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The Industrywide Studies Branch, DSHEFS, of the National Institute for Occupational Safety and Health (NIOSH) conducted a series of four industrial hygiene surveys in 1985 and 1986 to assess worker exposures to phosphine during the treatment of grain with aluminum phosphide fumigant products. Full-shift breathing zone sampling to measure workers' exposures to phosphine and area monitoring were conducted. In addition, short-term measurements were made to evaluate very brief (2–5 min) peak exposures during specific job tasks and peak concentrations from suspected sources of high concentrations. Results indicate that the use of aluminum phosphide can result in demonstrable, and frequently excessive, exposures when compared to relevant occupational evaluation criteria, even under very cold air temperatures ranging as low as −8°C (18°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 Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) (both 0.3 ppm). Short-term personal exposures during filling and emptying an automatic phosphide tablet dispenser averaged 2.5 ppm and ranged from 0.1–52 ppm over sampling periods ranging from 2–5 minutes. Many of these greatly exceeded the recommended ACGIH short-term exposure limit of 1 ppm. Examination of the sampling data suggested that the exposures to phosphine were partially a result of uncontrolled point sources and lack of appropriate local exhaust ventilation and depended on the general level of fumigation activity. General recommendations for reducing exposures through improved local exhaust ventilation, work practices, and respiratory protection are made. Zaebst, D.D.; Blade, L.M.; Burroughs, G.E.; Morelli-Schroth, P.; Woodfin, W.J.: Phosphine Exposures in Grain Elevators during Fumigation with Aluminum Phosphide. Appl. Ind. Hyg. 3:146–154; 1988.

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, the modes of pesticide use generally can be described as protectant, fumigant, or space treatment. The fumigants (used to treat grain with existing infestations and which kill insects primarily through their respiratory organs) are perhaps the most important insecticides used in the grain industry, primarily because of their volume of use and their economic impact in reducing grain loss or damage. From an occupational exposure standpoint, they present a significant worker inhalation hazard since in order to work, fumigants must produce a high airborne concentration of gas or vapor over a time period sufficient to eliminate infestation in the grain.

As a result of changing regulations, the pattern of fumigant use in the United States in the last few years has changed drastically. A 1980 report indicated that the market share for the three most regularly used fumigants were 45 percent liquid mixtures (e.g., 80% carbon tetrachloride/20% carbon disulfide mixtures, known as 80/20), 50 percent aluminum phosphide, and 5 percent methyl bromide.[2]

Since June 1986, liquid-mixture fumigants containing carbon tetrachloride or carbon disulfide may no longer be used.[3] Since there are currently few other suitable substitutes, the market share for phosphide products for fumigant purposes in the grain industry is much higher, essentially supplanting the use of the liquid formulations.

Phosphide products are classified by the U.S. Environmental Protection Agency (EPA) as restricted-use pesticides.[4] Thus, they may only be used by trained and certified applicators under controlled conditions. However, due partly to lack of recent empirical exposure data and due to the assumption that the release of phosphine (the actual fumigant evolved when phosphide products are used) is delayed for several hours after initial exposure of the phosphide tablets or pellets to air, 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 "if the label instructions are followed, applicators should not be exposed to measurable levels . . .".[4] Strictly speaking, this is partly true since the standard requires, and the labelling recommends, exposure monitoring to verify acceptable concentrations prior to re-entry to a fumigated area. However, empirical data were available which indicated measureable and excessive exposures could occur under actual use conditions.[4,5]

This paper presents the results of four industrial hygiene surveys conducted in 1985 and 1986 to evaluate elevator employees' exposures to phosphine during the active application of aluminum phosphide in grain elevators. 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, identification of pesticide residues in consumer products, and changing technology. The objective of these studies was to provide exposure characterizations where currently predominant types of pesticides were being used and to provide a data base for use in any future health studies of this workforce.

Chemistry, Toxicity, and Exposure Criteria

Phosphide pellets (spherically shaped) or tablets (disk shaped), which are composed of aluminum phosphide, urea, and ammonium carbamate, decompose in the presence of moisture (in the air or in the grain) to yield phosphine gas, ammonia, and carbon dioxide.[9,10] The aluminum phosphide reacts with water to yield phosphine as follows:

$$2AlP + 6H_2O \rightarrow 2Al(OH)_3 + 2PH_3$$

Phosphide products have been reported to begin decomposing one to four hours after the original container is opened.[9,10] 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.[10] 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.

Phosphine is an acutely toxic gas by inhalation.[11,12] An Australian report in 1964 found 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 symptoms were exhibited by phosphine-exposed workers, ranging from chest tightness to vomiting, diarrhea, and central nervous system effects.[5] In another article, 59 cases of acute phosphine poisoning, including 26 deaths, were reported between 1900 and 1958. One death, in a worker operating an acetylene generator, apparently occurred from pulmonary edema after one- to two-hour per day exposures of 1–14 ppm over a period of one month.[13]

The U.S. EPA's Pesticide Incident Monitoring System (1981) reported 29 incidents of human exposure from 1966 to 1981 affecting 80–90 people; of those involved, 71 received medical treatment, 33 were hospitalized, and 2 died.[4] 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.

The effects of chronic, low-level exposure to phosphine in humans has not been clearly defined. These effects have been stated to include anemia, bronchitis, gastrointestinal disturbances, and nervous disorders including visual, speech, and motor disturbances.[14] Other authorities state that chronic phosphine poisoning is similar to that of phosphorous, including embrittlement of bones and teeth.[12,15] The evidence for these effects is not well documented, being limited to sparse case reports. A possible case of chronic phosphine toxicity was reported in Germany in which three years of exposure to phosphine, in a facility producing acetylene from calcium carbide, produced chronic bronchitis, anemia, and digestive disorders in one worker. In this article, it was reported that the anemia may have been related to a latent gastric hemorrhage.[16]

The acute and subchronic toxicity of phosphine in animals has been previously described.[4,17-20] Four-hour LC_{50} values on the order of 10–11 ppm have been determined.[17-18]

The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV)[21] and the OSHA Permissible Exposure Limit (PEL)[22] for full-shift (8-hour) exposures to phosphine are 0.3 ppm. The ACGIH has also established a short-term exposure limit (STEL) of 1 ppm for exposures time weighted over any 15-minute period, encompassing no more than four such exposures per day. NIOSH has not recommended an exposure limit.[11]

Previous reports are contradictory regarding the odor threshold and warning properties of phosphine. The odor threshold of phosphine has been reported to be 0.02 ppm, well below the TLV of 0.3 ppm, suggesting that phosphine has adequate warning properties.[23] However, another authority[15] states that "phosphine has a characteristic decayed fish odor barely perceptible at concentrations of 1.5 to 3 ppm", thus giving no warning of its threshold concentration. A third report 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.[24] The odor threshold of phosphine purified with a molecular sieve has been reported to be on the order of 1–2 ppm, while that of phosphine generated from a technical grade of aluminum phosphide ranged from 0.1 to 0.2 ppm, and from Phostoxin™ (a commercial product containing a mixture of aluminum phosphide and ammonium carbamate) 0.01–0.02 ppm. In this article, it was stated that the origin of the garlic-like odor was unknown.[25] Finally, experiments have been conducted which indicate that olfactory fatigue may result in unreliable detection of phosphine by odor.[26]

Methods

Long-term (full-shift) exposures to airborne phosphine, both personal and area, were evaluated using battery-operated portable sampling pumps calibrated to draw air at a flowrate of 50 cc/min through glass tubes containing silica gel impregnated with mercuric cyanide, as specified by NIOSH method S-332.[27] Frequently, dual-tube manifolds were used to allow 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 TWA exposure criteria and to evaluate many area concentrations in terms of sources of exposure. Short-term samples of a few minutes duration were also collected in inert gas sampling bags as necessary to evaluate peak exposures during certain cycles of activity and to evaluate specific sources of potential exposure.

TABLE I. Grain Fumigation Study Elevator Characteristics

Inland Elevator	Capacity (MM bu)[A]	Year(s) of Construction	No. of Workers	Date of Evaluation	Ventilation Characteristics	
					Local[B]	General[C]
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

[A]Million bushels.
[B]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.
[C]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.

Short-term samples were obtained by collecting air in inert (Tedlar®) gas sampling bags. The samples of air were then analyzed 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® portable gas chromatograph incorporating an 11-eV source and photoionization detector. Separation was accomplished with a 6′ × 1/8″ teflon column containing 3 percent SE30 on 80/100 mesh supelcoport. All samples were analyzed two or more times for increased accuracy. The sensitivity obtained varied somewhat during the surveys but was on the order of 0.06 ppm. The general principle for direct analysis of air samples by portable gas chromatography is outlined in the NIOSH *Manual of Analytical Methods*.[25]

Ventilation characteristics at each facility (Table I) 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 velocities 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 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 in application techniques were described depending on factors such as the type and age of the grain storage structures, the fumigation procedures as described in this report appear to be representative of techniques used throughout the industry.

The following descriptions assume some familiarity with the grain industry and its unique terminology. The grain industry, grain elevators, and general fumigation procedures have been described elsewhere.[1,28]

The surveys were conducted at four midwestern elevators of varying sizes and characteristics (Table I). All four of the elevators surveyed used similar procedures to treat the grain. This technique consisted of mixing the aluminum phosphide pellets or tablets with the grain as it was moved within the elevator ("turned"), or as the grain was received at the elevator. At three of the elevators (A, C, and D), the tablets or pellets were dispensed one at a time (at a rate of approximately 6–7 per minute) into the grain stream as the grain was conveyed past the point of addition on an open belt, or as it fell directly into a bin opening from an electrically-operated automatic dispenser. The dispenser (Figure 1a) is a portable device on wheels which can be positioned at an advantageous point, typically on the bin deck upstream of the tripper car.

A variation of this procedure was used at elevator B. At this

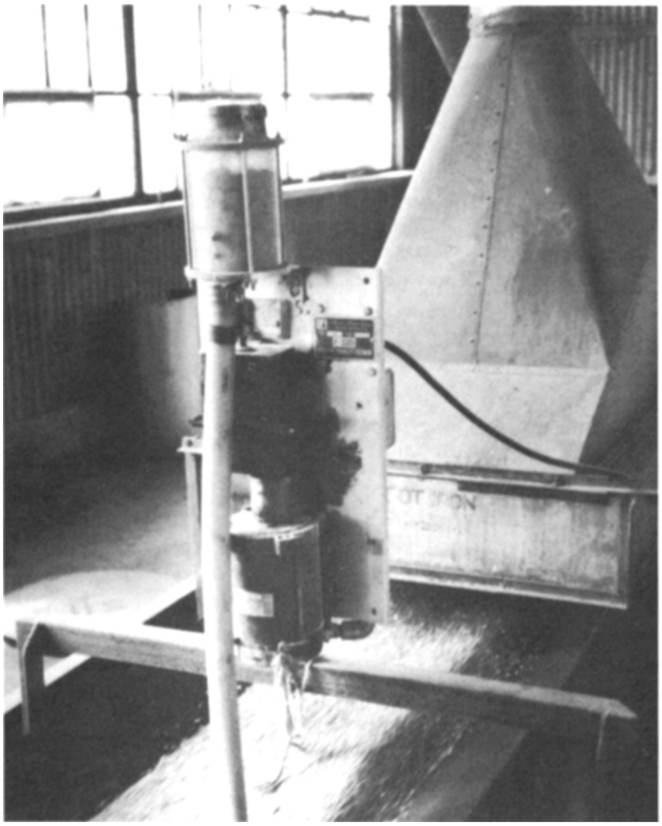

FIGURE 1a. Automatic aluminum phosphide tablet dispenser, permanently mounted above open-belt conveyor on bin deck.

FIGURE 1b. Manual addition of aluminum phosphide tablets through grain-leg access door in basement.

facility, no automatic dispenser was used. Instead, the "blender," who worked mainly in the tunnel (under the grain storage bins) and boot areas, manually poured the tablets from the original container into a grain-leg housing through an access door in the basement near the boot (Figure 1b). At this point, the tablets were mixed with the grain stream being carried within the leg and subsequently routed with the grain to the bin deck.

At all of the elevators, the treated grain containing the tablets or pellets was then directed to a storage bin. During storage, the tablets/pellets decomposed in the presence of the moisture in the grain, releasing large quantities of phosphine into the confined space in the bin (approximately 20–60 grams per 1000 cubic feet at normal treatment rates).

Table II summarizes information gathered regarding environmental conditions (air temperatures and relative humidity) and the type and quantity of the grain treated (when available) during each survey. One would expect that most of these factors would potentially influence the exposure of workers to phosphine since the rate of generation of phosphine from aluminum phosphide is dependent on temperature and moisture.[10] However, many other factors, such as work practices used and quality of general dilution and local exhaust ventilation at critical points (Table I), would also undoubtedly influence exposures.

Results

Figures 2–6 present the geometric means of full-shift (or near full-shift) samples obtained using the silica gel tubes. These samples were obtained either as personal breathing zone samples or as area samples. The concentrations reported in Table III are the results of short-term samples obtained using the inert gas-sampling bags and on-site chromatographic analyses. Such short-term samples were obtained either in the breathing zone of an employee as he conducted a brief task or were obtained at or near supposed sources of phosphine contamination. The first column of Table III indicates the type of short-term sample.

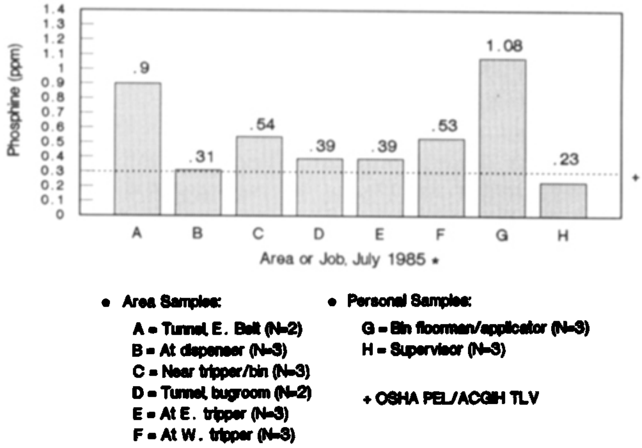

FIGURE 2. Geometric mean PH_3 exposures and area concentrations, elevator A.

Figures 2, 3, and 4 summarize the area and personal phosphine sampling results from elevators A, C, and D, respectively. No corresponding graph is shown for elevator B because all integrated sample results obtained in comparable areas and jobs at this elevator were near or below the analytical limit of detection (< 0.01 ppm) for phosphine. The geometric mean of all full-shift samples obtained in several specific areas within each elevator and the geometric means for personal samples in those jobs sampled are presented. In addition, Figure 5 presents selected grouped data from all four elevators.

In order to facilitate discussion of results between elevators, similar jobs or areas have been grouped (e.g., bin floorman/

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

Elevator	Date of Survey	Air Temp. Range C° (F°)	Relative Humidity (%)	Grain Type & Quantity (1000 bu)[A]	Grain Temp. C° (F°)	Grain Moisture (%)
A	7/85	28–35 (82–95)	40–60	Wheat (25–49)	NA[B]	NA
B	9/85	28	72	Wheat (40)	NA	NA
C	11/85	6–9 (43–46)	74–86	Wheat (22–43)	24–29 (75–85)	11–13
D	11/86	−8–+1 (18–34)	—	Wheat (40–53)	17–22 (62–71)	11–12

[A]Quantity of grain treated per shift in thousands of bushels.
[B]Information unavailable during survey.

TABLE III. Summary of Analyses for Phosphine by Portable Gas Chromatography; Elevators B, C, and D

Sample Description						
Sample Type	Location	Description*	N	Min. (ppm)	Max. (ppm)	Geo. 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	3000	—	—
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 empty pellet dispenser	1	1000	—	—
Ambient	Outside elevator	Background samples, away from fumigation activity	2	<0.06	<0.06	—

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

applicator or "at dispenser"). The bin floorman/applicator worked mainly on the bin deck or the distributor level of the headhouse. This person was responsible for applying the fumigant and tending the automatic dispensers, trippers, and associated apparatus at elevators A, C, and D. At elevator B, however, the "blender," working mainly in the tunnel and boot areas, conducted the fumigation procedure although his general duties were analogous to the basement mix man at elevator D.

Personal Sampling Results

Figures 2–4 indicate, not surprisingly, that the applicators' (i.e., bin floormen's) exposures to phosphine at elevators A, C, and D were far above any other workers' exposures. In addition, individual full-shift samples were frequently in excess of the OSHA PEL and ACGIH TLV of 0.3 ppm. An exception to this pattern was found at elevator B where the blender (applicator) conducted the fumigation of the grain. As indicated in Figure 5, the blender's exposure was below the limit of detection (< 0.05 ppm).

Area Sampling Results

At elevators A and D (Figures 2 and 4, respectively), high concentrations of phosphine, relative to other areas, were found near the receiving bins and at the trippers, indicating that phosphine-contaminated air was being flushed (from the head space of the bin receiving treated grain) back into the bin deck's work space as the bins filled with treated grain over a period of several hours. In contrast, relatively low concentrations were found at comparable locations in elevator C. This was very likely due to factors at elevator C such as the local exhaust present at the tripper chutes and to a good seal between the bottom of the tripper discharge chute and the floor surrounding the bin opening. In contrast, the tripper chutes at elevators A and D were not equipped with mechanical local exhaust ventilation. General dilution ventilation at elevator C was also more efficient than at elevators A or D.

The results obtained by full-shift area measurements near the dispenser (Figures 2–4) also suggest (although not conclusively) that the dispenser was a potential source of exposure. Based on preliminary results obtained during the first survey at elevator A, 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. It was also hypothesized that 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 indicated that exposures to applicators may occur as soon as the original phosphide flasks are opened. Based on the nature of the chemical reaction, it was previously assumed that aluminum phosphide tablets or pellets would begin reacting slowly and that significant generation of phosphine would not

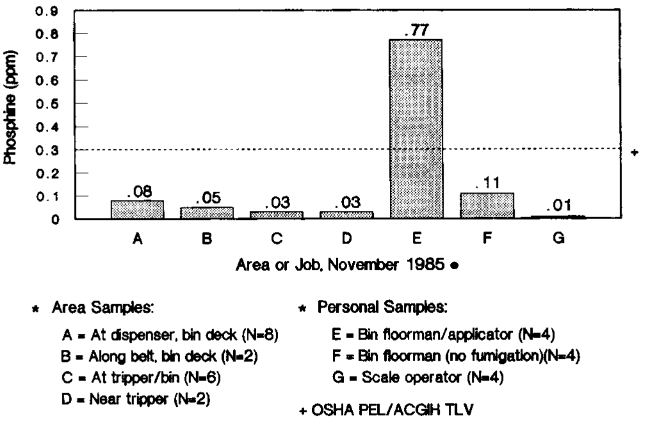

FIGURE 3. Geometric mean PH_3 exposures and area concentrations, elevator C.

occur for several hours.[4,10] These hypotheses were more fully investigated at elevators B, C, and D 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, helped to clarify and confirm some of the hypothesized sources of exposure during and subsequent to the fumigation process.

Short-term Sample Results

Short-term samples were obtained at elevators B, C, and D, and analyzed on site by portable gas chromatography (Table III). As listed in Table III, several locations or processes were identified as potential sources of worker exposure. These included the processes of filling and emptying the dispenser's holding vessel (usually done by the same operator four to six times during a typical fumigation run), the point at which phosphine-contaminated air escapes from a bin being filled with treated grain, and the dispenser's holding vessel containing aluminum phosphide tablets or pellets.

During one 2-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. During similar operations (i.e., dispenser filling and emptying) at elevator D, exposures ranged from 0.1 ppm to 52 ppm and averaged approximately 2.5 ppm (geometric mean) during each 2- to 3-minute time period. Some of the higher exposures were recorded at the start of a fumigation run, indicating that the exposures were due not only to phosphine escaping from the dispenser's holding vessel, but also to phosphine released (under pressure) when the original flask was opened, or (less likely) that the phosphide began to react immediately when exposed to the air. This conclusion was corroborated by the concentration of phosphine (110 ppm) found inside a just-emptied phosphide flask.

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. Although this person conducted the procedure six times during the shift, the cumulative effect of these short exposures at elevator B were not reflected in the single, full-shift sample obtained from the breathing zone of this employee (< 0.05 ppm). The blender's low full-shift exposure may have been 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.

In general, an exposure during such a short procedure would exceed the ACGIH STEL (1 ppm) if the concentration exceeded 5 ppm over three minutes or more. Overall, 6 of 13 such short-term measurements, all obtained during filling and/or emptying the dispenser at elevators C and D, exceeded this concentration.

Short-term 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 backflushed from the bin's head space (as the bin filled with grain) 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 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.

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), 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 (integrated) in the bin deck areas on the shifts following fumigation averaged 0.05 ppm (Figure 4), and the bin floorman's exposure on this shift (when no fumigation was being conducted) was 0.09 ppm (Figure 4, bar J).

Finally, two short-term samples obtained inside the pellet dispensers' holding vessels, obtained either during or immediately following the fumigation process, 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 5 presents the results of phosphine monitoring at all four sites for selected areas and jobs which were considered to be generally comparable based on process and activities. In general,

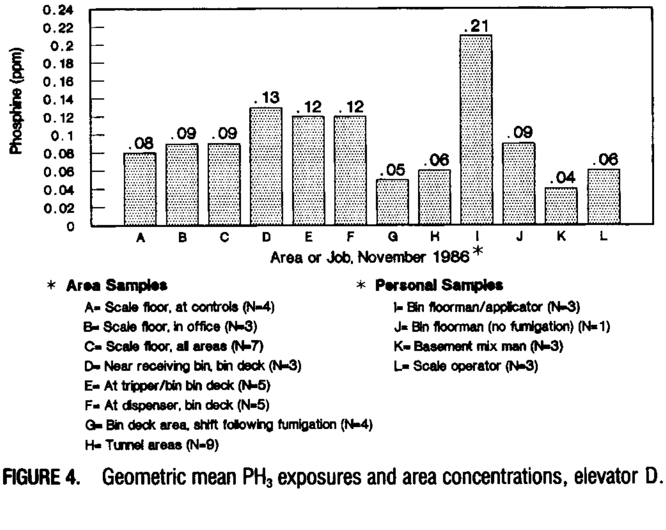

FIGURE 4. Geometric mean PH_3 exposures and area concentrations, elevator D.

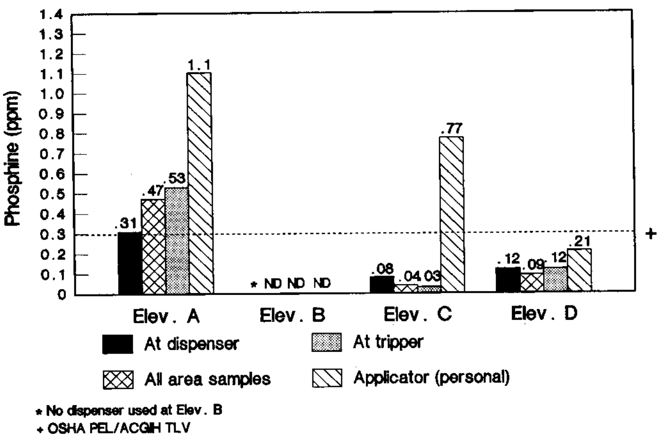

FIGURE 5. Geometric mean PH_3 exposures and area concentrations, elevators A-D.

area concentrations of phosphine and personal exposures were substantially higher at elevator A than at elevators B, C, or D. This may be due in part to the lack of adequate general ventilation and specific local exhaust ventilation at the tripper in elevator A compared with elevator C.

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 applicator's exposures to phosphine. At elevator B, perhaps due 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 parameters, such as ambient temperature, relative humidity, and grain temperature and moisture, cannot be assessed fully based on the limited data collected, although some trends are evident. Comparison of Figure 5 with Table II 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 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 the two elevators for which such data were available (Table II). 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.

Figure 6 presents pertinent phosphine sampling results obtained at elevator A over a two-week period (i.e., sampling one day each week during each of three consecutive weeks). At this elevator, the bin floorman (applicator) conducted and controlled the fumigation process, while the supervisor conducted various activities on the bin deck, tunnel areas, and outside the elevator. Prior to the survey, it was hypothesized that concentrations (and exposures) would rise gradually over time due to an increase in volume of treated grain stored in the bins and due to the general lack of room ventilation at the bin deck level.

The data indicate that the expected upward trend in concentrations did not occur. It is more likely that the measured exposures 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 volumes appear to reflect a trend similar to the bin floorman's exposures. In addition, at elevator D exposures were higher on the last of three days of sampling despite a drop in environmental temperature from the 1°C (34°F) range to −8°C (18°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 up to and in excess of 50 ppm for several minutes. Although an odor was frequently detectable during these activities (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. Respirators (except single-use dust respirators) were not seen in regular use by applicators or other exposed personnel at any of the elevators in this study although several (not all) had appropriate respirators and phosphine canisters available (stored) on site.

Conclusions

The data obtained during these surveys indicate that the use of aluminum phosphide can result in demonstrable, and occasionally excessive, exposures to phosphine (particularly to the applicator) when compared to relevent criteria, even under very cold −8 to 1°C (18–34°F) air temperatures. It also appears that, based on integrated area samples and short-term samples analyzed by portable gas chromatography, significant sources of the exposures to personnel include:

1. The processes of charging, recharging, and emptying the automatic dispensers, which in the case of the applicators appeared to be a major contributor. The specific sources during these procedures were a) the immediate release of phosphine from the original phosphide flask and b) release of phosphine from the dispenser's holding vessel when the lid was opened during the charging or emptying process.
2. The backflush of contaminated air from the headspaces of bins being filled with phosphide-treated grain into the bin deck work spaces.

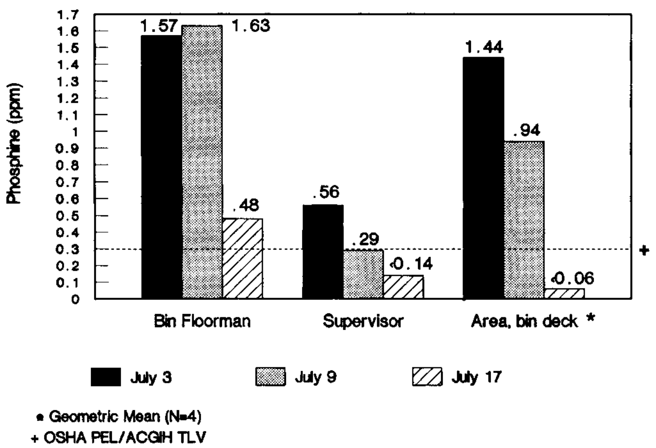

FIGURE 6. Phosphine concentrations over a two-week period, elevator A.

3. Infiltration from these bins into the bin deck and tunnel areas on the same shift during the fumigation and during subsequent shifts after the bins were closed, particularly where efforts to seal the bin were minimal.
4. To a lesser extent, the dispenser itself (i.e., the tablets held within) over the course of a fumigation run. Although the lids incorporated seals to reduce leakage of phosphine, other parts of the dispenser (e.g., the outlet tubing) were not sealed.

Several of the short-term samples obtained at the start of fumigation runs suggested that substantial applicator exposures to phosphine can and do occur as soon as the original containers of aluminum phosphide are opened. These exposures 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 with air inside the container, in which case the phosphine would be released (under pressure) when the flask is opened.

The contributions of environmental parameters, such as grain temperatures, moisture, and ambient temperatures and relative humidity, cannot be assessed properly 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 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, such as those discussed above, also substantially influence exposure levels, apparently to a much greater extent.

Based on measured short-term concentrations of airborne phosphine and observations of work practices during fumigation activities, the warning properties of phosphine may not be adequate, contrary to some previous reports. This indicates the need for more careful exposure monitoring and proper training of applicators, the lack of which may lead in many cases to unnecessary overexposures.

When using solid phosphide formulations to fumigate grain, applicators should not become complacent in the handling of these products because of the seemingly innocuous nature of the solid tablets or pellets used. Compared with many other fumigants (such as the liquid mixtures, or gases such as methyl bromide), aluminum phosphide products, because of their physical state, appear to be relatively safe to use. 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.

Recommendations

Although demonstrable and sometimes excessive exposures to phosphine were measured during these surveys, control of exposures during active fumigation activities should be economically and technically feasible. The following considerations apply at facilities using or contemplating use of aluminum phosphide to fumigate grain.

1. Installation of local exhaust ventilation systems at the phosphide dispenser and at the tripper car's discharge chute would undoubtedly reduce exposures. The system 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 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.
2. Careful attention should be given to sealing storage bins being filled with, or containing, recently treated grain. At the tripper car's discharge chutes, good seals should be provided between the floor and the chute. Good sealing of storage bins, both at the bin deck and in the tunnel area, is also important during the period when they contain treated grain. Simply replacing the steel cover is not sufficient.
3. As a temporary measure, until exposure monitoring indicates that phosphine concentrations are controlled to within acceptable limits, exposures to phosphine should be controlled during the filling and emptying of the dispenser by requiring the use of appropriate personal protective equipment, including the use of a NIOSH-certified canister respirator for phosphine or other respiratory protective equipment appropriate to the exposure levels.[11]
4. Adequate training should be implemented for applicators and all other employees required to use phosphide products for fumigation of grain or for those required to work in facilities in which phosphide products are used.

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