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An Overview of Phosphine-Generating Pesticides Used in California in 2005

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Executive Summary

Phosphine-generating materials have been in use as pesticides in the United States for more than 50 years. The metal phosphides (aluminum phosphide and magnesium phosphide) are primarily used for insect control in stored commodities and vertebrate pest control. These metal phosphides are usually applied as solids (pellets or granular-containing sachets) that react with water vapor in the air to form phosphine gas (PH_3), the actual toxic agent.

In addition to the metal phosphides, phosphine gas itself has been registered as a pesticide since 2001. The gas materials presently come in either a 100% formulation (VAPORPH_3OS), to be diluted and injected by a proprietary application device (Horn Diluphos System) or a 2% formulation (ECO_2FUME) for direct injection. Phosphine gas is classified as flammable.

If metal phosphides are ingested, phosphine gas evolves in the digestive tract producing symptoms such as nausea, vomiting, diarrhea, pain in the chest and abdominal areas, tightness in the chest, coughing, headache and dizziness. In severe cases, this may progress to cardiovascular collapse, pulmonary edema, cyanosis and respiratory failure. Inhalation exposure to phosphine gas can result in severe pulmonary irritation, mucous membrane irritation, as well as similar symptomology associated with ingestion.

All 28 phosphide/phosphine materials registered in California are Category I (signal word Danger/Poison). The greatest use is in commodity fumigation (22%), followed by landscape maintenance (15%). Fresno County has the highest use by poundage, followed by Los Angeles County.

In general, when used as a commodity fumigant, the phosphide/phosphine labels require the use of a fumigant management plan. All phosphine gas and phosphine gas-generating materials are federally classified as "restricted use pesticides". However, only aluminum phosphide is also a California "restricted material" (requiring a permit from the County Agricultural Commissioner for use). California also places other worker safety restrictions, via regulation, on the use of fumigants, including phosphide/phosphine materials.

From 1994 through 2005, 88 illnesses related to exposure to phosphine-generating products have been reported to the Department of Pesticide Regulation's (DPR) Pesticide Illnesses Surveillance Program (PISP). Twenty-four of these involved pesticide handlers using aluminum phosphide. Many of the handler illnesses were the result of violations of regulations or label requirements. Lack of appropriate training and required personal protective equipment were the common factors in several illnesses. Bystander exposure occurred during fumigation, aeration and post-aeration. Inadequate monitoring of the work area, inadequate posting of treated commodity, allowing people not engaged in the fumigation to be present were some of the problems noted for bystander exposure.

DPR has conducted worksite evaluations of several commodity fumigation facilities that use phosphide/phosphine materials and has done extensive review of illness data, enforcement activities and regulatory requirements. The labels do not appear to be providing sufficient guidance to facility operators, as they are not familiar with proper monitoring procedures,

monitoring equipment or interpreting the results of monitoring conducted. In addition, some facility operators do not seem to understand how to use exhaust or ventilation to control exposure. More diligent and comprehensive monitoring of phosphine throughout its use-cycle is needed. Inadequate storage of gas cylinders was also noted as a safety hazard at some facilities.

DPR recommends several approaches to ensure worker safety in the use of these materials, including application of exposure control technology, real-time monitoring of worksites, specific training and licensing requirements, on-site evaluations and compliance assistance.

Introduction

Pesticide products containing metal phosphides (aluminum, magnesium, and zinc) were patented in Germany in 1930. Aluminum-based products were introduced into the United States and California in 1958. Magnesium phosphide was first registered as a pesticide in the United States and California in 1979. Their principal uses are to control invertebrate pests of stored commodities via volumetric fumigation (aluminum and magnesium) and for rodent control (zinc) in agricultural areas and rights-of-way as well as in and about residential and recreational areas. The major application method is via hand or mechanical placement; aerial and ground applications are allowed on some zinc phosphide labels. Most products are solid formulations (pellets, granules, dusts, or baits) that react with moisture to produce phosphine gas, the biologically active chemical ingredient. Phosphine gas, the most recently registered product, was first registered in the United States in 1999 and in California in 2001. It is a compressed gas formulated pesticide used for volumetric fumigation of stored commodities and also for small rodent control.

The Department of Pesticide Regulation (DPR) conducted an evaluation of phosphine-generating pesticides to determine whether current labeling and regulations are adequate to protect workers and the public. The results of this review will determine if any further action is needed to ensure these products can be used safely. This report will concentrate on the gas and gas-generating products and not address zinc phosphide, since its use (solely vertebrate control), physical state of the killing agent (solid/paste as opposed to a gas) and method of application (broadcast, burrow introduction) are very different from the gas/gas-generating materials.

Physical and Chemical Properties

In the technical state (> 90%), aluminum phosphide and magnesium phosphide exist as yellowish to dark grey and chartreuse crystals, respectively (Tomlin, 2001). Phosphine is a colorless and odorless gas (US EPA, 1986) that has a lower explosive limit of 1.87% in air (vol/vol) (Cytec Industries, Inc., 2004; Tomlin, 2001; US EPA, 1999; World Health Organization [WHO], 1988); it reacts violently in the presence of halides and halide compounds (NIOSH, 1999; US EPA, 1999; WHO, 1988). It reacts with a variety of metals including copper, gold, silver, and brass (NIOSH, 1999; WHO, 1988). No olfactory characteristic for the solid states of the metal phosphides was found in the public domain literature. Reports of the odor of phosphine are not consistent; some report it as garlic or rotting fish (Cytec Industries, Inc., 2004; Tomlin, 2001; US EPA, 1999) or no detectable odor at concentrations as great as 200 ppm (WHO, 1988; Zaebst *et al*., 1988). The odor may be from the contaminant arsine, often found in phosphide formulations. The National Institute of Occupational Safety and Health (NIOSH) does not recognize an odor threshold as a means to alert workers or bystanders of the presence of phosphine (NIOSH, 1999). Table 1 details the physical and chemical properties of these compounds.

Table 1. Physicochemical properties of the phosphine generating compounds[1]

Active Ingredient	Empirical formula	Molecular weight	Vapor pressure	Melting point	Boiling point	Half-life ($t_{½}$)	Stability
Aluminum phosphide Al – P	AlP	58	Negligible at normal temperature and pressure	> 1000 °C			Stable when dry; reacts with moist air, reacts violently with acids producing phosphine
Magnesium phosphide P | Mg – Mg – Mg | P	Mg_3P_2	134.9	0 mm Hg at 25 °C	> 750 °C			Stable when dry; reacts with moist air, reacts violently with acids producing phosphine; more reactive than aluminum phosphide
Phosphine H – P - H | H	H_3P	34	High: 4132 k Pa (=31,400 mm Hg at 20 °C)[2]	-132.5 °C[1,3]	-87.4 °C[1,3]	28 hours (in air)[4] < 5 hours (sunlight)[4]	Lower explosive limit of 1.87% in air

1/Tomlin, 2001 (unless otherwise referenced)
2/ U.S. Department of Labor, 2005
3/ Kovacs, 2001
4/ World Health Organization, 1988

Based on the similarity of their chemistry, toxicity and uses, the US EPA and DPR grouped aluminum and magnesium phosphide together toxicologically for risk assessment (US EPA 1986; US EPA 1998; DPR, 2004).

Adverse Health Effects

Depending on the route of exposure, the symptoms may vary. When ingested, symptoms may include nausea, vomiting, diarrhea, pain in the chest and abdominal areas, tightness in the chest, coughing, headache and dizziness. In severe cases this may progress to cardiovascular collapse, pulmonary edema, cyanosis and respiratory failure, with a delayed onset of pericarditis, renal failure, and hepatic damage including jaundice (WHO, 1988). These symptoms may be delayed and death may occur up to one week after severe poisoning (WHO, 1988). Pathological findings may include fatty degeneration and necrosis of the liver and pulmonary hyperemia and edema (Chan *et al*., 1983).

Inhalation exposure may result in severe pulmonary irritation (Childs and Coates, 1971; WHO, 1988). Mild exposure may cause only mucous membrane irritation, with initial symptoms mimicking an upper respiratory tract infection. Other symptoms may include nausea, vomiting, diarrhea, headache, fatigue, and coughing, while more severe symptoms may include ataxia, prickling sensation in the abdominal area, intention tremor, double vision, and jaundice (Wilson *et al*., 1980; WHO, 1988). Death can be sudden or delayed for up to two weeks (Curry *et al*., 1959; Childs and Coates, 1971; WHO, 1988). Post-mortem examinations have revealed focal

myocardial infiltration and necrosis, pulmonary edema and widespread small vessel injury (WHO, 1988). According to the World Health Organization (WHO), there is no evidence for cumulative effects from intermittent low-level exposure averaging 14 mg/m^3 (10 ppm) or less (WHO, 1988). Based on the current knowledge of toxicology and adverse effects, the NIOSH recommended exposure limit (REL) for phosphine is 0.3 ppm as a time-weighted average (TWA) for up to 10 hours per day during a 40-hour work week, and 1 ppm as a TWA 15-minute short-term exposure limit (STEL) that should only occur up to four times during a work shift, with a minimum of 1 hour between exposures. The California Department of Industrial Relations, Division of Occupational Safety and Health (Cal/OSHA) Permissible Exposure Limit (PEL) is also 0.3 ppm (Title 8, Section 5155: Airborne Contaminants). The U.S. Environmental Protection Agency (US EPA) developed a reference concentration (RfC) for phosphine chronic effects of 0.0003 mg/m^3 (US EPA, 1995). California's Office of Environmental Health Hazards Assessment (OEHHA) established a REL for chronic effects of 0.0008 mg/m^3 (OEHHA, 2002).

Severity of effects from over-exposure to phosphine is summarized in Table 2.

Table 2. Toxic effects of phosphine[1]

Effect	Concentration	
	mg/m^3	ppm
Rapidly fatal	2800	2000
Death after ½-1 hr	560 - 840	400 - 600
Dangerous to life after ½-1 hr	400 - 600	290 - 430
Serious effect after ½-1 hr	140 - 260	100 - 190
No serious effects after ½-1 hr	10	7
1/ Childs & Coates (1971)		

Illnesses Related to Phosphine-Generating Pesticides

Reported cases of inadvertent exposure of the general population to phosphine have been published (Wilson et al., 1980; Maddy et al., 1983; O'Malley, 1998). There have been cases of accidental or suicidal ingestion of phosphide pesticides (Chan *et al*., 1983; Mehler, 2005a). There have been occasional cases of fatal occupational exposure to phosphine (Harger and Spolyar, 1958; Ziemer, 1963; WHO, 1988). Between 1900 and 1958, Harger and Spolyar (1958) identified 26 fatalities involving phosphine poisoning following exposure to pesticide products. These fatalities include a resident of an apartment complex near a large grain elevator in which grain was being fumigated with aluminum phosphide, three residents of a house sharing a wall with a granary under fumigation, and a child passenger on a grain freighter under fumigation.

From 1994 through 2005, 88 illnesses related to exposure to pesticide use of phosphine gas and phosphine-generating products have been reported to DPR's Pesticide Illnesses Surveillance Program (PISP). Of these 88 reported cases, 69 involved aluminum phosphide exposure (Mehler, 2005a; Yanga 2007a), five involved magnesium phosphide (Mehler, 2005b; Yanga 2007b) and 14 involved exposure following use of phosphine gas (Yanga, 2007c).

Four cases involved suicide attempts (three fatal). Twenty-four cases involved handlers. Of these handler cases, nine involved handlers applying bait in rodent burrows, and the remaining 15 cases involved various other handler activities. The handlers involved in vertebrate control appeared to be exposed to either dust residue from their gloves or the container, or to associate the exposure with phosphine gas emissions from the treated burrows. In the gas exposure events, the actual proximity of the worker to the gas source or sources is unclear.

The following brief narratives describe the exposure of the 15 non-rodenticide handler incidents:

1994 Stanislaus County	A worker was placing a box of aluminum phosphide tablets under a tarp when wind blew gas into his face. He had not been trained for using pesticides nor was he provided with the required personal protective equipment (PPE).
1995 Butte County	While applying aluminum phosphide tablets atop a large rice storage bin, a worker noted garlic-like odor and became ill. No PPE was provided or worn. He was observed at a hospital for 21 hours before his release.
1995 Orange County	A worker, unloading a sea container, scraped against a paper bag taped to the container ceiling. Powder fell from the bag onto his skin. He washed it off immediately. He developed symptoms that resolved by the time he saw a doctor.
1996 Tulare County	Upon opening a flask of aluminum phosphide pellets, pressurized gas (probably from moisture introduced when the flask was previously opened) was ejected from the flask and was inhaled by the employee. No training or PPE was provided to the applicator.
1996 Fresno County	While removing spent material, a worker may have had contact with the dust, developing a rash.
1996 Butte County	A worker opened a shipping container filled with almonds under fumigation. Apparently there was inadequate aeration and the worker detected garlic-like odor, becoming ill. This was the second time in four days the worker had been exposed to inadequately aerated commodity.
1997 Alameda County	While attempting to consolidate the contents of two aluminum phosphide containers, the worker was exposed to gas that had evolved within the containers. The worker was wearing gloves and work clothes at the time of exposure.
1999 San Joaquin County	While atop a rail car taking multiple phosphine gas readings of the contents, a worker began to feel ill. He violated company procedure by staying on top between readings, instead of exiting the area as required.
1999 Fresno County	Under windy conditions, a worker was applying aluminum phosphide to covered bins of almonds on a very windy day. He was found unconscious three hours after completing the bin fumigation.

cont'	No specific exposure was noted by the applicator and no violations were found during the investigation.
2000 Santa Clara County	An untrained worker started aerating a rail car treated with aluminum phosphide and was exposed to phosphine gas.
2002 Glenn County	A worker was placing plastic sheeting and metal lids on bins freshly treated with aluminum phosphide and became ill.
2003 Stanislaus County	A forklift driver attributed a rash to contact with dust remaining from fumigations. She handled and discarded the trays of spent tablets before dumping the almonds. The investigator identified shortcomings in fumigation safeguards and procedures.
2004 Fresno County	An almond processing plant worker mistakenly fumigated 22 extra bins of almonds with phosphine gas. The next morning, two workers helped to open the bins and dump the almonds onto the sorting belt.
2004 Kern County	A sanitation worker felt ill after his supervisor ordered him to remove tarps from pistachio bins still undergoing fumigation with aluminum phosphide. That night he developed chest pains and difficulty breathing and sought medical attention. Eight days later he was again untarping pistachios and developed a rash on his chest and arms; the doctor subsequently hospitalized him because of poor liver function test results possibly related to phosphine exposure.

Other than the handler incidents, 4 cases involved suicide attempts (3 fatal), 32 cases involved exposure of workers processing commodity, 13 involved other bystanders, 8 were people responding to emergencies (suicides, fire) and 7 involved miscellaneous exposures. Workers processing commodity were generally exposed to phosphine via inadequately aerated commodity. The 13 bystanders exposures included maintenance workers in warehouses where commodity fumigations were taking, workers in rooms or areas adjacent to treated commodity, and a receiving dock employee handling boxes of treated wicker furniture. In one incident employees in a break room developed headaches and nausea the morning after fumigation of raisins in the warehouse. Draeger tube readings showed 1 ppm phosphine in the break room. In another incident, two mill workers were working in or about a silo filled with fumigated wheat that had been aerated 19 days prior. Draeger tube readings of the ambient air detected 2 ppm phosphine. Three people hopped a train a rode in a fumigated rail car for 2-3 hours; two died. In another incident, two workers were exposed to smoke when an employee put the "spent" aluminum phosphide dust into a barrel and then a wooden box. The dust caught fire. A county inspector entered an unposted fumigation chamber used three days prior and not yet aerated. Draeger tube readings found 4 ppm phosphine.

In many cases, the incidents appear to have resulted from violations of regulations, label requirements or other conditions of use. Unplacarded or unposted fumigations, inadequate aeration, allowing employees not engaged in the fumigation to be present were some of the violative causes of exposure. However, in several incidents no violative behavior was noted. Events not involving pesticide application were also responsible for several illnesses and deaths. Seven cases involved a HAZMAT, emergency responders, medical personnel and coroners'

office employees handling suicide victims. One other case involved a firefighter who inhaled smoke from spent aluminum phosphide ash nearly three hours after he arrived on the scene.

Registered Phosphine-Generating Products

As of April 2007, the DPR Product/Label database contains 28 actively registered phosphine-generating products registered (Table 3): aluminum phosphide (22), magnesium phosphide (4), and phosphine (2). Of these 28 registered products, all are Category I (Danger/Poison or Danger).

Table 3. Phosphine-generating products registered in California[1]

Product Name	EPA Registration No.	Formulation	Percent AI[2]
Aluminum Phosphide			
Degesch Phostoxin Pellets	72959-5-AA	Pellet/tablet/cake/briquet	55
Degesch Phostoxin Prepac Rope	72959-8-AA	Pellet/tablet/cake/briquet	55
Degesch Phostoxin Tablet Prepac	72959-9-AA	Pellet/tablet/cake/briquet	55
Degesch Phostoxin Tablets	72959-4-ZB	Pellet/tablet/cake/briquet	55
Detia Fumex	72959-10-AA	Pellet/tablet/cake/briquet	57
Detia Phos Pellets	72959-5-ZA	Pellet/tablet/cake/briquet	55
Detia Phos Tablets	72959-4-ZA	Pellet/tablet/cake/briquet	55
Drex-PH_3 Aluminum Phosphide Fumigant Pellets	19713-569-AA	Pellet/tablet/cake/briquet	60
Drex-PH_3 Aluminum Phosphide Fumigant Tablets	19713-571-AA	Pellet/tablet/cake/briquet	60
Fumitoxin Pellets	72959- 2-ZA	Pellet/tablet/cake/briquet	55
Fumitoxin Pellets	72959-2-AA-5857	Pellet/tablet/cake/briquet	55
Fumitoxin Tablets	72959-1-ZA	Pellet/tablet/cake/briquet	55
Fumitoxin Tablets	72959-1-AA-5857	Pellet/tablet/cake/briquet	55
Gastoxin Fumigation Pellets	43743-2-AA	Pellet/tablet/cake/briquet	57
Gastoxin Fumigation Sachet Chain	43743-3-ZA	Dust/powder	57
Gastoxin Fumigation Sachets	43743-3-AA	Dust/powder	57
Gastoxin Fumigation Tablets	43743-1-AA	Pellet/tablet/cake/briquet	57
Phosfume Fumigation Tablets	70506-13-AA-1015	Pellet/tablet/cake/briquet	60
Quickphlo-R Granules	70506-69-AA	Granular/flake	77.5
Weevil-Cide Gas Bags	70506-15-AA	Granular/flake	60
Weevil-Cide Pellets	70506-14-AA	Pellet/tablet/cake/briquet	60
Weevil-Cide Tablets	70506-13-AA	Pellet/tablet/cake/briquet	60
Magnesium Phosphide			
Degesch Fumi-Cel	72959-6-AA	Pellet/tablet/cake/briquet	56
Degesch Fumi-Strip	72959-6-ZA	Pellet/tablet/cake/briquet	56
Degesch Magtoxin Granules	72959-11-AA	Granular/flake	94.6
Degesch Magtoxin Prepac Spot Fumigant	2959-7-AA	Pellet/tablet/cake/briquet	34
Phosphine Gas			
Eco$_2$fume	68387-7-AA	Pressurized gas	98
Vaporph$_3$os Phosphine Fumigant	68387-8-AA	Pressurized gas	99.3

1/ Registered as of March 2006
2/ AI – Active ingredient

Reported Use of Phosphine-Generating Pesticides

A search for all reported uses of phosphine-generating products for the years 1993 through 2005 was conducted using the California Pesticide Information Portal (CalPIP) querying the DPR pesticide use report database (DPR, 2007). Of the three active ingredients, aluminum phosphide accounted for 97% of the total used in the 13-year span (Table 4).

Table 4. Total pounds of active ingredients (AI) applied in California (1993-2005)[1]

Year	Aluminum Phosphide	Magnesium Phosphide	Phosphine[2]
2005	133,969	3,156	2,699
2004	131,864	2,621	1,690
2003	119,533	2,844	1,141
2002	171,181	4,853	901
2001	129,677	2,521	44
2000	122,397	3,660	
1999	133,141	3,540	
1998	84,002	4,140	
1997	94,636	3,931	
1996	112,279	3,615	
1995	90,968	4,929	
1994	99,647	3,735	
1993	171,522	1,539	
Total	1,598,816	45,084	6,475

1/ DPR, 2007
2/ Registered for use in 2001

Of the 65 different products listed in the PUR database from 1993 through 2005, 17 products accounted for greater than 91% of the total AIs applied (Table 5). Sixteen of these 17 products contain aluminum phosphide; the other contains magnesium phosphide.

Table 5. Top 20 phosphine-generating products used in California (1993–2005)[1]

Product	Amount Active Ingredient Applied	Percent of Grand Total
Fumitoxin Tablets	197,838	12
Degesch Phostoxin New Coated Tablets [2]	186,421	11
Fumitoxin New Coated Tablets-R [2]	156,837	10
Degesch Phostoxin Coated Pellets [2]	127,546	8
Phostoxin New Coated Tablets [2]	122,834	7
Detia Gas-Ex-B [2]	102,324	6
Phostoxin Coated Pellets [2]	98,030	6
Gastoxin Fumigation Tablets	97,567	6
Degesch Phostoxin Tablets	89,445	5
Fumitoxin Pellets	79,650	5
Degesch Phostoxin Pellets	52,679	3
Weevil-Cide Tablets	35,160	2
Degesch Phostoxin Tablets-R [2]	34,701	2
Degesch Fumi-Cel Plates [2, 3]	31,676	2
Degesch Phostoxin Tablet Prepac	31,368	2
Detia Fumex	28,045	2
Fumitoxin Coated Pellets [2]	26,551	2

1/ DPR, 2007. Represents 91% of all uses
2/ No longer registered in California.
3/ All of the products listed contain the active ingredient, aluminum phosphide, except for Degesch Fumi-Cel Plates. It contains magnesium phosphide.

Based on total use from 1993 through 2005, approximately 96% of the use occurred in 21 of California's 58 counties; the top 10 counties accounted for approximately 72% of the use (Table 6). Geographically, these counties were generally clustered in the rice-growing region, along the west side of the Central Valley from San Joaquin to Kern and major California shipping ports.

Table 6. Use of phosphine-generating products in California by county (1993-2005)[1]

County	Lbs Active Ingredient used	Percent of Grand Total
Fresno	174,001	13
Los Angeles	134,794	10
Merced	131,437	10
Yolo	110,706	8
Imperial	105,565	8
Stanislaus	105,274	8
Kern	67,968	5
Colusa	50,302	4
Tulare	47,436	3
Sutter	41,983	3
San Joaquin	41,612	3
Butte	37,774	3
Monterey	31,307	2
Madera	31,065	2
Orange	29,110	2
Riverside	27,502	2
Sacramento	26,224	2
Ventura	22,772	2
San Bernardino	22,576	2
Santa Clara	21,721	2
San Diego	20,524	2
		Total: > 96%

1/ DPR, 2007

A summary of the top 10 use-sites is shown in Table 7. Of the 158 sites reported in the PUR (DPR, 2007), approximately 90% of the phosphine-generating pesticides were used in these 10 sites. Two of these use-sites might include residential areas (landscaping and vertebrate pest control) and account for approximately 19% of the total use. The landscaping and vertebrate control uses are primarily aimed at subterranean rodents (moles, voles, gophers, field mice, etc.). Structural pest control uses involve space fumigation of mills, processing plants and warehouses.

Table 7. Top 10 uses of phosphine-generating products in California from 1993 through 2005[1/]

Use Site	Pounds Active Ingredient Applied	Percent of Grand Total
Commodity fumigation	298,722	22
Landscape maintenance	199,739	15
Fumigation, other	184,422	14
Almonds	183,497	13
Grapes	83,319	6
Structural pest control	72,155	5
Vertebrate pest control	58,441	4
Rights-of-way	57,387	4
Rice	54,816	4
Pistachio	35,646	3
	Total:	90

1/ DPR, 2007. The PUR database did not always differentiate "commodity fumigation" from the specific listed commodities.

Historical US EPA Actions

Aluminum phosphide was first registered as a pesticide in the U.S. in 1958 while magnesium phosphide was first registered in 1979. In 1981 and 1982, US EPA issued Pesticide Registration Standards that discussed safety data and required labeling for products containing aluminum phosphide and magnesium phosphide, respectively. At this time the US EPA also issued a data call-in for both the metallic phosphides. Subsequently, US EPA issued PR Notice 84-5, a "Label Improvement Program for Fumigants" and PR Notice 85-6, which partially revised PR Notice 84-5, but did not alter the portions of PR Notice 84-5 that pertained to aluminum phosphide. In response to the data call-in US EPA issued an amended Registration Standard that superceded the PR notices and the previous standard. This amended standard required additional data submissions and labeling changes for aluminum and magnesium phosphide products.

The US EPA completed a Reregistration Eligibility Decision (RED) for aluminum/magnesium phosphide in 1998. The RED outlined needed mitigation measures for handlers and entry workers as well as occupational and non-occupational bystanders. Subsequent to public comment, the RED was amended and the phosphine-generating registrants and US EPA (US EPA, 2000; US EPA, 2004) signed a Memorandum of Agreement (MOA). Currently registered aluminum and magnesium phosphide and phosphine gas products are bound by the terms of the MOA. The major provisions of the MOA include the requirement for site-specific fumigation management plans, incident reporting to US EPA, monitoring studies, establishment of worker exposure limits, development of a training and certification program and other label modifications discussed below.

All phosphine-generating pesticides are on the US EPA Restricted Use Pesticides list based on the active agent, phosphine (US EPA, 1986; US EPA, 1998). The active ingredients aluminum

phosphide, magnesium phosphide, and phosphine are categorized as Toxicity Category I for acute inhalation exposure (US EPA 1986, 1998, 1999).

Label Requirements

Currently, phosphine and phosphine-generating products are not within the scope of the Worker Protection Standard because their registered uses are not directly related to the production of agricultural products (US EPA, 1998). Restricted entry intervals (REI) are not required for the phosphine-generating products (40 CFR 156.208.d).

Aluminum/magnesium phosphide products and phosphine gas may be sold only to persons who hold a dealer or qualified applicator certificate (referred to federally as a certified applicators' license). Only those persons who hold a qualified applicator certificate or trained personnel under the direct supervision of a certified applicator may use these products. There must be at least one certified applicator physically present, and this person is responsible for each fumigation. The certified applicator must maintain visual and/or voice contact with all fumigation workers during the application of the fumigant and the initial opening of the fumigation structure for aeration. Once the aeration process is secured and monitoring has established that aeration can be completed safely, a trained person can complete the process. An emergency response plan is required for each site.

The label requirements include:

a. *Fumigation Management Plans* – Site-specific fumigation management plans (FMP) are required prior to any application. The US EPA defines the FMP as a written description of the steps to conduct a safe, legal and effective fumigation. The plan must characterize the structure or site/area involved in the fumigation and include all safety requirements in the plan. Safety measures, emergency procedures, and monitoring, as well as an evaluation of the suitability of the site for fumigation, are also required.
b. *Worker Exposure Limits* – The current PEL of 0.3 ppm must be referenced on the labels and Time-Weighted Average (TWA) exposure must be maintained below the PEL.
c. *Applicator's Manual* – An applicator's manual is referenced by aluminum/magnesium phosphide and phosphine labels; the manual holds the same legal authority as the label. The applicator's manual defines how to conduct all aspects of a fumigation operation.
d. *Handler Requirements* – Any person handling the product must wear dry gloves since metal phosphides react with moisture, including perspiration. After use, gloves must be aerated and the applicator is directed to wash his hands. For phosphine gas, handlers must wear leather or leather-faced cotton gloves while connecting or disconnecting the cylinders. In addition, eye protection must be worn when working with pressurized equipment. A self-contained breathing apparatus (SCBA) is required when entering structures under fumigation and when air concentrations are unknown or above 15 ppm. Approved full-face gas masks with a phosphine gas canister can be used when phosphine concentrations are known to be below 15 ppm. Respiratory protection must be available when applying metal phosphides within an enclosed structure. If monitoring equipment is not available, an approved canister respirator or SCBA must be worn during application. Products packaged in cells or strips may be applied in enclosed structures without respiratory protection. The slow gas release is

expected to permit applicators to deposit the fumigant and exit the structure before air concentrations increase to hazardous levels.

e. *Enclosed Areas Around the Fumigation Site* – People in enclosed areas around the fumigation site must not be exposed to phosphine with a TWA above the 0.3 ppm PEL.

f. *Other Label Requirements* – Product labeling also includes the following:
   - A prohibition of aeration of railcars, railroad boxcars, shipping containers and other vehicles en route. Written notification must be provided to the receiver of railcars, railroad boxcars, shipping containers and other vehicles, which are being fumigated in-transit. Notification must be made prior to the actual receipt of a fumigated vehicle or container by a consignee. Upon receipt of the railcar, railroad boxcars, shipping containers or other vehicle a trained person must perform the aeration process and must document in writing that monitoring has been conducted and that aeration has been completed.
   - The fumigated area must be placarded. At minimum the signs must contain the date and time fumigation is initiated and completed; name of fumigant; name, address and telephone number of the fumigation company and/or applicator; and a 24-hour emergency response telephone number. The signs must not be removed until the area contains 0.3 ppm phosphine or less. For phosphine gas, the perimeter of the fumigation area must be monitored to ensure that phosphine and, if applicable, carbon dioxide (the diluent gas used in ECO_2FUME) are kept within acceptable levels. If high levels are detected outside the fumigation area, the addition of phosphine must be stopped. Leaks must be repaired to limit bystander exposure. Users are not allowed to enter space under fumigation without first assessing the concentration (while wearing SCBA). Workers not associated with the fumigation may not be present in the enclosed area of a commodity fumigation during the fumigation and aeration phases until phosphine levels are shown to be below the 0.3 ppm PEL.
   - All thefts of phosphine-generating products must be reported to local law enforcement.
   - The fumigation area must be aerated until the level of gas is at or below the PEL. The area or site must be monitored to ensure that further off-gassing from the treated commodity does not result in the development of unacceptable levels of phosphine. Reentry into treated areas by any person before aeration is complete is prohibited unless wearing appropriate respiratory protection.
   - The fumigated area must be carefully sealed to ensure that adequate gas levels are retained. Proper application procedures must be followed to provide satisfactory distribution of phosphine gas.
   - The products may not be applied into a burrow system that is within 15 feet of any occupied structure.
   - Prior to treating a rodent burrow on a property containing an inhabited structure, the applicator must provide the customer with an MSDS or appropriate sections of the Applicator's Manual.
   - The employer must monitor and document phosphine exposures in an operations log or manual for each site and operation.
   - If monitoring shows that workers could be exposed to concentrations in excess of the permitted limits, engineering controls, modified work practices, or personal protective equipment must be used to reduce exposure to within permitted limits.

- A discussion of the explosiveness of phosphine-air mixtures; concentrations above the lower explosive limit of 1.8 % (v/v) can ignite and higher levels can spontaneously ignite on contact with air. Never allow the buildup of hydrogen phosphide to exceed explosive concentrations. Do not confine spent or partially spent dust from metal phosphide fumigants as the slow release of hydrogen phosphide from this material may result in formation of an explosive atmosphere. Monitoring will ensure that explosive concentrations are not exceeded
- Adjacent, enclosed areas likely to be occupied must be tested to ensure that significant leakage does not occur.

California Regulatory Requirements

All phosphine gas and phosphine-gas generating materials are federally classified as "Restricted Use Pesticides" (due to high acute inhalation toxicity of phosphine gas), which limits their use to certified private or certified commercial applicators. California also has a restricted use category that not only encompasses the federal standards, but places a permitting requirement, via Title 3 of the California Code of Regulations, Section 6412(a) (3 CCR 6412[a]), on specific materials. These materials, found in 3 CCR Section 6400(e), include only aluminum phosphide. Thus, even though magnesium phosphide and phosphine gas (the ultimate material generated by the metal phosphides) are federally restricted, they do not require a permit for use in California (3 CCR Section 6414[b.

California regulations (3 CCR 6780 & 6782) impose additional requirements for the safe use of fumigants, including aluminum phosphide, magnesium phosphide and phosphine gas. These include:

- **3 CCR 6780(a).** When concentrations cannot be controlled and an employee's exposure exceeds the PEL of 0.3 ppm, the employer must provide and require the employee to wear approved respiratory protective equipment. Gas masks (TC-14G) may be used in phosphine concentration ranging from 0.3 to 15 ppm. When concentrations are unknown or greater than 15 ppm the use of self-contained breathing apparatus (SCBA, TC-13F) is required. The respiratory requirement can be waived if using continuous monitoring to warn employees before the PEL of 0.3 ppm is reached.
- **3 CCR 6780(c).** Employers shall submit a "Fumigation Safety Program" to the DPR director for approval. The program must describe practices used to insure the employee will not be exposed to phosphine concentrations in excess of the PEL.
- **3CCR 6780(d).** In addition, the employer must have an accident response plan that provides instructions to employees in case of spills, fire or leaks. Employees must also be trained to respond based on the plan.
- **3CCR 6782(a).** Fumigations using phosphide products in enclosed spaces such as vaults, chambers, vans, boxcars, ships, vehicles, tarpaulin-covered structures and tarpaulin-covered commodities inside buildings, require at least two trained employees be present during the application. When solid fumigants (such as aluminum and magnesium phosphide) are introduced from outside the enclosed space, then only one trained person need be present. Two trained employees are necessary when entering the space to

facilitate aeration and when determining the fumigant concentration (no exception for solid fumigants).

- **3CCR 6782(b).** The second employee must have SCBA immediately available should it become necessary to enter the space for rescue.
- **3CCR 6782(c).** Warning signs must be posted prior to fumigation. These signs must be visible from all entrances to the space under fumigation and are not to be removed until the fumigation and ventilation is completed and the space has been cleared for safe reentry. The signs should be in English and Spanish and contain the following statement "DANGER-FUMIGATION" with skull and crossbones.
- **3CCR 6782(d).** Employees are not allowed into the enclosed fumigated areas, unless the concentration in the area is known to be at or below 0.3 ppm.
- **3CCR 6782(e).** The fumigant is not to be released into an occupied area.
- **3CCR 6782(f).** Management of the treated area or areas where treated commodities are stored requires that levels of phosphine gas be maintained at or below 0.3 ppm for unprotected employee entry.

Finally, in situations where off-gassing from treated product may cause air concentrations of phosphine to reach hazardous levels, Title 3 CCR Section 6706: Hazardous Areas, allows that

> "[w]hen there is a reasonable suspicion by the director or commissioner that a specific workplace has been or may be unsafe for workers due to exposure to active or inert ingredients in pesticide products, or breakdown products of these ingredients, the director or commissioner may require the employer to prohibit entry of employees into that workplace… The director or commissioner may also specify exposure time limits and protective clothing and equipment to be worn by employees under these circumstances."

California Enforcement Actions

Table 8 shows the types of enforcement actions involving phosphine-generating pesticides taken from the years 1998 to 2005. In that time, there were 76 violations of the Food and Agricultural Code and the California Code of Regulations. The actions involving administrative and record keeping requirements, such as not registering as an applicator in the county or not filing use reports, that usually do not directly threaten health, property or the environment. Other actions found could possibly threaten the health of workers or bystanders. Use of aluminum phosphide accounted for well over half the actions taken and magnesium phosphide and phosphine gas accounted for a much smaller portion. Less than 15% of the violations involved use for fumigation of nuts, dried fruits, or other commodities. The great majority of violations occurred with users applying these products to burrows for rodent control.

Table 8. Types of violations found for phosphine-generating products from 1998 to 2005[1].

Grouping of enforcement for violation	Number of violations issued
Failed to follow applicable label and/or permit requirements	23
Did not provide worker with PPE, training, or emergency medical information	14
Failed to notify persons likely to be exposed to pesticide	1
Failed to properly store or secure pesticide containers	1
Failed to file required records within the county of use	37

[1] Enforcement Tracking Data System.

California's Worksite Evaluations

From 2003 to 2005, the Department of Pesticide Regulation's Worker Health and Safety Branch (WHS) industrial hygienists made five worksite evaluations of processing facilities that used phosphine or phosphine-generating pesticides. Additionally, in 1982, WHS conducted a study of fugitive emissions into a business adjoining a rice warehouse fumigated with a phosphine-generating material.

Unlike the later worksite evaluations, the 1982 study (Maddy *et al*., 1983) was an onsite investigation of a potential exposure event resulting from tarped bulk fumigation of rice using the phosphine-generating material aluminum phosphide. The rice storage facility also housed a computer repair business that shared space within the building envelope. Though inconclusive as to the phosphine concentration employees were exposed to, the study did establish that infiltration of phosphine gas into the work area of the computer repair business did occur. The report also concluded that fumigation applicators must consider "…proximity of workers not involved in the fumigation process when choosing a site for commodity tarp-fumigation." In this case, the structure was not a dedicated commodity warehouse, but an under-utilized commercial structure with a large amount of empty space and only the computer repair company as tenant.

The more recent worksite evaluations were initiated by requests from either the local agricultural commissioner's (CAC) office or from DPR's Enforcement Branch. Two evaluations were conducted in Stanislaus County, two in Kern County and one in Fresno County. All cases involved the use of either phosphine gas (ECO$_2$FUME® or VAPORPH$_3$OS®) or a phosphine-generating material (GASTOXIN®). Unless otherwise noted, all ambient air samples were taken from worker's breathing zone height (approximately 5 ft) or in locations normally accessible to workers. The following are summaries of the worksites evaluated.

Kern County

At the request of DPR's Enforcement Branch, DPR industrial hygienists conducted a worksite evaluation of a nut-processing facility in Kern County. WHS monitoring equipment was unavailable for this evaluation. The facility used a method for bin fumigation that was not explicitly defined on the $ECO_2FUME^{®}$ label or in the Applicator's Manual. The application procedure used involved injecting the phosphine gas directly into a plastic bag lining a bin (approximate volume of 64 ft^3) filled with commodity (almonds), then sealing the puncture with duct-tape. This procedure is not found in the Applicator's Manual, but appears to loosely combine elements of the "Application to Tarpaulin Fumigations" section and the "Application to Bulk Commodity"section. However, these bins can fail to contain the fumigant for many reasons that include insufficient tightening of the bag opening, permeation through the plastic and integrity failure of the bag.

The facility manager stated that the actual fumigation procedure was done either outside the facility or next to a fully opened rollup door. Fumigated product was stored outside of enclosing structures, as per order by Kern CAC. Under these conditions, the potential for phosphine exposure to other workers should be low. A walk-around of the facility indicated that fumigation outside or next to large openings should not result in worker exposure to hazardous concentrations of phosphine. However, the facility manager also stated that they wished to store fumigated product within the enclosed structure and to also do spot re-fumigation to stored bins. Such operations could result in detectable, and possibly hazardous, concentrations within the structure. Monitoring procedures for both applicators and the areas where other workers may occupy, as required by the Applicator's Manual, were recommended for application and storage within an enclosed structure (Fong, 2003).

A second facility in Kern County had been using $ECO_2FUME^{®}$for phosphine fumigations and was bringing a $VAPORPH_3OS^{®}$ unit (Horn Diluphos System, HDS-200C) into operation. The Horn Diluphos System meters gas from a 100% phosphine cylinder, combining the phosphine with air in an enclosed mixing vessel, yielding a 1% phosphine dilution gas. The diluted material is then pumped out via large diameter hoses to the container under fumigation. The DPR Enforcement Regional Office requested a consultation to review their use of these materials (Fong, 2005).

The facility processed pistachios and stored pre-processed nuts in silos located in an unenclosed, but roofed, structure. Using the INNOVA-ST to test the air over a conveyor belt that was unloading one of the silos, concentrations of phosphine between 0.03 and 0.04 ppm were detected. Following the processing path into the enclosed processing structure, many of the nuts are heat-treated for 20 minutes at 400° F within a rotating drum. This may have some effect on any residual phosphine in the nutmeat, driving it out of the product; though further research would be necessary to validate this as an exposure control procedure. Exhaust air from the heating process is vented outside.

Within the processing structure, stacked bins that had been fumigated as described in the previous evaluation were noted. These bins shared the same air parcel as the employees on the processing line. Air sampling detected phosphine in both the bin headspace (0.27 ppm) and the bulk mass of the pistachios (1.87 ppm). These concentrations were not unexpected nor were the

concentrations applicable to potential inhalation exposure. However, these results did establish that phosphine was present in the bins and in the air immediately surrounding them. The facility manager was advised that even though ambient air concentration of phosphine was non-detectable, increasing the number of treated bins stored in this area could result in detectable or even hazardous concentrations of phosphine. The Applicator's Manual explicitly states, "*The area or site must be monitored to ensure that liberation of gas from treated commodity does not result in the development of unacceptable levels of phosphine and carbon dioxide*." This would appear to require the facility manager to have a phosphine air-monitoring protocol for storage areas post-aeration.

The HDS-200C system was examined and the facility manager explained its operating procedures. Supposedly, the computer control of the phosphine/air mixing precludes operator errors that may result in explosive conditions. Any attempt to override computer-controlled mixing protocols, that lead to phosphine levels in the delivery conduit greater than 1% (lower explosive level is 1.8% by volume) will abort or otherwise discontinue the application process.

Stanislaus County

DPR industrial hygienists evaluated a nut processing facility using phosphine gas [$ECO_2FUME^{®}$] in Stanislaus County (Fong, 2004b). The hygienists inspected several storage and fumigation areas. The facility injected phosphine gas into plastic-lined bins containing nuts as described previously. The storage facilities had the capacity to hold hundreds of bins. Workers were performing various activities, unrelated to the application, in the warehouses where the nuts were stored following fumigation.

This nut-processing facility had several areas where detectable concentrations of phosphine gas were found. Of three storage structures sampled using DPR's INNOVA-ST detector, two showed detectable phosphine concentrations, ranging from 0.1 to 0.15 ppm in the ambient air. Sampling in the confined airspace between stacked bins resulted in readings as high as 0.37 ppm.

Two intermodal containers had been converted into fumigation chambers, replacing the steel doors with canvas tarpaulin covers. No phosphine was detected at the doors; however, high levels (>1.95 ppm) were discovered along the side of one of the containers. It is suspected that the floor of the container had some defect, allowing phosphine to seep out. High concentrations (up to 1.0 ppm) were also detected in the pit of an adjoining loading dock. This is believed to be related to the suspected leak in the fumigation container.

Though this facility had potential worker exposure problems with the use of phosphine gas, the storage area for the phosphine cylinders was of exemplary design. Cylinders were properly stowed and strapped, the cage-structure allowed free flow of air, the cylinders were securely locked within and there was excellent housekeeping within and around the storage area.

Mitigation measures of exhaust ventilation and/or real-time monitoring were suggested. Though a real-time phosphine detector was available at the facility, it was stored in an office desk and not in use on the day of the worksite evaluation. No other method of phosphine detection was available at the facility. Monitoring of indoor areas where both fumigation crews and other

workers have access to during fumigation, aeration and post-aeration storage is required by the Applicator's Manual, as is maintaining a log of such measurements.

DPR industrial hygienists evaluated a second nut-processing facility in Stanislaus County (Fong, 2004a). The primary purpose of this evaluation was to observe both the application procedure for a phosphine-generating material (Gastoxin®) and to review the storage area for phosphine gas cylinders (ECO_2FUME®). WHS monitoring equipment was unavailable for this evaluation.

The Gastoxin® application procedures, which occurred exterior to the processing facility, consisted of opening the material flask, pouring out the required number of tablets onto a paper filter previously placed on the nuts within each bin, then sealing the plastic tarpaulin. Only one application was observed. Though the application was very straightforward, the applicator, who was wearing a short-sleeved shirt, was in violation of the label requirement for "…loose fitting, long-sleeved shirt…" When queried as to their method for monitoring phosphine concentrations, the facility operator responded that they used Dräger colorimetric detector tubes. On close inspection of the Dräger tubes, it was discovered that their expiration date was 1998. The facility operator was advised that expired tubes are not considered valid sampling devices. Periodic air sampling of applicator's breathing zone and air parcels where unprotected workers may be present is required by the Gastoxin® Applicator's Manual.

During the walkthrough of the processing facility, it was noted that not all phosphine-treated bins were identified as such. Local agricultural staff advised the facility operator that each bin must be identified if treated.

Examination of the storage area for the ECO_2FUME® phosphine cylinders revealed a potentially unsafe storage site. A pallet full of tanks was located within the processing facility, sharing the same air parcel as the workers. This is not a recommended storage protocol, either on the label, the applicator's manual or on the MSDS. It was suggested that a well-ventilated remote storage structure be erected for cylinder storage. The facility operator concurred with the suggestion and planned to construct an outdoor storage area for the cylinders.

Fresno County

An illness event in a nut processing facility engendered a request by DPR's Enforcement Branch to provide a worksite evaluation of the facility. The fundamental cause of the illness had been processing of freshly treated nuts from bins, which had been inadequately labeled, a violation of both Title 3 CCR Section 6782 (posting of warning signs) and the Applicator's Manual (fumigation placarding). The information on the treatment time was incorrect, so when the recently treated bin was dumped into the processing hopper, all the phosphine gas within escaped into the ambient air of surrounding workers. Though this had been addressed by the time of the evaluation, Enforcement requested an industrial hygiene assessment of the facility's use of phosphine (ECO_2FUME®).

A walk-around of the processing and storage areas did not reveal any conditions of immediate health concern (Fong, 2004c). The INNOVA-ST phosphine detector did not register any phosphine in the ambient air in these areas, though placing the probe deep within a bin stack did produce a reading of 0.6 ppm. This was not unexpected, since the bins had been treated a several

days earlier. The facility manager stated they use personal air monitors for measuring handler exposure but that the company is considering the purchase and installation of a stationary monitoring system with remote sensors for phosphine.

Observation overview of worksites

Through the various worksite evaluations, we noted several label violations. However, it was also clear that the labels for the phosphine gas materials ($ECO_2FUME^{®}$ and $VAPORPH_3OS$) were not providing sufficient guidance in regards to worker health and potential phosphine exposure. Facility operators/managers did not seem to be familiar with proper procedures for monitoring airborne concentrations of hazardous materials that are introduced into their structures. These operators may also not be fully aware of the implications of concentrations of hazardous materials above and below the PEL or how to conduct TWA monitoring for worker exposure. As noted by the American Conference of Governmental Industrial Hygienists (ACGIH), allowed air concentrations of hazardous materials set by regulatory or consensus standards do not represent a fine line between healthy versus unhealthy work environments or the point at which impairment of health will occur. Rather, some workers may experience discomfort or even serious adverse effects when exposed to levels below recognized or regulatory standards. Exposure to air concentrations just below the PEL, or even at half the PEL, though not illegal, is not considered a good work practice. Concentrations of phosphine gas greater that 0.15 ppm should either be investigated and corrected (if a point source is suspected) or continuous monitoring must be implemented to prevent hazardous exposure of workers. Simple, bare compliance with the PEL may not be in the best health and safety interests of the employer or the employee.

Employers did not seem to be familiar with standard industrial hygiene practices for monitoring worker breathing zones, understand local exhaust versus general ventilation, know how to calibrate monitoring equipment, or know about alternative methods of exposure control. Though not explicitly addressed in the above-mentioned worksite evaluations, which involved direct phosphine gas applications, such problems may also apply to the phosphine-generating materials. Colorimetric tube measuring systems (e.g. Draeger) are not appropriate for application monitoring, since they are only capable of taking grab samples. Applications are dynamic events, where phosphine is constantly being released, resulting in potentially large changes in exposure over time, conditions that are not conducive to accurate assessment of worker exposure using grab sampling. Colorimetric tubes are inadequate for conditions under flux. In addition, the PEL is a time-weighted average (measured or calculated over and 8-hour period) and grab sampling cannot be used to determine PELs. Colorimetric tubes are most often appropriate for measuring air masses where the concentration of phosphine has stabilized, such as storage facilities for treated commodity that have not had any new material added in the past 24 hours.

Given that conditions in the leaking intermodal container could expose workers to potentially hazardous concentrations of phosphine, more diligent and comprehensive monitoring of phosphine throughout its use-cycle is of paramount importance. Likewise, enclosed storage of hundreds of treated bins could also lead to low-level but long-term exposure to employees working in the same air parcel. Issues like this must be included and addressed in the Fumigation Safety Program.

Mitigation of many exposure conditions should not be an unreasonable task. The primary mitigation measure should be adequate ventilation of processing and storage facilities. By the use of forced air general ventilation, local exhaust ventilation, or whole-structure exhaust ventilation, the levels of phosphine within the structures could be kept below levels of concern or even to undetectable levels. This would be the preferred method of control. Consultation with a ventilation engineer is strongly advised if this is pursued. Periodic air monitoring of structures using ventilation to control phosphine concentrations is necessary to ensure continued adequate function of the ventilation.

Approaches to risk reduction, other than forced ventilation, could include pole-barn storage of treated bins (avoiding confinement of off-gassing phosphine), equipping storage and processing areas with real-time phosphine detectors that log their data to a central control console and constantly monitor phosphine concentrations within the structure, conducting all applications outside to allow for dilution of any fugitive emissions during gas injection, and equipping all employees either directly involved with gas application or those who enter the structures where fumigated product (either by gas or by phosphine-generating materials) is stored with a personal real-time phosphine detector (if stationary detectors are not deployed).

Finally, storage of gas cylinders or phosphine-generating material containers must be in a manner that not only complies with Title 3 CCR Section 6674, but also protects personnel if there is a failure of containment. Ideally, cylinders should be stored outside, in a secured cage structure, to allow dissipation of any leakage. If cylinders are stored within a structure, either isolated from workers or within the work area, a real-time detection system must be dedicated to the storage area, to warn of leakage. Enclosed structures should also have adequate ventilation to remove any minor leakage.

Discussion

Phosphine Gas Monitoring

Personal real-time monitoring devices for applicators and other persons assisting with application of phosphine gas or phosphine-generating materials should be the primary method of monitoring worker exposure and ensuring compliance with the PEL. Real-time monitoring provides constant measurements in a work place where phosphine concentrations may change constantly, thus ensuring workers are not exposed to hazardous concentrations of phosphine. Grab samples (colorimetric tubes, like Draeger) are inadequate to capture the variability in gas concentrations. Unlike the vast majority of gasses used in agricultural fumigation, phosphine personal real-time monitors and area monitors are readily available, capable of measuring at levels critical for health and safety, robust in operation, and the personal monitors are easily and unobtrusively attached to workers' clothing. Not only do they alert the worker of excursions above the PEL, most are also capable, via internal data-loggers, of TWA calculations. In many instances, had real-time monitors been deployed in facilities using phosphides/phosphine, exposure situations that led to illness or injury might have been avoided. This is especially true in cases where handlers report noting a "garlic" odor, but are not alerted as to the real concentration of phosphine until hazardous exposure has occurred. Likewise, exposures to non-handlers, from prematurely open bins of treated commodity, within a properly monitored facility

may have been avoided had real-time monitoring equipment been installed at strategic locations (e.g. bin unloading stations). NIOSH-certified respiratory protective equipment for use in phosphine-containing atmospheres may be necessary for conditions where phosphine concentrations exceed the PEL and engineering controls are not feasible.

The practicality of remote monitoring systems has been demonstrated at a nut processing facility in Fresno County in April of 2006. This was the same facility cited earlier that had experienced a phosphine-related illness event in 2004 and had asked for an industrial hygiene consultation with WHS after the illness event. One of the suggestions made by WHS was the installation of a remote monitoring system for phosphine, which the facility brought on-line in late 2005. The system monitors phosphine concentrations in critical work areas (warehouse storage, bin dump, sizing area, shipping, manual sorting) using hardwired remote sensors. These sensors feed into a monitor/display device located outside the monitored structures. The system is designed to trigger an intermittent alarm on detection of 0.3 PPM and a continuous alarm at 0.6 PPM. Employees are trained to evacuate the structure on alarm notification. This approach to managing phosphine gas, from injection to final dissipation, serves as a model of good stewardship for this material. The company is able to track emissions of phosphine from treated bins and can potentially respond immediately to phosphine exposure events before they become hazardous conditions. This level of phosphine monitoring replicates the engineering controls found in other industries that also use phosphine (e.g.. semiconductor fabrication) and goes far in ensuring that workers are not exposed to conditions which could adversely effect their health.

Labels, Applicator's Manuals

Since 2004, WHS staff has reviewed five Applicator's Manuals for both metal phosphides and phosphine gasses and has consistently found the same shortcomings:

- The manuals do not consistently use the regulatory-defined term "permissible exposure limit (PEL)", to define acceptable limits but may use ambiguous terms such as "safe levels" or "allowable limits".

- Respiratory protection recommendations do not include any specifically defining nomenclature such as TC-14G for full-face gas mask or TC-13F for SCBA.

- Not all labels sufficiently explain the limitations of using colorimetric tubes as a monitoring device.

- Expertise in air monitoring for assessing worker exposure is assumed without defining qualifications of monitoring personnel.

- The PEL is sometimes used as an acceptable level for nearby residents. PELs are occupational exposure limits, developed for "healthy" working adult populations whose exposure periods would be defined by 8-hour workdays. As such, the use of the phosphine PEL for non-occupational exposures, which can include infants, children and

persons in ill health (possible lasting 24 hours), is inappropriate as an exposure standard for non-occupational exposure.

A model Fumigation Management Plan (FMP) developed by industry has been reviewed by WHS and is undergoing further modification in response to DPR comments. FMPs are required to be developed by fumigant users and must reflect conditions unique to the covered site. The model FMP acts as a template to remind fumigant users of the information that must be contained in the FMP. This approach, using check boxes, fill-ins and multiple choice, attempts to ensure that fumigant users have considered the environmental and worker safety conditions involved in the fumigation.

Cross Regulatory Approaches

Not only does phosphine have pesticidal properties, it also has many applications in industrial settings, especially in the semiconductor industries, where it is used as a doping agent for solid-state electronic components. It also has uses in metal recovery and sulfide processing. Cal/OSHA regulates phosphine exposure to workers primarily through the following Title 8 regulations:

- **Title 8, Section 5141: Control of harmful exposures to employees.** This regulation formally establishes the hierarchy of control (engineering/administrative/PPE) and specifies that respiratory PPE can only be used under the following conditions: (1) During the time period necessary to install or implement feasible engineering controls; (2) Where feasible engineering controls and administrative controls fail to achieve full compliance; and (3) In emergencies.
- **Title 8, Section 5155 (e): Airborne contaminates; workplace monitoring**. This is the operative part of 5155 concerning air monitoring. It requires the employer to monitor (or cause to have monitored) the work environment so that exposures to employees can be measured or calculated whenever it is reasonable to suspect that employees may be exposed to concentrations of airborne contaminants in excess of levels permitted in Section 5155(c) (the PELs).
- **Title 8, Section 5155 (e)(3):** For the adequate protection of employees, the person supervising, directing or evaluating the monitoring and control methods shall be versed in this standard and shall be competent in industrial hygiene practice.
- **Note (in Section 5155):** To facilitate the detection of conditions leading to serious overexposures, the screening of the work environment by any person authorized by the employer, using appropriate measuring devices, is encouraged.
- **Title 8, Section 5189: Process Safety Management of Acutely Hazardous Materials.** This deals with prevention of employee exposure from a catastrophic event when the hazardous material is present in the process at a Threshold Quantity (TQ), currently 100 lbs.

The above-cited sections are the primary requirements that Cal/OSHA applies to phosphine. The use of phosphine in the commodity processing industries is congruent with its use in other industries, and as such Cal/OSHA regulations may point to further actions that DPR could take in insuring worker health and safety. In particular, the primacy of engineering controls for maintaining acceptable air concentrations, the continuous use of air monitoring equipment, and

the requirement for competent persons being charged with monitoring phosphine levels should be considered.

In assessing phosphine exposure conditions, there have been recommendations that the methyl bromide permit conditions for commodity fumigation be used as a template for phosphine fumigation conditions. This may not be the best approach for phosphine. The methyl bromide requirements are prescriptive in part because of the difficulty in measuring air concentrations of this material. There are no effective real-time methyl bromide monitors available. The requirements reflect the results of several years of study by DPR and industry of various commodity use conditions, using industrial hygiene and environmental sampling, something not readily available to most commodity fumigators. The requirements also reflect a "design standard" approach to mitigation of worker exposure. Essentially, if a fumigator follows the methyl bromide requirements, worker exposure is assumed to be sufficiently mitigated. However, for phosphine, there are real time monitors capable of detection at levels associated with human health and safety risk. Because phosphine has industrial applications other than as a fumigant, monitoring of this material has been a requirement at industrial use applications. Thus for commodity use of phosphine, a "performance standard" may be used, where fumigators, by the judicious and appropriate deployment of real-time monitors, can maintain a holistic awareness of phosphine levels throughout the use cycle of the material.

Recommendations

Phosphine gas, properly controlled, is a viable alternative to methyl bromide in many fumigation conditions. The following are some recommendations to consider to ensure worker and bystander safety at and around phosphine fumigation sites.

Hierarchy of Exposure Control

For phosphine used in industries other than agriculture, Cal/OSHA requires establishment of a hierarchy of exposure control for workers. That hierarchy assigns top priority to using engineering controls as a first method of reducing potential exposure. For phosphine gas users, this can include gas-tight tank lockers, shielded or pressurized coaxial tubing and local-exhaust ventilation. Administrative controls, such as work-time restrictions, must be considered if engineering controls are not feasible, and personal protective equipment (respiratory protection) is a last resort. The agricultural industry has generally looked at exposure control in the reverse order. DPR should evaluate revising 3CCR 6780(b) to require employers to use the standard industrial hygiene hierarchy of control for work situations where fumigants are used.

Controlling Exposure at or Below the PEL

To maintain worker exposure to phosphine gas at or below the PEL, DPR should evaluate and consider the following requirements, either as regulations, permit conditions or as part of an approved Fumigation Management Plan, to augment the safety requirements found on labels or within Applicator's Manuals:

All applications must be performed either outdoors or, if within an enclosing structure where other workers may be present, the area must be monitored by real-time phosphine monitoring device(s), subject to restrictions imposed by Title 3, CCR Section 6782 (enclosures housing a

stack fumigation become fumigated enclosures; fumigant may not be released into an occupied work area).

All fumigated product must be stored such that potentially hazardous concentrations of phosphine gas cannot occur undetected. This may be accomplished by:

- Engineering controls
  - Outdoor storage,
  - Pole-barn (screened or unscreened) storage,
  - Forced-air mechanical general dilution ventilation or high-volume exhaust ventilation certified by a ventilation engineer to be sufficient to maintain phosphine concentrations below 0.3 ppm under all foreseeable loading conditions,
  - Cylinder storage should be such that leakage is not an immediate hazard to people in the work area, or should be both ventilated and monitored with real-time detectors. In this situation, colorimetric tubes may be used to establish whether an enclosed storage area has any phosphine contamination in the air before worker entry.
- Administrative controls
  - Real-time personnel monitoring devices for ***all*** persons entering the air volume of the stored product,
  - Real-time stationary remote monitoring systems, with a sufficient number of sensors strategically placed to adequately characterize potential phosphine concentrations in a worker's breathing zone for any location within the storage area that workers may be required to occupy,
  - Colorimetric detector tubes may be used to establish that a fumigated space (e.g. chamber, tarpaulin) has been adequately aerated or that active ventilation is maintaining phosphine gas concentrations from off-gassing commodity at acceptable levels.
  - Processing lines involving fumigated product may require real-time monitoring at appropriate strategic points.
  - Before bringing product that has been stored under fumigation into the processing facility, it may be necessary to confirm that fumigant concentrations have decreased to acceptable levels. Sampling of the air over the transportation system (conveyor belt, auger, etc.) can be performed to establish concentrations. This will also prevent erroneous selection of recently fumigated product.
  - If facility managers are unsure of proper procedures for monitoring phosphine gas to provide adequate protection of employees, the manager shall consult and arrange training from persons versed in label and regulatory requirements and competent in industrial hygiene practice.

Training and Licensing

The current labels and applicator's manuals require that these products only be used by persons with certified applicator license (or qualified applicator's certificate in California) or trained personnel under the direct supervision of a certified applicator. In addition, at least one certified applicator must be physically present, and this person is responsible for each fumigation. However, as noted in illness investigations, enforcement actions and workplace evaluations, these certified applicators may not have all the proper knowledge to conduct fumigations safely. Fumigation work areas present very different problems and hazards than other application situations. To ensure fumigators have the appropriate knowledge and abilities, DPR should

evaluate creating a new licensing category for fumigators. A training manual specific to fumigators would need to be developed.

Work Practice Evaluation
DPR should consider requiring a workplace or work practice investigation when concentrations of phosphine gas greater than ½ the PEL are found in work areas where people are present. The employer would be required to maintain a log of monitoring results; documentation of the workplace investigation, the findings and corrective actions taken should also be maintained in a log. This could be similar to the workplace evaluation required in the medical supervision regulations.

Compliance Assistance and Training
Outreach and training are needed to inform applicators and employers about appropriate monitoring methods, the meaning of PELs, ventilation requirements, and maintaining a safe workplace in general.

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