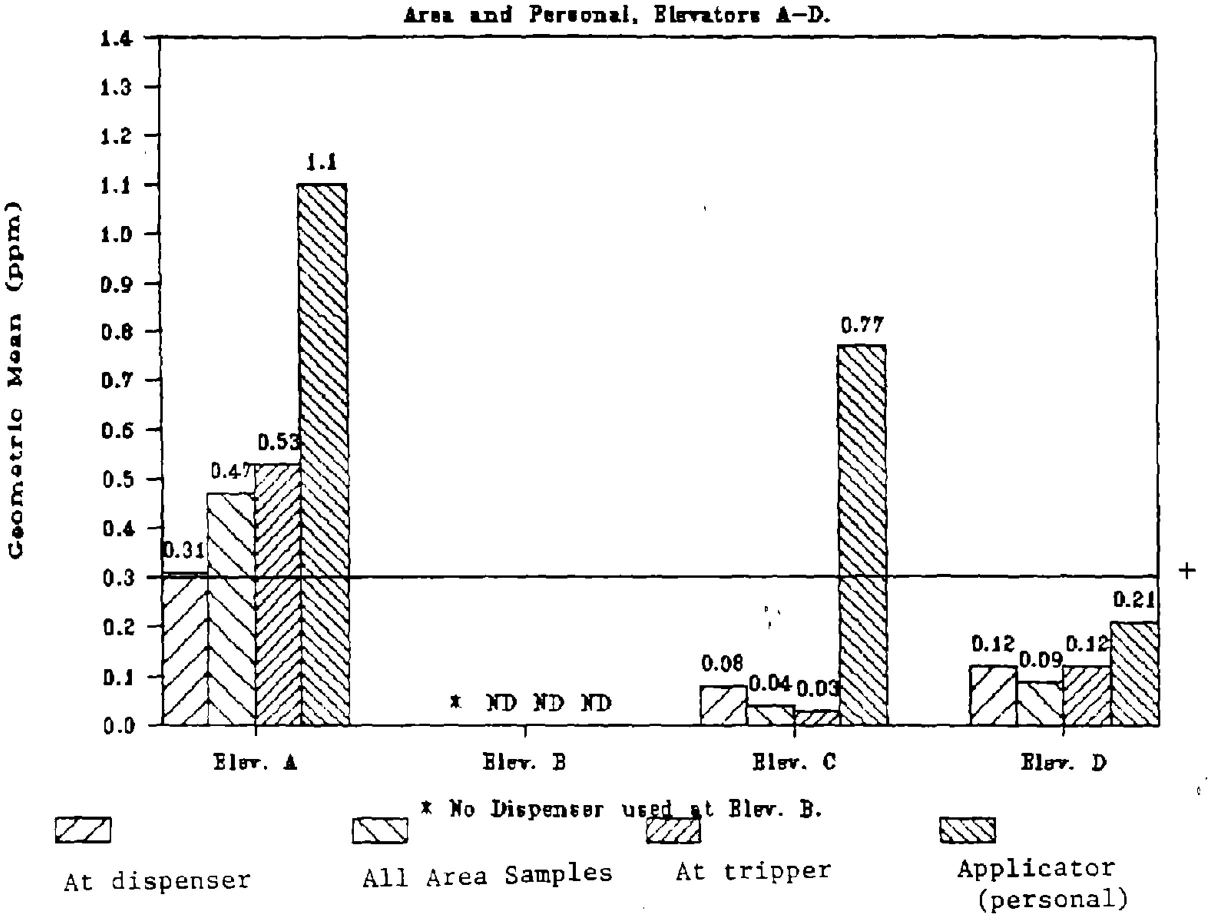
I= Bin floorman/applicator (N=3)

J= Bin floorman (no fumigation activity) (N=1)

K= Basement mix man (N=3)

L= Scale operator (N=3)

Figure 6. Comparison of PH3 Levels



+ OSHA PEL/ACGIH TLV

Appendix A
(Statistical Summary Data; Elevators A, C, D)

Table A1
Area and Personal Phosphine Exposure Summary By Job/Area[1]
Elevator A, July 1985
(ppm)

Job/Area	N	Range Min	Range Max	Arithmetic Mean	Standard Error	Geometric Mean	Geometric Standard Deviation
All Areas	16	0.06	2.3	0.81	0.16	0.47	3.7
Basement, E. Belt	2	0.61	1.3	0.97	0.35	0.90	1.7
Bin Floor, at dispenser, N. end	3	0.06	0.82	0.50	0.23	0.31	4.4
Bin Floor, near W. tripper	3	0.07	1.7	1.1	0.51	0.54	6.1
Basement, bug room	2	0.23	0.66	0.44	0.22	0.39	2.1
Frame of E. Tripper	3	0.06	1.2	0.68	0.33	0.39	5.0
Frame of W. Tripper	3	0.07	2.3	1.1	0.64	0.53	6.3
Bin Floorman	3	0.48	1.6	1.2	0.37	1.1	2.0
Roving Supervisor	3	0.07	0.56	0.31	0.14	0.23	2.9

1 Results below detection limit incorporated by using a value equal to one half of detection limit (L/2)

Table A2
Area and Personal Phosphine Exposure Summary
By Job or Area[1]
Elevator C, November 1985
(ppm)

Description of Data	N	Mean, ppm	Standard Deviation, ppm	Geometric Mean, ppm	Geometric Standard Deviation
Personal TWA[2]					
All	12	0.36*	0.43*+	0.13*	6.0*+
All 11/14/85	6	0.44*	0.59*+	0.12*	7.4*+
All 11/15/85	6	0.28	0.24+	0.13	5.8+
All Spouters	8	0.51	0.46	0.29	4.1
Spouter #1	4	0.85	0.42	0.77	1.6
Spouter #2	4	0.17	0.15+	0.11	3.7+
Area TWA					
All	22	0.06*	0.06*+	0.04*	2.8*+
All 11/14/85	12	0.07*	0.07*+	0.04*	3.1*+
All 11/15/85	10	0.06*	0.06*+	0.04*	2.4*+
At Dispenser	8	0.1*	0.07*	0.08*	1.9*
Along belt	2	0.06	0.02	0.05	1.5
At tripper/bin	6	0.06	0.07+	0.03	3.0+
Fumigated grain entering "nearby" bin	2	0.06	0.06+	0.03	5.1+
Source					
At tripper/bin opening, TWA	3	0.2	0.2+	0.1	5.3+
Inside bin/bin vent outlet, "instantaneous"	2	0.9	0.5	0.8	1.9

1 Results below detection limit incorporated by using a value equal to one half of detection limit (L/2).

2 Time-Weighted Average

* One sample included is equal to or greater than reported value; reported value used to calculate statistics.

\+ Standard deviation may lack precision because between 20 and 50% of values were "L/2" (due to being below detection limit).

Table A3
Area and Personal Phosphine
Exposure Summary By Job or Area[1]
Elevator D, November 1986
(ppm)

Job/Area and shift	N	Range Minimum	Range Maximum	Arithmetic Mean	Standard Error	Geometric Mean	Geometric Std. Dev.
Personal Samples							
Galley man (2nd)	3	0.13	0.37	0.25	0.06	0.21	1.50
Galley man (1st)	1	0.09	--	--	--	--	--
Basement Mix Man (2nd)	3	0.01	0.07	0.04	0.01	0.04	1.71
Night Foreman (scale room, 2nd)	3	0.01	0.08	0.06	0.02	0.06	1.77
Area Samples							
Scale floor, at controls (1st & 2nd)	4	0.07	0.10	0.08	0.01	0.08	1.15
Scale floor, office (1st)	3	0.07	0.12	0.10	0.01	0.09	1.30
Scale floor, all areas (1st & 2nd)	7	0.07	0.12	0.09	0.01	0.09	1.21
Near receiving bin, bin deck (2nd)	3	0.08	0.27	0.15	0.06	0.13	1.89
On tripper, bin deck (2nd)	5	0.08	0.25	0.14	0.03	0.12	1.67
At dispenser, bin deck (2nd)	5	0.08	0.21	0.13	0.02	0.12	1.41
Bin deck, area (1st)	4	0.01	0.20	0.11	0.04	0.05	5.57
B-house, tunnel #4 (1st and 2nd)	9	0.02	0.17	0.08	0.02	0.06	2.41

[1] Results below detection limit incorporated by using a value equal to one half of detection limit (L/2)

Appendix B
(Raw data Tables B1-B7, Elevators A-D)

Table B1
Sampling Results, Phosphine
Elevator A

Date 1986	Sample Number	Job/Area	Time Start	Time Stop	Flow (cc/min)	Weight (ug)	Time (min)	Vol. (L)	Concentration (ppm) Replicate	Concentration (ppm) Mean*
7/09	N58P	Area, basement	12 25	15 43	50.02	7.4	198	9.9	0.55	
7/09	N59P	Area, basement	12 25	15 43	48.72	8.8	198	9.6	0.67	0.61
7/17	N83PA	Area, basement	12 14	16 5	43.7	19.6	231	10.1	1.42	
7/17	N83PB	Area, basement	12 14	16 5	44.06	17	231	10.2	1.22	1.32
7/17	N84PA	Area, bin floor N	8 11	15 58	50.84	3.5	467	23.7	0.11	
7/17	N84PB	Area, bin floor N	8 11	15 58	48.88	3.5	467	22.8	0.11	0.11
7/03	N44P	Area, bin floor N	8 13	15 19	45.41	22.1	426	19.3	0.83	
7/03	N45P	Area, bin floor N	8 13	15 19	50.21	23.7	426	21.4	0.80	
7/09	N62P	Area, bin floor N	8 9	15 35	45.64	16	446	20.4	0.58	
7/09	N63P	Area, bin floor N	8 9	15 35	45.26	19	446	20.2	0.69	0.63
7/17	N82PA	Area, bin floor Cntr	8 5	15 53	42.29	3.5	468	19.8	0.13	
7/17	N82PB	Area, bin floor Cntr	8 5	15 53	39.33	3.5	468	18.4	0.14	0.13
7/03	N46P	Area, bin floor Cntr	8 19	15 22	46.6	45.8	423	19.7	1.69	
7/03	N47P	Area, bin floor Cntr	8 19	15 22	41.48	42.6	423	17.5	1.77	1.73
7/09	N54P	Area, bin floor Cntr	8 9	15 36	51.62	43.8	447	23.1	1.40	
7/09	N55P	Area, bin floor Cntr	8 9	15 36	51.28	42.6	447	22.9	1.37	1.38
7/09	N66P	Area, bug room	12 22	15 43	50.2	6.2	201	10.1	0.45	
7/09	N67P	Area, bug room	12 22	15 43	50.11	6.2	201	10.1	0.45	0.45
7/17	N85PA	Area, bug room	12 12	16 4	42.43	8.9	232	9.8	0.66	
7/17	N85PB	Area, bug room	12 12	16 4	44.02	9.1	232	10.2	0.65	0.66
7/03	N50P	Area, East tripper	8 26	15 23	47.82	32.2	417	19.9	1.18	
7/03	N51P	Area, East tripper	8 26	15 23	45.76	31.2	417	19.1	1.19	1.18
7/09	N52P	Area, East tripper	8 16	15 37	44.55	21.3	441	19.6	0.80	
7/09	N53P	Area, East tripper	8 16	15 37	41.78	20	441	18.4	0.80	0.80
7/17	N87PA	Area, East tripper	8 1	15 54	44.32	3.5	473	21	0.12	
7/17	N87PB	Area, East tripper	8 1	15 54	44.18	3.5	473	20.9	0.12	0.12
7/03	N48P	Area, West tripper	8 23	15 25	42.76	56.1	422	18	2.26	
7/03	N49P	Area, West tripper	8 23	15 25	43.21	57.6	422	18.2	2.30	2.28
7/09	N56P	Area, West tripper	8 12	15 36	42.08	25	444	18.7	0.98	
7/09	N57P	Area, West tripper	8 12	15 36	44.21	26.7	444	19.6	1.00	0.99
7/17	N86PA	Area, West tripper	8 9	15 56	40.38	3.5	467	18.9	0.14	
7/17	N86PB	Area, West tripper	8 9	15 56	40.85	3.5	467	19.1	0.13	0.13
7/03	N42P	Bin Floor Operator	7 37	15 27	50.34	53	470	23.7	1.62	
7/03	N43P	Bin Floor Operator	7 37	15 27	52.76	51.7	470	24.8	1.51	1.57

Table B1 (Continued)
Sampling Results, Phosphine
Elevator A

Date 1986	Sample Number	Job/Area	Time Start	Time Stop	Flow (cc/min)	Weight (ug)	Time (min)	Vol. (L)	Concentration (ppm) Replicate	Concentration (ppm) Mean*
7/09	N64P	Bin Floor Operator	7 59	15 28	45.34	44.4	449	20.4	1.60	
7/09	N65P	Bin Floor Operator	7 59	15 28	47.92	48.7	449	21.5	1.67	1.63
7/17	N80PA	Bin Floor Operator	7 58	15 43	44.56	14	465	20.7	0.49	
7/17	N80PB	Bin Floor Operator	7 58	15 43	42.98	13	465	20	0.48	0.48
7/03	N40P	Roving Supervisor	7 27	15 36	45.07	16	489	22	0.53	
7/03	N41P	Roving Supervisor	7 27	15 36	44.94	18	489	22	0.59	0.56
7/09	N60P	Roving Supervisor	7 48	15 47	45.64	8.2	479	21.9	0.28	
7/09	N61P	Roving Supervisor	7 48	15 47	44.16	8.6	479	21.2	0.30	0.29
7/17	N81PA	Roving Supervisor	8 39	16 0	39.04	3.5	441	17.2	0.15	
7/17	N81PB	Roving Supervisor	8 39	16 0	42.41	3.5	441	18.7	0.14	0.14

* Arithmetic mean of the two replicate samples shown on the same line, and the line immediately above the mean.

Table B-2
Sampling Results, Phosphine
Elevator B

Date 1986	Sample Number	Job/Area	Time Start	Time Stop	Flow (cc/min)	Weight (ug)	Time (min)	Vol. (L)	Concentration (ppm) Replicate	Concentration (ppm) Mean*
9/06	P3	Headhouse, transfer floor, at N. end (tripper)	1005	1544	42.5	1	339	14.4	0.05	
9/06	P17	Replicate, P3	1005	1544	42.9	2	339	14.5	0.10	0.08
9/06	P24	Scale room, scale floor	1014	1540	40.7	< 1	326	13.3	< 0.05	
9/06	P8	Replicate, P24	1014	1540	44.2	< 1	326	14.4	< 0.05	< 0.05
9/06	P1	W. annex bin floor, S. end, at #2 stand	0952	1551	42.1	< 1	359	15.1	< 0.05	
9/06	P2	Replicate, P1	0952	1551	43.7	< 1	359	15.7	< 0.05	< 0.05
9/06	P28	Bin Floorman	0821	1152	44.8	< 1	211	9.5	< 0.08	
9/06	P26	Replicate, P28	0821	1152	49.4	< 1	211	10.4	< 0.07	< 0.07
9/06	P9	Headhouse, transfer floor, S. end, at #2 stand	0959	1542	41.9	< 1	343	14.4	< 0.05	
9/06	P29	Replicate, P9	0959	1542	42.8	< 1	343	14.7	< 0.05	< 0.05
9/06	P18	Blender operator	0821	1553	42.9	< 1	419	18	< 0.04	
9/06	P10	Replicate, P18	0821	1553	43.2	< 1	419	18.1	< 0.04	< 0.04
9/06	P6	Chief Weighmaster	0848	1539	38.9	< 1	377	14.7	< 0.05	
9/06	P5	Replicate, P6	0848	1539	42	< 1	377	15.8	< 0.05	< 0.05
9/06	P4	Bin Floorman	0855	1547	42.3	< 1	374	15.8	< 0.05	
9/06	P23	Replicate, P4	0855	1547	43.3	< 1	374	16.2	< 0.04	< 0.05
9/06	P15	Headhouse, @ base of leg, access door	0943	1600	45.5	< 1	377	17.2	< 0.04	
9/06	P25	Replicate, P15	0943	1600	44.7	< 1	377	16.9	< 0.04	< 0.04
9/06	P21	Vapor spike, 2.98 ug	--	--	-	2		Recovery:	0.67	
9/06	P14	Vapor spike, 3.97 ug	--	--	-	4		Recovery:	1.01	0.84

*Arithmetic mean of the two replicate samples shown on the same line, and the line immediately above the mean.

Table B-3
Elevator C
Personal Air Sampling Results for Phosphine.
November, 1985.

JOB TITLE	LOCATION: FLOOR	DESCRIPTION	DATE	TIME OF SAMPLE COLLECTION	FIELD SAMPLE NUMBER	SAMPLE VOLUME, L	CONCENTRATION, PPM
Weighmaster	Scale	---	11/14	Full Shift	BKC-01	19.7	≥ 0.2*
					BKC-06	19.6	< 0.02**
			11/15	Full Shift	BKC-45	20.8	< 0.02
				8:25a-3:05p	BKC-28	16.8	< 0.03
Spouter #1	Distributor, Galleries	Loads dispenser	11/14	Full Shift	BKC-09	18.3	1.4
					BKC-12	19.6	0.93
				2:15p	BKI-06	INST[1]	12
			11/15	Full Shift	BKC-41	19.6	0.45
				8:14a-2:50p	BKC-46	16.5	0.61
Spouter #2	Distributor, Galleries	---	11/14	Full Shift	BKC-17	18.4	(0.07)+
					BKC-23	18.1	<0.03
			11/15	Full Shift	BKC-40	18.8++	0.3++
				8:19a-2:48p	BKC-37	14.0++	0.3++

* More than 30% of analyte on backup section of sample tube. Therefore, either breakthrough or migration assumed to have occurred; true concentration thus equals or exceeds reported value.

** The "less than" symbol (<) indicates a result below the limit of detection (value listed is detection limit for the sample).

1 "Instantaneous" sample (collection in sample bag); volume not measured (not relevant).

\+ Sample results in parentheses are between the limits of detection and quantitation, and are considered to have less-than-normal precision.

++ Value could be affected by unusually high variation in pump flow rate.

Table B4
Elevator C
Area Air Sampling Results for Phosphine.
November 1985

Location: House	Floor	Belt	Description	Operation: Bin Filling & Time	Date	Time Of Sample Collection	Field Sample Number	Sample Volume L	Concentration PPM
Gallery, No Fumigation Occurring in House									
Middle	Gallery	-	Center	---	11/14	---*	BKC-10	---*	---*
Treated Grain Entering "Nearby" Bin									
Old	Gallery	-	Bin 93(20'E of 133)	133/8:30a-12:00p	11/14	Full Shift	BKC-11	20.3	0.02**
							BKC-19	17.5	0.1
Along Belt, Not Near Dispenser or Bin									
Head	Gallery	N	Belt to bin 133	133/8:30a-12:00p	11/14	Full Shift	BKC-22	18.4	(0.07)***
						10:43a	BKI-03	INST[1]	0.11+
		S	Belt to bin 51	51/12:30p-3:20p	11/14	2:31p	BKI-08	INST	0.16+
Middle	Gallery	S	Belt to bin 391	391/9:00a-2:10p	11/15	Full shift	BKC-24	19.1	(0.04)
Head	Below Distr.	S	Belt to bin 391	391/9:00a-2:10p	11/15	11:08a	BKI-15	INST	****
Scale Floor, Work Floor									
Head	Scale	-	Center	---	11/14	Full shift	BKC-07	20.9	0.02
					11/15	Full shift	BKC-21	17.8	0.03
Head	Work	-	Center	---	11/14	Full shift	BKC-15	18.6	0.03
						10:34a	BKI-01	INST	0.097+
						2:54p	BKI-11	INST	0.097+
			N. Wall, center	---	11/15	Full shift	BKC-26	19.1	0.02
At Tripper/Bin									
Old	Gallery	N	Tripper at bin 133	133/8:30a-12:00p	11/14	Full shift	BKC-14	21.4	0.02
						9:30a-12:30p	BKC-04	8.63	0.05
						10:48a	BKI-04	INST	0.097+
		S	Tripper at bin 51	51/12:30p-3:20p	11/14	12:52p-4:10p	BKC-05	9.19	(0.07)
						2:35p	BKI-09	INST	0.13+
New	Gallery	S	Bin 391	391/9:00a-2:10p	11/15	Full shift	BKC-36	19.2	(0.02)
							BKC-30	18.4	0.03
						10:59a	BKI-14	INST	****
		N	Bin 115	115/8:15a-10:00a	11/15	10:04a-4:32p	BKC-33	20.5	0.2

Table B4 (continued)
Elevator C
Area Air Sampling Results for Phosphine.
November 1985

Location: House	Location: Floor	Location: Belt	Location: Description	Operation: Bin Filling & Time	Date	Time Of Sample Collection	Field Sample Number	Sample Volume L	Concentration PPM
At Dispenser									
Head	Distributor	N	Dispenser	133/8:30a-12:00p	11/14	9:40a-12:58p	BKC-16	11.6	0.2
						Full Shift	BKC-08	19.4	0.1
						10:40a	BKI-02	INST	0.081[+]
		S	Dispenser	51/12:30p-3:20p	11/14	Full Shift	BKC-13	20.5	(0.03)
						1:01p-4:04p	BKC-02	10.7	|(0.2)[++]
			Dispenser, close to spout	51/12:30p-3:20p	11/14	2:19p	BKI-07	INST	0.11[+]
		N	Dispenser, near	115/8:15a-10:00a	11/15	9:42a-10:35a	BKC-38	2.63	0.2
						Full Shift	BKC-35	23.0	(0.06)
		S	Dispenser, near	391/9:00a-2:10p	11/15	9:44a-2:41p	BKC-43	14.4	(0.05)
						Full Shift	BKC-39	21.8	|(0.06)[++]
Background									
---	---	–	Bridge over RR trks.	---	11/15	11:17a	BKT-1[+++]	INST	****
						11:22a	BKI-16	INST	****
			Outside office bldg.	---	11/15	10:05a	---	INST	0.081
						10:40a	---	INST	0.097
						12:30p	---	INST	0.11
			Inside office bldg.	---	11/15	10:00a	---	INST	0.21
						10:10a	---	INST	0.27
						10:45a	---	INST	0.21

* Pump failure

** The "less than" symbol ( ) indicates a result below the limit of detection (value listed is detection limit for the sample).

*** Sample results in parentheses are between the limits of detection and quantitation, and are considered to have less-than-normal precision.

**** Sample contamination due to phosphine carryover in the sampling train.

1 "Instantaneous" sample (collection in sample bag); volume not measured (not relevant).

\+ Indistinguishable from apparent background and/or interference.

++ More than 30% of analyte on backup section of sample tube. Therefore, either breakthrough or migration assumed to have occurred; true concentration thus equals or exceeds reported value.

+++ Sample collected in Tedlar[2] bag.

Table B5
Elevator C
Source Air Sampling Results for Phosphine
November 1985

Location: House	Floor	Belt	Description	Operation: Bin Filling & Time	Date	Time Of Sample Collection	Feild Sample Number	Sample Volume, L	Concentration, PPM
Old	Gallery	N	Tripper at bin 133, near bin opening	133/8:30a-12:00p	11/14	10:05a-12:34p	BKC-20	7.51	(0.2)*
			Inside bin 133			10:51a	BKI-05	INST[1]	1.3
		S	Tripper at bin 51, at bin opening	51/12:30p-3:20p	11/14	12:50p-2:16p	BKC-03	4.34	0.5
			Vent outlet, bin 51			2:40p	BKI-10	INST	0.54
New	Gallery	S	Tripper at bin 391, at bin opening	391/9:00a-2:10p	11/15	Full shift	BKC-31	17.4	0.03**
			Inside bin 391			10:54a	BKI-13	INST	***
Head	Distributor	-	Inside empty pellet can	---	11/15	10:38a	BKI-12	INST	110
		N	Inside just emptied tablet dispenser	---	11/15	2:52p	BKI-17	INST	3000

* Sample results in parentheses are between the limits of detection and quantitation, and are considered to have less-than-normal precision.

** The "less than" symbol ( ) indicates a result below the limit of detection (value listed is detection limit for the sample).

*** Sample contamination due to phosphine carryover in the sampling train.

1 "Instantaneous" sample (collection in sample bag); volume not measured (not relevant).

Table B6
Phosphine Concentrations (Personal and Area)
Elevator D
November 1986

Date-Shift 11/86	Sample Number	Job/Area	Time Start	Stop	Flow (cc/min)	Weight (ug)	Time (min)	Volume (L)	Concentration (ppm)
11-2nd	SCP-44	At dispenser, A-house, bin deck	21 44	2 14	48.8	2	270	13.2	0.10
10-2nd	SCP-08	At dispenser, B-house, bin deck	20 47	2 11	49.2	2	324	15.9	0.08
11-2nd	SCP-43	At dispenser, B-house, bin deck	21 44	2 11	48.2	4	267	12.9	0.21
12-2nd	SCP-71	At dispenser, B-house, bin deck	20 9	2 2	51.3	4	353	18.1	0.14
12-2nd	SCP-67	At dispenser, C-house, bin deck	20 28	2 12	46.8	3	344	16.1	0.12
12-1st	SCP-53	Bin deck, center, A-house	14 0	22 0	45.9	2	480	22.0	0.06
12-1st	SCP-63	Bin deck, center, A-house	14 0	22 0	45.2	0.3	480	21.7	0.01
10-2nd	SCP-11	Basement Mix Man	20 21	2 6	45.8	0.7	345	15.8	0.03
10-2nd	SCP-09	Replicate, SCP-11	20 21	2 6	45.1	1	345	15.6	0.04
11-2nd	SCP-50	Basement Mix Man	20 42	2 32	47.3	0.7	350	16.6	0.03
11-2nd	SCP-48	Replicate, SCP-50	20 42	2 32	47.0	1	350	16.5	0.04
12-2nd	SCP-66	Basement Mix Man	19 47	2 19	45.5	0.4	392	17.8	0.01
12-2nd	SCP-65	Replicate, SCP-66	19 47	2 19	45.2	2	392	17.7	0.07
12-1st	SCP-55	Bin deck area, B-house	9 23	18 30	48.6	6	547	26.6	0.15
12-1st	SCP-59	Bin deck area, B-house	9 25	17 25	48.5	7	480	23.3	0.20
10-2nd	SCP-01	B-house, tunnel #4	21 7	2 6	48.2	2	299	14.4	0.09
10-2nd	SCP-03	B-house, tunnel #4	21 24	2 6	48.8	2	282	13.8	0.10
11-1st	SCP-23	B-house, tunnel #4	8 55	17 40	57.4	2	525	30.1	0.04
11-1st	SCP-26	B-house, tunnel #4	13 45	18 0	45.2	0.3	255	11.5	0.02
11-1st	SCP-17	B-house, tunnel #4	14 50	17 40	45.6	2	170	7.8	0.17
11-1st	SCP-22	B-house, tunnel #4	14 50	17 40	46.8	2	170	8.0	0.17
11-1st	SCP-25	B-house, tunnel #4	13 45	18 0	45.9	2	255	11.7	0.12
12-1st	SCP-52	B-house, tunnel #4	9 0	17 0	44.8	1	480	21.5	0.03
12-1st	SCP-47	B-house, tunnel #4	8 53	16 53	47.4	0.7	480	22.8	0.02
10-2nd	SCP-05	Galley man	20 24	2 12	45.2	4	348	15.7	0.17
10-2nd	SCP-07	Replicate, SCP-05	20 24	2 12	45.5	3	348	15.8	0.13
11-1st	SCP-19	Galley man	9 30	15 30	43.3	2	360	15.6	0.09
11-1st	SCP-14	Replicate, SCP-19	9 30	15 30	41.7	2	360	15.0	0.09
11-2nd	SCP-45	Galley man	20 32	2 5	45.8	5	333	15.3	0.22
11-2nd	SCP-40	Replicate, SCP-45	20 32	2 5	45.1	5	333	15.0	0.22
12-2nd	SCP-57	Galley man	19 54	2 12	45.6	10	378	17.2	0.37
12-2nd	SCP-18	Replicate, SCP-57	19 54	2 12	46.8	6	378	17.7	0.22
10-2nd	SCP-06	Near receiving bin, B-house, bin deck	20 37	2 15	46.1	2	338	15.6	0.08

Table B6 (Continued)
Phosphine Concentrations (Personal and Area)
Elevator D
November 1986

Date-Shift 11/86	Sample Number	Job/Area	Time Start	Time Stop	Flow (cc/min)	Weight (ug)	Time (min)	Volume (L)	Concentration (ppm)
11-1st	SCP-21	Near receiving bin, B-house, bin deck	9 17	16 25	48.5	3	428	20.8	0.10
11-2nd	SCP-42	Near receiving bin, B-house, bin deck	20 25	2 5	50.2	7	340	17.1	0.27
10-2nd	SCP-12	Night Foreman (scale room)	20 21	2 11	47.3	2	350	16.6	0.08
10-2nd	SCP-10	Replicate, SCP-12	20 21	2 11	47.0	0.3	350	16.5	0.01
11-2nd	SCP-46	Night Foreman (scale room)	20 11	2 5	45.2	0.7	354	16.0	0.03
11-2nd	SCP-51	Replicate, SCP-46	20 11	2 5	45.5	1	354	16.1	0.04
12-2nd	SCP-56	Night Foreman (scale room)	19 47	2 1	45.1	2	374	16.9	0.08
11-2nd	SCP-49	On tripper, A-house, bin deck	20 36	2 17	49.2	2	341	16.8	0.08
10-2nd	SCP-04	On tripper, B-house, bin deck	20 38	2 14	47.4	2	336	15.9	0.08
11-2nd	SCP-15	On tripper, B-house, bin deck	20 27	2 7	46.1	6	340	15.7	0.25
12-2nd	SCP-61	On tripper, B-house, bin deck	20 1	2 7	48.8	5	366	17.9	0.18
12-2nd	SCP-58	On tripper, C-house, bin deck	20 32	22 50	46.1	1	138	6.4	0.10
11-1st	SCP-20	Scale Floor, office	9 40	16 17	48.6	2	397	19.3	0.07
12-1st	SCP-54	Scale Floor, office	9 15	17 15	48.2	4	480	23.1	0.12
12-1st	SCP-60	Scale Floor, office	13 50	18 20	50.2	2	270	13.6	0.10
10-2nd	SCP-02	Scale Floor - at scale controls	21 2	2 11	50.2	2	309	15.5	0.09
11-1st	SCP-24	Scale Floor - at scale controls	9 12	16 20	44.8	2	428	19.2	0.07
11-2nd	SCP-41	Scale Floor - at scale controls	20 10	2 6	47.4	2	356	16.9	0.08
12-2nd	SCP-70	Scale floor - at scale controls	20 16	2 0	57.4	3	344	19.7	0.10

Table B7
Results of Personal, Area, and Source Air Samples
For Phosphine by Portable Gas Chromatography
Elevator D
November 1986

No.	Location/Description*	Date/Time of Collection Nov., 1986	Conc. (ppm)
	Personal Breathing Zone Samples		
T	Galley Man, Filling Dispenser, (1st of 2 cans added)	10th/20:36	0.20
Q	Galley Man, Filling Dispenser, (2nd of 2 cans added)	10th/20:37	0.10
G	Galley Man, Filling Dispenser, B-house	11th/21:30	10
D	Galley Man, Filling Dispenser, A-house	11th/22:02	52
C	Galley Man, Filling Dispenser, B-house	12th/19:56	25
S	Galley Man, Filling Dispenser, C-house	12th/20:47	1.5
M	Galley Man, Emptying Dispenser, B-house	11th/1:44	4.5
F	Galley Man, Emptying Dispenser, B-house (5 min.)	12th/00:05	9.0
V	Galley Man, Emptying Dispenser, A-house	12th/00:54	30
R	Galley Man, Emptying Dispenser, C-house	12th/22:50	0.90
T	Galley Man, Continuation of Sample R, above	12th/22:52	0.30
H	Galley Man, Emptying Dispenser, B-house	13th/00:30	0.90
	Area/Source Samples		
N	Inside dispenser's holding vessel (source sample, 20 min. after refill, start of second run)	10th/11:43	1000
	At Dispenser*:		
R	B-house, at start of fumigation	10th/20:49	0.06
P	B-house, 20 min. after refill	10th/23:38	0.44
U	B-house, holding vessel 1/3 full	11th/00:34	0.33
C	B-house, near end fumig. (1/5 full)	11th/1:32	0.20
H	B-house, at start fumigation	11th/21:32	0.18
F	A-house, at start of fumigation	11th/22:10	0.12
S	A-house, holding vessel 1/2 full	11th/23:44	0.06
U	B-house, holding vessel 1/2 full	12th/23:38	0.44

Table B7 (continued)
Results of Personal, Area, and Source Air Samples
For Phosphine by Portable Gas Chromatography
Elevator D
November 1986

No.	Location/Description*	Date/Time of Collection Nov., 1986	Conc. (ppm)
	At Tripper Discharge:		
V	B-house, at bin #557 opening, start of 1st fumig.	10th/20:42	0.06
O	B-house, at bin #562 opening, 1 hr. after start of fumigation	11th/00:40	2.7
R	A-house, at bin # 611 opening, 2 hr. after start of fumigation	11th/23:55	0.3
K	B-house, at bin #662 opening, 1.5 hr. after start of fumigation	12th/23:30	4.2
	Inside bins, First shift Source Samples:		
I	B-house, inside bin opening, bin #557 (fumigated night before)	11th/14:12	50
Q	B-house, inside bin opening, bin #557, fumigated 11/10/87, second shift	12th/10:40	100
K	B-house, inside bin opening, bin #256, labeled as fumigated 8/19. Adjacent to bin #358;	11th/15:40	2.3
L	B-house, inside bin opening, bin #358, odor detected but no label warning of fumigation.	11th/12:04	77
E	B-house, same location as L, above	11th/14:01	47
	Miscellaneous:		
V	Tunnel, No. 2 line, No grain running, odor detected	12th/16:00	0.35
S	B-house, far end of bin deck, away from fumigation	10th/20:53	0.06
P	A-house, at end of fumigation, near end of discharge tubing on dispenser, a few minutes after the vessel was emptied.	13th/1:03	25
T	A-house, bin deck, inside fumigant storage shed, where phosphide (sealed) canisters are stored.	12th/8:50	0.06

Table B7 (continued)
Results of Personal, Area, and Source Air Samples
For Phosphine by Portable Gas Chromatography
Elevator D
November 1986

No.	Location/Description*	Date/Time of Collection Nov., 1986	Conc. (ppm)
	Background samples:		
P	At entrance of elevator, about 1 foot above ground, upwind of elevator	12th/10:05	0.06
R	Downwind of elevator, approximately 20 yards past office building.	12th/10:15	0.06

* Samples were collected in 2-10L Tedlar(tm) bags over sampling periods of 2 to 5 minutes. Bag samples were then analyzed on site using a Photovac (tm) Model No. 10A10 portable gas chromatograph incorporating a photoionization detector.