FUMIGANTS: PHOSPHINE AND PHOSPHINE-GENERATING COMPOUNDS

RISK CHARACTERIZATION DOCUMENT

Environmental Fate

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INTRODUCTION

Phosphine, along with methyl bromide and sulfuryl fluoride, are among several active ingredients frequently used as agricultural fumigants against insects in stored commodities. Phosphine is also used for rodent control in landscape maintenance and rights-of-way. In its use as a fumigant, application of aluminum, magnesium or zinc phosphide pellets generates phosphine gas when exposed to moisture. Phosphine gas also can be applied directly as a fumigant.

In California, phosphine and two phosphine-generating compounds (aluminum and magnesium phosphide) are used as fumigants on stored commodities. Phosphine is a compound that penetrates deeply into materials such as large bulks of grain or tightly packed materials and it diffuses quickly.

This environmental review is part of the Department of Pesticide Regulation's (DPR) risk characterization document for phosphine and phosphine-generating products. The risk assessment process was initiated for phosphine and phosphine-generating compounds for the following two reasons:

- California law requires DPR to list in regulation as toxic air contaminants (TACs) those pesticides previously identified under federal law as hazardous air pollutants (HAPs) (TAC Control and Identification Act). Federal law classifies phosphine as a HAP (42 Code of Federal Regulations [CFR] §7412). Therefore, in 2003 DPR listed phosphine and phosphine-generating compounds as TACs in regulation (3 CCR §6860). Chemicals the federal government classifies as HAPs are administratively listed as TACs and not subject to the evaluation and control provisions of the TAC Identification and Control Act. However, they are subject to reevaluation and possible restrictions under other statutory mandates. In 2007 and 2008, DPR requested ARB to monitor for phosphine to determine the levels of phosphine in air from an agricultural application, as required by FAC §14022(c) (TAC Control and Identification Act; Warmerdam 2007 & 2008).
- They fall under the Birth Defect Prevention Act-mandated review of toxicology data for all active ingredients, which requires DPR to initiate a risk assessment for registered pesticide products containing the active ingredient phosphine and the phosphine generating active ingredients, aluminum phosphide and magnesium phosphine (Birth Defect Prevention Act; DPR 2007 & 2011).

This review summarizes the scientific literature about the environmental fate, physical and chemical properties, and DPR's databases about specific uses and formulations of phosphine and phosphine-generating products in California.

However, the review does not address zinc phosphide. Zinc phosphide is used to control rodents in agricultural and residential settings. It converts to phosphine gas in the presence of moisture and acid in the stomach. Due to its formulation (i.e., a solid pellet, tablet or cake) and method of application (inside rodent burrows), and its effectiveness as a rodenticide only when ingested, one would expect exposure to be low (US Environmental Protection Agency [EPA] 1998b). Therefore, risk to humans, fish and wildlife, and the environment from these baits would be negligible, so zinc phosphide products are not included in this review.

2. PHYSICAL AND CHEMICAL DESCRIPTION

Aluminum and magnesium phosphide exist as yellowish to dark grey and chartreuse crystals, respectively (World Health Organization [WHO] 1988). These solids are stable when dry. However, they react with water as shown below to produce phosphine gas (Bond, 1984).

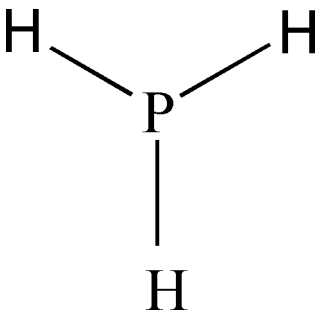
$AlP + 3H_2O \rightarrow PH_3 + Al(OH)_3$

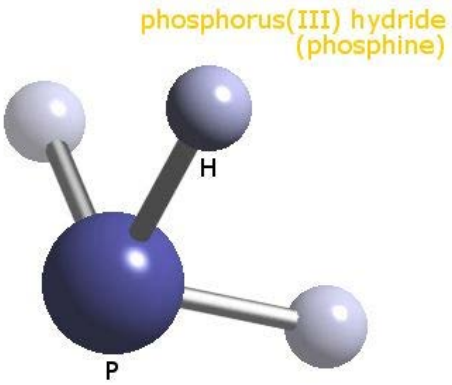
$Mg_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Mg(OH)_2$

Phosphine gas in its pure form is odorless and colorless. Technical grade phosphine, due to impurities from the manufacturing process, has an odor similar to garlic or decaying fish (Fluck 1976; International Programme on Chemical Safety [IPCS] 1997). Figure 1 shows the structure of phosphine.

Table 1 lists some physical and chemical properties of aluminum phosphide, magnesium phosphide and phosphine. In addition to the chemical properties shown in Table 1, phosphine reacts with copper and precious metals (Bond 1984). It is also a flammable gas, igniting spontaneously in air.

Figure 1. Structure of phosphine gas **(**3D structure: WebEments.com 2012**)**





Phosphine is a triagonal pyramidal molecule with C_{3v} molecular symmetry. The length of P-H bond is 1.42 A^0, the H-P-H bond angles are 93.5^0.

Table 1. Physical and chemical properties of aluminum phosphide, magnesium phosphide and phosphine

	Aluminum phosphide	**Magnesium phosphide**	**Phosphine**
Property	Aluminum phosphide	Magnesium phosphide	Phosphine gas
Common name	Phostoxin	Magtoxin	Hydrogen phosphide Phosphorus trihydrite
CAS Registry number[1]	20859-73-8	12057-74-8	7803-51-2
Chemical family	Inorganic phosphide	Inorganic phosphide	Inorganic phosphide
Physical state[1]	Solid	Solid	Gas
Color	Greenish gray[2]	Grey[3]	Colorless
Odor	Not available	Not available	Garlic, decomposing fish
Molecular formula	AlP	Mg_3P_2	PH_3
Molecular weight (g/mol)	58	135	34
Boiling Point at 1 atm (^{0}C)	>1,000[2]	> 1,000[3]	-87.7[4]
Melting point (^{0}C)	>1,000[2]	> 1,000[3]	-134[4]
Relative density (g/cm^3) (water = 1)	2.9[2]	2.1[3]	0.8[4]
Solubility in water (ml/100 ml at 17 ^{0}C)	Insoluble, reacts with water to form PH_3[2]	Insoluble, reacts[3]	26[4]
Octanol-water partition coefficient (K_{ow})	Not available	Not available	-0.271 (log L/kg)[5]
Diffusion coefficient in water ($cm^2 \cdot s^{-1}$)	Not available	Not available	1.82e-005[5]
Diffusion coefficient in air ($cm^2 \cdot s^{-1}$)	Not available	Not available	0.381[5]
Henry's Law Constant ($atm \cdot m^3/mol$ at 25 ^{0}C)	Not available	Not available	2.44 x 10^{-2} [6]
Vapor pressure (mm Hg at 25 ^{0}C)	0[2]	0[3]	31388[5]
Relative vapor density (air = 1)	Not available	Not available	1.17[7]

[1]DPR 2012a & b
[2]DEGESCH America, Inc. 2011
[3]DEGESCH America, Inc. 2010
[4]IPCS 1997
[5]Groundwater Services, Inc. 2010
[6]Hazardous Substances Data Bank 2012
[7]WHO 1988

3. REGULATION

Table 2 shows the years aluminum phosphide, magnesium phosphide, and phosphine were first registered in the US and California (US EPA 1998a & b; US EPA 1999; DPR 2012c).

Table 2. Years aluminum phosphide, magnesium phosphide and phosphine were first registered in the US and California

	Year registered	
Compound	**US**	**CA**
Aluminum phosphide	1958	1958
Magnesium phosphide	1979	1979
Phosphine	1999	2001

At the federal level, registered aluminum and magnesium phosphide and phosphine gas products fall under provisions of a Memorandum of Agreement (MOA) between registrants and the US EPA (2000 &, 2004). The major requirements of the MOA include site-specific fumigation management plans, incident reporting to US EPA, monitoring studies, establishment of worker exposure limits, development of training and certification programs and other label modifications. All phosphine and phosphine-gas generating products are federally classified as "Restricted Use Materials" (due to the high acute inhalation toxicity of phosphine gas), which limits their use to certified private or certified commercial applicators.

In California, aluminum phosphide, magnesium phosphide and phosphine are also restricted materials. With certain exceptions, restricted materials may be purchased and used only by or under the supervision of a certified commercial or private applicator under a permit issued by the County Agricultural Commissioner. Permits are time- and site-specific, and may include use practices to reduce adverse effects. [3 CCR §6400(e) & §6412(a)(3)]

In 2003, DPR listed phosphine and phosphine-generating compounds in regulation as TACs (3 CCR §6860), which is one of the factors that triggered monitoring and may lead to changes in use.

4. USE PROFILE

Many phosphine and phosphine-generating products are used in California. Currently, 27 products contain or produce phosphine gas with 20 of the products containing aluminum phosphide, 5 of the products containing magnesium phosphide. Two of the products consist of pressurized gas mixtures containing phosphine (Table 3) (DPR 2012d).

Table 3. Registered phosphine and phosphine-generating products in California, their formulations, percent active ingredient t(a.i.), and registration number as of December 2012 (DPR 2012d).

Active Ingredient	Formulation	A.I. (%)	Registration Number
Aluminum phosphide			
Fumitoxin Tablets	Tablet	55	72951-1-ZA
Fumitoxin Pellets	Pellets	55	72959-2-ZA
Weevil-cide Tablets	Tablets	60	70506-13-AA
Degesch Phostoxin Tablets-R	Tablets	55	72959-4-ZB
Degesch Phostoxin Prepac Rope	Gas permeable blister packs	55	72959-8-AA
Degesch Phostoxin Pellets	Pellets	55	72959-5-AA
Degesch Phosphine Tablet Prepac	Tablets	55	72959-9-AA
Detia Fumex	Gas permeable bags	57	72959-10-AA
Detia Phos Pellets	Pellets	55	72959-5-ZA
Detia Phos Tablets	Tablets	55	72959-4-ZA
Fumitoxin Pellets	Pellets	55	72959-2-ZA
Gastoxin Fumigation Pellets	Pellets	57	43743-2-AA
Gastoxin Fumigation Sachet Chain	Sachets	57	43743-3-ZA
Gastoxin Fumigation Sachet	Sachets	57	43743-3-AA
Gastoxin Fumigation Tablets	Tablets	57	43743-1-AA
Phosfume Fumigation Tablets	Tablets	60	70506-13-AA-1015
Quickflo-R Granules	Granules for Generator	77.5	70506-69-AA
Weevil-Cide Gas Bags	Gas permeable bags	60	70506-15-AA
Weevil-Cide Pellets	Pellets	60	70506-14-AA
Weevil-Cide Tablets	Tablets	60	70506-13-AA
Magnesium phosphide			
Degesch Fumi-Cel	Trays	56	72959-6-AA
Degesch Fumi-Strip	Strip	56	72959-6-ZA
Degesch Magtoxin Granules	Granules	94.6	72959-11-AA
Degesch Magtoxin Prepac Spot Fumigant	Gas permeable blister packs	66	72959-7-AA
Magnaphos Gas Bags	Gas permeable bags	66	70506-17-AA
Gaseous phosphine			
Eco2Fume	Dilute gas	2	68387-7-AA
Vaporph3os Phosphine Fumigant	Concentrated gas	99.3	68387-8-AA

4.1 Formulations and Methods of Application

Table 3 lists the formulations for phosphine and phosphine-generating products. Phosphine can be applied directly by injection or by way of aluminum phosphide or magnesium phosphide, which are solids that react with moisture in the air to generate phosphine gas.

Whether the pesticide is applied as a gas or as a solid metal phosphide in the fumigation structure, the fumigation typically lasts a few days to a month, depending on the type of structure and the ambient temperature. At the end of the fumigation period, the remaining phosphine gas in the chamber is vented out to the ambient air (Adler 2010; Dieterich et al. 1967).

Table 4 lists the general application rates for phosphine and phosphine-generating products registered for use in California (Cytec Industries, Inc. 2003; US EPA 1998a).

Table 4. General application rates for Al and Mg phosphide and phosphine in spaces (e.g., mills, warehouses, dried fruits and nuts) and bulk stored commodities (e.g., vertical storages, tanks, railcars and barges).

Product	**Application rate (g phosphine / 1,000 ft ^{3})**	
	Lowest	***Highest***
Aluminum phosphide	20	180
Magnesium phosphide	20	180
Phosphine	8	20

4.2 Use

Aluminum and magnesium phosphide fumigants are used primarily to control insects in stored grain and other agricultural commodities (US EPA 1998a). They are also used to control burrowing rodents in outdoor agricultural and other non-domestic areas, e.g., landscape maintenance and rights-of-way. The fumigants are restricted to use by specially trained pesticide applicators and in only narrow circumstances.

Phosphine is widely used indoors to control a wide range of insects for non-food and non-feed commodities (e.g., cotton, wool, leather, and tobacco) stored in sealed containers or structures (US EPA 1999).

Table 5 shows reported annual use of phosphine and phosphine-generating fumigants from 2005 through 2010 (DPR 2012d). In 2010, 109,656 pounds active ingredient phosphine were applied in California.

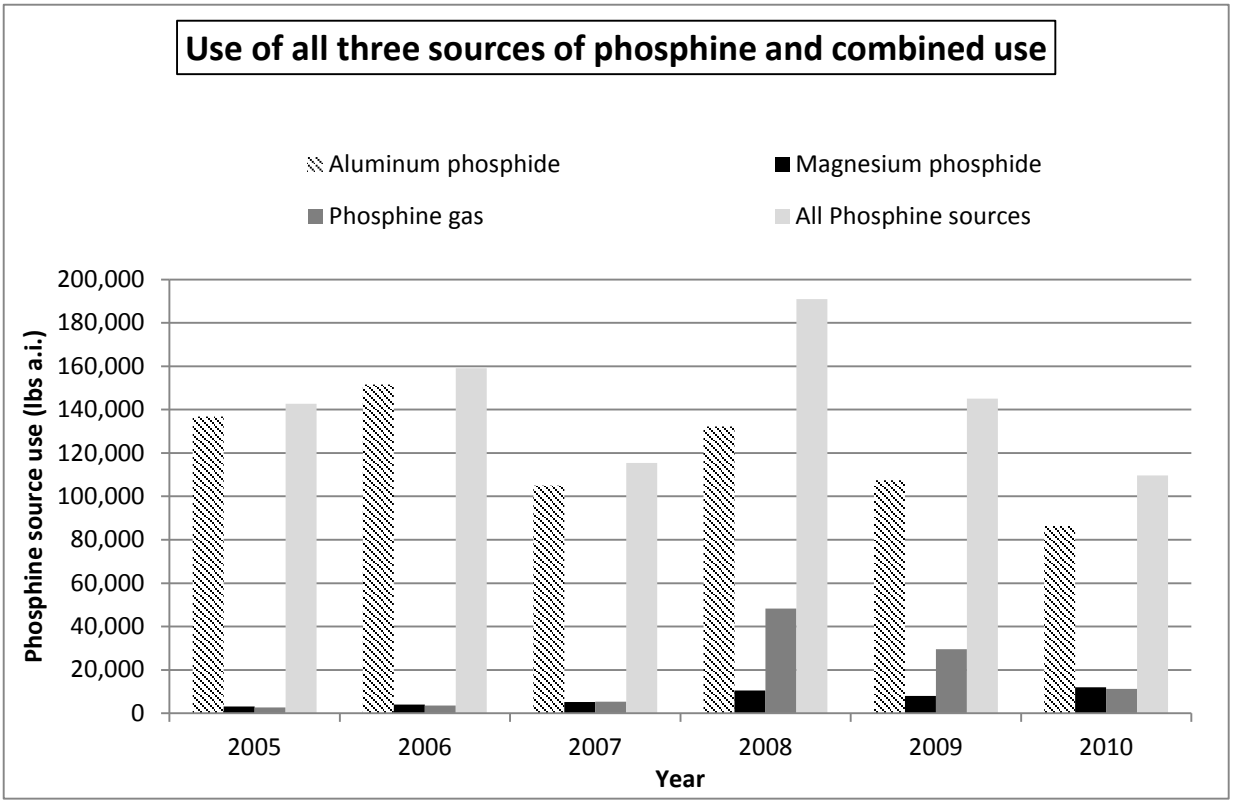
Table 5. Annual use of phosphine-generating fumigants and phosphine in California (2005 – 2010)

Year	**Aluminum phosphide**	**Magnesium phosphide**	**Phosphine**	**Total**
	Use (Pounds a.i.)			
2005	136,829	3,144	2,699	**142,672**
2006	151,631	3,931	3,491	**159,053**
2007	104,994	5,132	5,286	**115,412**
2008	132,246	10,506	48,243	**190,995**
2009	107,487	8,009	29,527	**145,023**
2010	86,342	12,014	11,210	**109,656**
Total	**718,920**	**42,735**	**100,557**	**882,212**

4.2.1 Aluminum and Magnesium Phosphide

In general, aluminum phosphide use data follow the patterns seen with the total phosphine use data, since over 80% of the total use data come from aluminum phosphide use (Table 5 & Figure 2).

Figure 2: Annual use of phosphine generating products in California from 2005 to 2010 (lbs. a.i.) (DPR, 2012d).



From the above chart it is evident that the total phosphine use was generally stable, except for the spike seen in 2008. The last three years show a slight decreasing trend in use.

Table 6 shows the use data of three groups of phosphine-generating commercial products. Aluminum phosphide-based products dominate the phosphine pesticide market, and Fumitoxin tablets and pellets are the most used (annual average of about 39,000 and 20,000 pounds active ingredient [a.i.], respectively). Magnesium phosphide is a distant second with about 7,000 pounds a.i. used.

Table 6. Annual use of phosphine-generating brand-named products in California (2005-2010) (DPR 2012d).

Active Ingredient	Pounds A.I. applied					
	Year					
	2005	**2006**	**2007**	**2008**	**2009**	**2010**
Aluminum phosphide products						
FUMITOXIN TABLETS	36,989	43,007	37,474	53,666	30,599	32,480
FUMITOXIN PELLETS	14,507	18,120	18,992	25,007	28,657	16,275
WEEVIL-CIDE TABLETS	8,310	15,519	10,020	10,481	11,752	12,264
DEGESCH PHOSTOXIN TABLETS-R	12,272	9,455	4,465	8,521	4,586	5,815
FUMITOXIN NEW COATED TABLETS-R	9,721	9,498	7,997	4,455	3,856	3,210
PHOSTOXIN NEW COATED TABLETS	10,196	6,714	3,027	8,273	1,431	2,270
PHOSTOXIN COATED PELLETS	18,396	4,417	3,144	3,052	1,877	641
DEGESCH PHOSTOXIN PELLETS	7,880	10,827	6,438	1,936	1,131	1,541
DEGESCH PHOSTOXIN TABLET PREPAC	2,334	4,054	2,763	5,738	2,035	2,367
GASTOXIN FUMIGATION PELLETS	492	16,644	548	453	302	312
Aluminum phosphide products total	**136,829**	**151,022**	**104,994**	**132,246**	**107,487**	**86,342**
Magnesium phosphide products						
DEGESCH FUMI-CEL	1,885	3,053	3,431	9,425	6,006	10,769
DEGESCH FUMI-CEL PLATES	574	253	413	172	243	265
DEGESCH FUMI-STRIP	576	406	1,172	396	1,592	282
DEGESCH MAGTOXIN GRANULES	0	0	0	4	124	377
DEGESCH MAGTOXIN PELLETS	14	44	0	8	0	0
DEGESCH MAGTOXIN PELLETS-PREPAC	1	0	0	0	0	0
DEGESCH MAGTOXIN PREPAC SPOT FUMIGANT	94	175	113	501	38	27
DEGESCH MAGTOXIN TABLETS-R	0	0	3	0	5	1
MAGNAPHOS GAS BAGS	0	0	0	0	0	294
Magnesium phosphide products total	**3,144**	**3,931**	**5,132**	**10,506**	**8,009**	**12,014**

Table 7 summarizes the annual use data for aluminum phosphide by top ten counties. Leading aluminum phosphide use counties for this six-year period are Fresno, Kern, Los Angeles and San Joaquin Counties.

Table 7. Annual use of aluminum phosphide products by top ten counties (lbs. a.i.) (2005-2010) (DPR 2012d).

County (Co.)	**Pounds A.I.**							
	Year						***County-by-Year Average***	***County Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**		
Fresno	30,332	21,418	13,032	13,295	20,242	19,401	19,620	**117,720**
Kern	9,387	14,090	12,724	14,378	9,746	1,746	10,345	**62,070**
Los Angeles	6,505	9,598	9,655	15,426	7,013	4,364	8,760	**52,561**
San Joaquin	5,515	20,301	4,237	4,336	7,179	1,831	7,233	**43,400**
Orange	8,129	3,964	4,353	10,389	5,751	7,449	6,673	**40,036**
Stanislaus	7,290	7,711	5,106	3,796	3,459	3,291	5,109	**30,652**
Colusa	5,124	3,334	4,511	4,963	5,789	6,330	5,009	**30,052**
Yolo	6,036	6,949	5,563	3,970	2,590	4,806	4,986	**29,913**
Riverside	5,078	8,484	4,925	6,073	3,151	2,115	4,971	**29,826**
San Bernardino	2,745	9,782	5,350	4,655	2,384	1,806	4,454	**26,722**
Top ten county total	**86,140**	**105,631**	**69,456**	**81,279**	**67,304**	**53,140**	**77,159**	**462,952**
Top ten county average	**8,614**	**10,563**	**6,946**	**8,128**	**6,730**	**5,314**	**7,716**	**46,295**
All counties' total	**136,829**	**151,022**	**104,994**	**132,246**	**107,487**	**86,342**	**119,820**	**718,920**

The top ten aluminum phosphide use sites for this six-year period are given in Table 8. Landscape Maintenance, Commodity Fumigation and Almonds, respectively, are the leading use sites.

Table 8. Top ten use sites of aluminum phosphide products in California by year (2005 – 2010) (lbs. a.i) (DPR 2012d).

Site	**Pounds A.I.**						
	Year						***Site Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**	
Landscape maintenance	44,333	42,604	35,450	54,673	24,158	23,758	**224,976**
Commodity fumigation	15,905	31,333	12,307	14,715	10,531	11,332	**96,123**
Almond	13,895	18,195	12,960	11,310	9,839	10,540	**76,739**
Fruits (dried or dehydrated)	11,715	11,847	5,014	4,170	9,673	7,674	**50,092**
Pistachio	3,690	5,938	8,285	13,736	12,048	3,102	**46,799**
Structural pest control	9,253	8,031	6,584	8,988	2,931	3,108	**38,895**
Vertebrate pest control	7,624	11,546	2,646	3,365	10,017	3,676	**38,874**
Fumigation (other)	5,996	6,959	4,180	4,850	8,106	4,828	**34,919**
Rights of way	3,277	1,980	5,582	3,753	1,017	2,890	**18,499**
Grapes	2,320	2,353	3,687	2,822	3,887	2,506	**17,575**
Year total	**136,829**	**151,022**	**104,994**	**132,246**	**107,487**	**86,342**	**718,920**

The average month-by-county use data for aluminum phosphide is given in Table 9. October is the leading use month and most of the leading use counties had their biggest use on this month. The use in Fresno County is spread over the months, more than in Kern, Los Angeles, or San Joaquin Counties.

Table 9. Average monthly use of aluminum phosphide products by top ten counties during 2005 through 2010 (DPR 2012d).

County	Pounds A.I.												
	Month												*County Total*
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	
Fresno	2,884	1,115	1,679	1,310	1,145	1,056	1,110	1,519	2,824	2,391	1,448	1,113	**19,620**
Kern	708	349	568	1,311	688	606	675	1,076	1,840	1,794	394	335	**10,345**
Los Angeles	538	512	1,175	594	648	575	531	1,438	513	580	1,158	498	**8,760**
San Joaquin	317	213	359	352	416	1,099	193	189	329	3,005	431	329	**7,233**
Orange	347	468	881	832	517	828	388	405	631	494	485	397	**6,673**
Stanislaus	425	263	491	378	240	300	361	507	640	742	473	291	**5,109**
Colusa	96	66	208	581	811	703	797	547	549	282	301	67	**5,009**
Yolo	341	341	291	446	325	362	357	669	823	361	401	268	**4,986**
Riverside	388	375	511	447	478	631	333	290	334	327	474	382	**4,971**
San Bernardino	306	273	323	881	369	389	426	384	359	286	284	172	**4,454**
Average top ten county use total	**6,350**	**3,974**	**6,486**	**7,133**	**5,637**	**6,548**	**5,171**	**7,024**	**8,841**	**10,262**	**5,850**	**3,853**	**77,159**
Average monthly use of all counties	**8,241**	**6,761**	**10,090**	**11,289**	**9,045**	**10,448**	**8,498**	**10,856**	**13,571**	**14,554**	**10,396**	**6,043**	**119,820**

The average monthly use of aluminum phosphide by site is given in Table 10. Landscape Maintenance is the leading average use site, and the use is evenly distributed over the months for this site. Most use is in October and September. Monthly use of aluminum phosphide by site (Table 10) follows almost the same pattern exhibited by all phosphine sources (Table 5 and Figure 2). The same three sites—landscape maintenance, commodity fumigation, and almond—are among the leaders for both source types.

Table 10. Average monthly use of aluminum phosphide products (lbs. a.i.) by top ten use sites (2005-2010) (DPR 2012d).

Site	**Pounds A.I.**												
	Year												***Site Total***
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	
Landscape maintenance	2,337	2,680	3,824	5,139	2,728	3,499	2,323	3,794	2,826	3,177	3,099	2,070	**224,976**
Commodity fumigation	507	504	935	648	1,018	764	1,191	1,764	2,764	4,312	1,215	398	**96,123**
Almond	507	509	761	826	646	380	487	1,316	2,872	2,736	1,076	655	**76,739**
Fruits (dried or dehydrated)	819	597	944	595	641	633	765	683	591	775	685	621	**50,092**
Pistachio	512	133	514	724	939	552	659	476	1,290	1,070	493	430	**46,799**
Structural pest control	668	495	450	408	731	1,029	352	310	557	663	550	269	**38,895**
Vertebrate pest control	392	438	715	1,121	433	434	352	406	189	179	1,486	333	**38,874**
Fumigation, other	242	292	243	411	338	429	413	821	998	679	541	412	**34,919**
Rights of way	187	135	487	245	209	456	407	301	204	94	213	146	**18,499**
Grapes	204	258	300	305	352	292	220	229	157	245	245	122	**17,575**
Total top ten monthly averages	**6,376**	**6,042**	**9,173**	**10,421**	**8,035**	**8,468**	**7,169**	**10,099**	**12,447**	**13,930**	**9,603**	**5,456**	
Total use in top ten counties for all six years	**49,445**	**40,563**	**60,539**	**67,734**	**54,268**	**62,690**	**50,987**	**65,138**	**81,425**	**87,325**	**62,375**	**36,256**	**718,920**

The annual use of magnesium phosphide products in top ten counties from 2005 to 2010 is given in Table 11. Yolo, Fresno and Solano are the top three use counties. County of Yolo had a more or less even distribution in use for this period. A large use in 2008 pushed the total use to second place in Fresno County. For Solano County, one large use year in 2010 pushed the average use up in this county.

Table 11. Magnesium phosphide use by top ten counties (lbs. a.i.) during years 2005-2010 (CDPR, 2012d).

County	**Pounds A.I.**							
	Year						***County Average***	***County Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**		
Yolo	615	765	1,750	1,328	2,532	2,168	1,526	**9,160**
Fresno	446	40	13	5,722	26	382	1,105	**6,630**
Solano	0.2	5	0	0	0	6,458	1,077	**6,464**
San Joaquin	240	126	1,026	718	487	309	484	**2,908**
Colusa	238	140	202	410	925	821	456	**2,739**
Sacramento	205	1,406	557	485	0	1	442	**2,656**
Stanislaus	119	33	48	79	2,211	101	432	**2,592**
Butte	329	288	218	414	605	335	365	**2,189**
Glenn	272	242	344	228	522	512	353	**2,122**
Merced	81	111	224	179	173	161	155	**930**
Year average	**255**	**316**	**438**	**957**	**749**	**1126**	**640**	
Year total	**3,144**	**3,931**	**5,132**	**10,506**	**8,009**	**12,014**		**42,735**

Fumigation (other), commodity fumigation, and walnut fumigation were the top ten use sites (Table 12), The highest amount of use was in 2010. The use in commodity fumigation is generally even except for in 2009, which gave about 1.5 times the average yearly use for this site. The use reported in walnuts in 2008 pushed the average use to third place.

Table 12. Top ten use sites of magnesium phosphide products in California by year (2005-2010, lbs. a.i.) (CDPR, 2012d).

Site	**Pounds A.I.**							
	Year						***Site Average***	***Site Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**		
Fumigation, other	535	1,779	1,281	1,926	1,059	6,794	2,229	**13,377**
Commodity fumigation	1329	1,204	1,945	1,011	3,205	2,859	1,926	**11,556**
Walnut	637	161	196	5,745	436	359	1,256	**7,536**
Almond	118	253	1,037	1,139	2,677	439	944	**5,664**
Structural pest control	156	52	201	411	366	119	217	**1,306**
Rice		143	210	29	8	731	187	**1,122**
Prune	156	176	5	35	156	260	131	**791**
Rights of way	17	30	117	144	0	51	60	**360**
Peach	0	0	0	0	0	293	49	**293**
Fruits (dried or dehydrated)	12	65	58	29	69	38	45	**274.2**
Top ten sites' average	**296**	**386**	**505**	**1,047**	**797**	**1,194**	**704**	
Year total of all sites	**3,144**	**3,931**	**5,132**	**10,506**	**8,009**	**12,014**		**42,735**

In Table 13, the top three counties in average use for magnesium phosphide by county and month are Yolo, Fresno, and Solano, in that order. The second highest user, Fresno, produced the highest average monthly use (947 pounds a.i.) in October.

Table 13. Average monthly use of magnesium phosphide products by top ten counties from 2005 to 2010 (lbs. a.i.) (CDPR, 2012d).

County	**Pounds A.I.**													
	Month												***County Average***	***County Total***
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**		
Yolo	73	77	69	180	91	142	110	341	146	131	130	33	127	**9,160**
Fresno	0	0	0	22	3	1	3	7	64	946	5	49	92	**6,630**
Solano	0	0	0	0	1073	0	0	0	0	0	0	0	89	**6,464**
San Joaquin	49	40	31	12	29	25	21	48	51	73	56	45	40	**2,908**
Colusa	17	16	12	18	91	44	60	47	99	11	23	14	38	**2,739**
Sacramento	51	51	47	30	16	25	1	16	71	56	42	32	36	**2,656**
Stanislaus	1	2	4	1	2	4	2	6	2	399	2	1	36	**2,592**
Butte	28	32	36	45	13	49	26	16	14	35	41	27	30	**2,189**
Glenn	9	5	2	3	3	0	7	0	52	133	123	14	29	**2,122**
Merced	3	3	3	3	2	3	9	24	55	21	14	8	12	**930**
Monthly average	**39**	**38**	**34**	**53**	**220**	**49**	**40**	**84**	**93**	**301**	**73**	**37**	**88**	
Total use in all counties	**1,523**	**1,501**	**1,407**	**2,111**	**8,288.8**	**2,149**	**1,738**	**3,310**	**3,755**	**11,872**	**3,360**	**1,717**		**42,735**

With respect to month by site distribution (Table 14), fumigation (other), commodity fumigation and walnuts were the leading use sites. Monthly average use of over 1,118 pounds a.i. in May for fumigation (other) gave the largest use. Commodity fumigation had a more or less even distribution through the months.

Table 14. Average monthly use of magnesium phosphide by top ten sites (lbs. a.i.) from 2005 to 2010 (CDPR, 2012).

Site	**Pounds A.I.**													
	Month												***Site Average***	***Site Total***
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**		
Fumigation (other)	63	76	89	75	1,118	79	86	95	174	204	125	44	186	**13,377**
Commodity fumigation	119	110	88	216	133	167	115	375	188	163	152	99	161	**11,556**
Walnut	8	4	3	2	1	0	0	0	74	1,042	106	15	105	**7,536**
Almond	44	41	42	28	31	23	19	19	105	504	63	23	79	**5,665**
Structural pest control	8	2	5	4	49	40	24	9	9	18	28	22	18	**1,307**
Rice	0	2	2	9	40	18	24	15	66	3	6	2	16	**1,123**
Prune	0	0	0	0	0	0	6	5	1	32	65	22	11	**791**
Rights of way	8	9	3	3	0	6	6	14	3	3	0	5	5	**361**
Peach	0	0	0	0	0	0	0	0	0	0	0	49	4	**294**
Fruits (dried or dehydrated)	0	3	0	13	5	15	2	0	0	0	1	5	4	**274**
Monthly average of top ten sites	**25**	**25**	**23**	**35**	**138**	**35**	**28**	**53**	**62**	**197**	**55**	**29**	**59**	
Monthly total for all sites	**1,523**	**1,502**	**1,407**	**2,111**	**8,289**	**2,149**	**1,739**	**3,310**	**3,755**	**11,872**	**3,360**	**1,717**		**42,735**

4.2.2 Phosphine

Tables 5, 6 and 15 summarize the annual use of phosphine gas products from 2005 through 2010; a total of 100,000 lbs. a.i. was applied during this period. The large use of Vaporph3os on almonds in 2008 (in Sacramento County) gave an unusual spike in general use for this period. In 2009, the same product was used in a relatively large amount on two different sites (Almonds, and Regulatory Pest Control).

Table 15. Annual use of phosphine gas products in California (2005-2010)

	Pounds A.I.					
	Year					
	2005	**2006**	**2007**	**2008**	**2009**	**2010**
Phosphine gas products						
Eco2Fume	1,706	2,082	2,586	3,519	3,627	4,189
Vaporph3os	994	1,409	2,699	44,724	25,900	7,101
Phosphine gas product total	**2699**	**3,491**	**5286**	**48,243**	**29,527**	**11,290**

Table 16 shows the annual use of phosphine gas products in the ten counties that used the most. The counties of Sacramento, followed by Stanislaus and Kern are the leading use counties. In 2010, Stanislaus County was the highest use county with over 3,500 lbs. of phosphine a.i. applied (Table 16).

Table 16. Annual use of phosphine gas products in California by the top ten counties from 2005-2010.

County	**Pounds A.I.**						
	Year						***County Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**	
Sacramento	0	11	32.0	37,668	16,106	1,036	**54,854**
Stanislaus	220	286	2,171	4,490	8,272	3,550	**18,991**
Kern	365	993	908	3,208	2,081	2,999	**10,557**
Fresno	459	640	315	466	958	983	**3,823**
San Joaquin	624	653	703	661	216	349	**3,209**
Butte	197	213	256	447	252	946	**2,313**
Merced	114	177	264	325	524	412	**1,819**
Glenn	61	95	213	368	455	409	**1,603**
Yolo	436	131	142	114	217	165	**1,206**
Kings	108	131	117	67	106	74	**605**
Top ten use total	**2,586**	**3,335**	**5,124**	**47,818**	**29,191**	**10,929**	**98,984**
Total use in all counties	**2,699**	**3,490**	**5,285**	**48,243**	**29,527**	**11,290**	**100,536**

From 2005 to 2010, the three sites with the most phosphine use were: almonds (an average of over 10,000 lbs. a.i.), regulatory pest control (one large use of over 15,000 lbs. a.i in 2009) and commodity fumigation (an average over 1,000 lbs. a.i) (Table 17).

Table 17. Annual use of phosphine gas by top ten sites in California by year (2005-2010)

Site	**Pounds A.I.**						
	Year						***Site Total***
	2005	**2006**	**2007**	**2008**	**2009**	**2010**	
Almond	929	1,791	2,860	43,154	10,061	3,026	**61,821**
Regulatory pest control	0	0	0	0	15,950	1	**15,951**
Commodity fumigation	695	510	576	757	1,128	2,952	**6,617**
Pistachio	107	149	369	2,164	1,079	1,952	**5,820**
Fumigation (other)	103	102	492	1,012	279	2,087	**4,075**
Walnut	361	604	585	543	286	501	**2,880**
Structural pest control	331	107	117	165	159	202	**1,080**
Dried fruit	86	100	0	106	289	192	**774**
Tomato, processing	18	0	50	113	160	167	**509**
Tomato	26	93	110	55	61	72	**416**
Top ten sites by year total	**2,657**	**3,456**	**5,159**	**48,069**	**29,451**	**11,152**	**99,943**
All sites' year total	**2,699**	**3,491**	**5,286**	**48,243**	**29,527**	**11,291**	**100,537**

Traditionally, October and November are months (6-year average) when most of the use of phosphine gas occurs in the top ten counties (Table 18).

Table 18 Average monthly use of phosphine gas products by top ten counties during 2005 through 2010 (DPR 2012d).

County	Pounds A.I.													
	Month												*County Average*	*County Total*
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**		
Sacramento	17	46	1,550	75	1,008	21	8	9	24	5,034	1,316	35	762	**54,854**
Stanislaus	1,068	133	95	86	85	63	33	129	326	467	466	214	264	**18,991**
Kern	185	161	75	58	84	301	61	139	166	253	170	106	147	**10,558**
Fresno	43	46	47	41	39	48	37	47	69	96	80	44	53	**3,823**
San Joaquin	13	23	9	10	15	18	23	23	23	189	169	21	45	**3,210**
Butte	19	5	48	42	11	24	20	53	32	39	63	29	32	**2,314**
Merced	21	15	14	15	29	15	15	20	39	60	48	13	25	**1,819**
Glenn	11	18	19	16	16	17	17	20	49	32	28	25	22	**1,604**
Yolo	16	7	8	8	12	8	8	14	85	17	12	4	17	**1,191**
Kings	1	4	12	12	17	6	14	14	5	8	7	2	8	**605**
Monthly average	**139**	**46**	**188**	**36**	**131**	**52**	**24**	**47**	**82**	**620**	**236**	**49**	**137**	
Total of all counties	**8,520**	**2,810**	**11,341**	**2,258**	**8,010**	**3,224**	**1,465**	**2,936**	**5,114**	**37,409**	**14,325**	**3,093**		**100,537**

The month with the highest reported average use was October (Table 19). As stated previously, the majority of the use of phosphine gas products is on Almonds.

Table 19. Average monthly use of phosphine gas products by top ten use sites (2005 through 2010) (DPR 2012d).

Site	Pounds A.I.												
	Month												***Site Total***
	JAN	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	
Almond	1,126	201	142	128	145	354	88	202	436	5,563	1,679	238	**61,821**
Regulatory pest control	0	0	1,542	63	996	11	0	0	0	36	11	0	**15,951**
Commodity fumigation	68	68	81	83	60	49	56	102	187	115	146	87	**6,617**
Pistachio	148	129	54	35	75	57	51	54	73	112	122	61	**5,820**
Fumigation (other)	19	15	14	18	25	21	10	76	68	116	215	82	**4,075**
Walnut	5	10	5	11	3	3	2	3	21	229	168	20	**2,880**
Structural pest control	33	14	10	10	12	10	6	15	20	27	15	8	**1,080**
Dried fruit	9	11	14	10	2	13	15	12	17	16	6	4	**774**
Tomato, processing	7	11	13	6	6	10	2	2	7	6	11	4	**509**
Tomato	4	1	3	7	5	3	12	9	3	10	6	7	**416**
Top ten sites' monthly average use	**142**	**46**	**188**	**37**	**133**	**53**	**24**	**48**	**83**	**623**	**238**	**51**	
Total of all sites by month	**8,520**	**2,810**	**11,341**	**2,258**	**8,010**	**3,224**	**1,465**	**2,936**	**5,114**	**37,409**	**14,325**	**3,093**	**100,537**

5. ENVIRONMENTAL FATE AND PERSISTENCE

The most likely routes of exposure to humans, fish, wildlife, and plants include air, water, and soil. Atmospheric exposure is not considered to be a significant route of exposure. In general, aluminum and magnesium phosphide may degrade rapidly to aluminum hydroxide, magnesium hydroxide, and phosphine (US EPA 1998a). Therefore, aluminum and magnesium phosphides and their residues do not appear to be persistent or mobile under most environmental conditions.

The following sections describe the environmental fate and persistence in air, water, and soil.

5.1 Air

The half-life of phosphine in air, exposed to light, is approximately five hours (Frank and Rippen 1987). It degrades due to photoreaction with hydroxyl radicals. The reaction products are non-volatile oxyacids of phosphorous and inorganic phosphate. Without light, the half-life can be as long as 28 hours.

5.2 Water

Phosphine has low solubility in water (Table 1). Phosphine degrades in days to phosphates and is at low risk for contaminating ground or surface water (WHO 1988).

5.3 Soil

Due to its high vapor pressure and high Henry's Law Constant (Table 1), phosphine near the soil's surface diffuses into the atmosphere where it degrades rapidly (Frank and Rippen 1987).

Hilton and Robison (1972) studied the degradation of phosphine in 3 types of soils at 5 different levels of moisture (0 – 100% saturation). They found that phosphine disappeared from air-dried soils within 18 days, but it took 40 days for it to disappear completely from 100% saturated soils. The interaction of phosphine with soil appears to be due to two processes--mixed chemisorption (irreversible) and physical adsorption (reversible)--with the extent of each depending on soil type (US EPA 1999).

6. NON-TARGET EFFECTS

Phosphine is very toxic to all forms of life; however, one would not expect exposure to occur. In general, risk of important environmental effects from phosphine or metal phosphides is low when proper transport, fumigation and industrial practices are used (WHO 1988; US EPA 1998a).

Given the characteristics and use patterns of aluminum and magnesium phosphide, these pesticides are not expected to pose a significant ecological risk to non-target organisms under most circumstances, with the exception of some endangered species. Since one of the uses of these pesticides is as a burrow fumigant for the control of rodents, concern exists that endangered or threatened species could be present in burrows targeted for fumigation. Also phosphine would be highly toxic to small mammals and birds that might remain in indoor sites (e.g., warehouses) during fumigation (US EPA 1999).

No research data exist on the wildlife toxicity of magnesium phosphide. Limited information on non-target effects, presented below, is available for aluminum phosphide and phosphine.

6.1 Birds

No oral or inhalation median lethal doses for aluminum phosphide or phosphine in birds have been identified. Klimmer (1969) reported that exposing male turkeys and hens to concentrations of 211 and 224 mg/m^3 for 74 and 59 minutes, respectively, resulted in apathy, restlessness, difficulty in breathing, and other symptoms. The birds died in less than 2 hours. One would expect these results to apply to other bird species. However, exposure at these concentrations is unlikely, as phosphine dissipates quickly in air.

6.2 Fish and Other Aquatic Species

The concentrations of aluminum phosphide that are toxic to fish vary greatly (Table 20) (EXTOXNET 1996; WHO 1988). No data are available for toxicity from magnesium phosphide or phosphine. Aluminum phosphide reacts with water, forming phosphine gas which quickly dissipates. Therefore, the probability of aquatic exposure is low (Meister 1992). No data are available about the toxicity of magnesium phosphide to fish or other aquatic species.

Table 20. Acute toxicity of aluminum phosphide for freshwater fish

Species	**96-h LC_{50}**
Rainbow trout (*Oncorhynchus mykiss*)	4.1 ug/L
Bluegill sunfish (*Lepomis macrochirus*)	0.178 mg / m^3

An LC_{50} for phosphine for the frog from a 30-minute exposure was reported to be 0.56 mg/L. The LC_{50} for a 15-min exposure was 0.84 mg/L (WHO 1988).

6.3 Seeds and Living Plants

Bond (1984) summarizes research that indicates that phosphine used to control insects does not normally affect seed germination. Little information exists on how growing plants are affected by exposure to phosphine.

7. RESIDUES OF PHOSPHINE FROM PHOSPHINE GAS AND PHOSPHINE-GENERATING PRODUCTS ON FUMIGATED COMMODITIES

Acceptable federal residue tolerances for various commodities vary from 0.01 to 0.1 ppm (US EPA 1985). According to several studies, residues of phosphine may remain on commodities fumigated with phosphine gas or phosphine-generating products (Table 21), however Dieterich et al. (1967) showed that residues in most fumigated foods are below a level of concern at 0.01 mg/m^3 (0.01 ppm) or less. In a National Residue Survey by the Australian Government (2006), residue of phosphine was assessed in bulk export grains at ports. Eight commodities were surveyed and none carried phosphine residues above the Maximum Residue Limit of 0.1 ppm for phosphine.

Table 21. Summary of some studies on residues in phosphine-fumigated commodities.

Fumigant, rate	Commodity	Residue/Observations	References
Phosphine @ 4000 ppm and 25 ^{0}C	Wheat Millet Milled Rice Soybeans Azuki beans	Wheat 0.46 Millet 1.16 Milled Rice 0.34 Soybeans 0.18 Azuki beans 0.24 12 days from fumigation	Sato & Suwanai, 1974
Phosphine @ 5 ppm	Wheat	After 4 days of aeration: 0.2ppb After 220 days of aeration:0.004ppb	Dumas, 1980
Phosfume® @ 2 tabs/ton 4 tabs/ton 8 tabs/ton	Legumes	Ranged from 0.66 to 1.33 ppm Below detection limit; 0.001 ppm by < 3 days in 2 tabs/ton < 6 days in 8 tabs/ton	Singh et al., 1983
Aluminum phosphide tabs @ 5 gm/ton	Wheat	Residue in wheat 12.01 ± 1.22 ppb	Pratt & Desmarchelier, 1988

8. ENVIRONMENTAL MONITORING

WHO (1988) reported a study that detected air concentrations of up to 280 mg phosphine/m^3 near outer walls of a facility fumigated with phosphine. When the distance was > 10 m from the buildings, all concentrations, except for one, were < 0.14 mg/m^3, which was below the exposure limit.

Thorn et al. (2002) described a method of monitoring inside and outside a sealed tobacco warehouse fumigated with phosphine, using a radio telemetry-based system. Phosphine was continuously monitored using two different types of electrochemical detectors. Phosphine concentrations outside the facility boundaries were < 0.3 ppm for five warehouses under simultaneous fumigation. Phosphine concentrations varied from 0 to 580 ppm inside sealed buildings.

In 2008, DPR requested that Air Resources Board (ARB) monitor one application site for phosphine because of its moderate pesticidal use, high volatility, and high priority for risk assessment (Warmerdam 2008). Therefore, ARB monitored an application of aluminum phosphide pellets at one application site for phosphine in Merced County in 2008 (Adler 2010). The fumigation lasted almost six days. The site, a large sealed chamber, was monitored before, during and after the use of phosphine as a post-harvest commodity fumigant. ARB conducted its monitoring at a commercial commodity fumigation facility. Monitoring occurred in December, historically one of the months with the highest phosphine use. A total of 75 samples were collected. Samples were collected from 8 locations (4 corners, 4 sides) from 15 to 40 feet away from the exterior walls of the chamber. One additional sampler was located inside the chamber. During the fumigation period, ambient samples ranged from 1 to 58.33 ug/m^3 phosphine; the samples from

inside the chamber were 510,000 to 7,000,000 ug/m^3. Concentrations of ambient samples taken during the venting of the chamber were < 1 – 6 ug/m^3.

Neither DPR nor ARB is monitoring phosphine in its air monitoring at this time (Vidrio et al. 2012, ARB 2012).

9. PHOSPHINE AND METAL PHOSPHIDES AS POSTHARVEST REPLACEMENTS FOR METHYL BROMIDE

For a variety of crops, methyl bromide is currently the chemical of choice for preplant soil fumigation, commodity, and quarantine treatment requirements. Under the Clean Air Act, methyl bromide was declared an ozone depleting compound in 1993, and its production and importation was phased out by 2001. Methyl bromide will be phased out internationally according to the provisions of the Montreal Protocol, established in 1995. For many uses of methyl bromide, no alternatives exist or alternative strategies are not well studied for applicability.

Phosphine and phosphine-generating phosphides are used as postharvest alternatives to replace methyl bromide (USDA 2011). As of 1999, the US EPA recommends the use of the phosphine product, ECO_2FUME, as an alternative to methyl bromide. This product is effective at controlling a broad spectrum of economically important insect pests on commodities in sealed containers or structures. When used properly, it offers greater control of application rates as compared with the metal phosphide fumigants; therefore, one would expect to reduce the levels of peak concentrations of phosphine necessary for satisfactory performance within the fumigated areas.

ECO_2FUME fumigant gas is a non-flammable pre-mixed cylinderized mixture of phosphine and carbon dioxide. In most cases ECO_2FUME can be dispensed from outside the storage facility, which eliminates the need for applicators to enter a closed space and dispense tablets or pellets, thereby greatly reducing the possibility of exposure. This product eliminates the need to dispose of waste pellets, tablets or both when using metal phosphide products.

USDA (2011) summarizes research results to improve the usefulness of phosphine as an alternative to methyl bromide.

10. REFERENCES

Adler, N. 2010. Report on air monitoring of the application of phosphine in Merced County in December 2008. ARB, Cal/EPA, Sacramento, CA.

ARB. 2012. California ambient toxics data statewide summaries. Cal/EPA, Sacramento, CA. Database. Accessed 11 January 2013. http://www.arb.ca.gov/adam/toxics/statesubstance.html

Australian Government. 2006. Department of Agriculture, Fisheries and Forestry, National Residue Survey, Bulk Export Grains Program, July 2005- to June 2006. Resource document. Accessed 11 January 2013. http://www.daff.gov.au/agriculture-food/nrs

Birth Defect Prevention Act. Cal. Food and Agricultural Code §§13121-13135 (West 2012).

Bond, E.J. 1984. Manual of fumigation for insect control. FAO Plant Production and Protection Paper 54. Food and Agriculture Organization, United Nations: Rome.

3 CCR 6400(e). California Code of Regulations. (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Chapter 2. Pesticides. Subchapter 4. Restricted Materials. Article 1. Restricted Materials. §6400(e).

3 CCR sections 6412(a)(3). California Code of Regulations. (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Chapter. 2. Pesticides. Subchapter 4. Restricted Materials. Article 2. Possession and Use Limitations. §6412(a)(3).

3 CCR 6860. California Code of Regulations. (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Chapter 4. Environmental Protection. Subchapter 2. Air. Article 1. Toxic Air Contaminants. §6860.

42 CFR 7412. 2013. Code of Federal Regulations: Title 42 Chapter 85, Subchapter 1, Part A, §7412. Office of the Federal Register National Archives and Records Administration. Washington, DC.

Cytec Industries, Inc. 2003. Applicator's manual for VAPORPH3OS™ Phosphine Fumigant. West Patterson, NJ.

DEGESCH America, Inc. 2010. Material safety data sheet: magnesium phosphide. Weyers Cave, VA. Resource document. Accessed 11 January 2013. http://www.degeschamerica.com/docs/MSDA/Mg3P2%20MSDS.pdf

DEGESCH America, Inc. 2011. Material safety data sheet: aluminum phosphide. Weyers Cave, VA. Resource document. Accessed 11 January 2013. http://www.degeschamerica.com/docs/MSDS/Mg3P2%20MSDS.pdf

Dieterich, W. H., G. Mayr, K. Hild, J. B. Sullivan & J. Murphy. 1967. Hydrogen phosphide as a fumigant for foods, feeds and processed food products. Residue Rev., 19: 135 – 149.

DPR. 2007. Notice to pesticide registrants regarding initiation of risk assessment process for the active ingredient phosphine. California Notice 2007-2. Cal/EPA, Sacramento, CA. Resource document. Accessed 11 January 2013. http://www.cdpr.ca.gov/docs/registration/canot/2007/ca2007-02.pdf

DPR. 2011. Prioritization and status of active ingredients for risk characterization: report #52. Memo to the Pesticide Registration and Evaluation Committee dated July 15 2011. Cal/EPA, Sacramento, CA. Resource document. Accessed 11 January 2013. http://www.cdpr.ca.gov/docs/risk/priot.pdf

DPR. 2012a. Pesticide Chemistry Database. Cal/EPA, Sacramento, CA. Database. Accessed 11 January 2013. http://www.cdpr.ca.gov/docs/county/dataflex/chemical/chmbynam.pdf.

DPR. 2012b. Pesticide Label Database. Cal/EPA, Sacramento, CA. Database. Accessed 11 January 2013. www.c**dpr**.ca.gov/docs/**label/label**que.htm.

DPR. 2012c. The Pesticide Chemical Information Report. Cal/EPA. Sacramento, CA. Resource document. Accesssed 5 December 2012. http://www.cdpr.ca.gov/docs/whs/pdf/hs1863.pdf.

DPR. 2012d. Annual Pesticide Use Reports: 2005-2010, Pesticide Use Report Database, Cal/EPA, Sacramento, CA. Accessed 5 December 2012. http://www.cdpr.ca.gov/docs/pur/purmain.htm.

Dumas, T. 1980. Phosphine sorption and desorption by stored wheat and corn. J. Agric. Food Chem., 28: 337-339.

EXTOXNET. 1996. Pesticide information profiles: Aluminum phosphide. Ithaca, NY. Resource document. Accessed 13 January 2013. http://pmep.cce.cornell.edu/profiles/extoxnet/24d-captan/aluminum-phosphide-ext.html

Fluck, E. 1976. The odor threshold of phosphine. J. Air Pollut. Control Assoc., 26 (8): 795.

Frank, R. & G. Rippen. 1987. Fate of phosphine in the atmosphere. Batelle-Institut, Frankfurt: Germany. Accessed 4 January 2013. http://legacy.library.ucsf.edu/tid/zjj13c00/pdf

Groundwater Services, Inc. 2010. Phosphine chemical properties. Houston, TX. Database. Accessed 11 January 2013. http://www.gsi-net.com/en/publications/gsi-chemical-database/single/448.html.

Hazardous Substances Data Bank. 2012. Phosphine. National Library of Medicine, National Institute of Health, Bethesda, MD. Database. Resource document. Accessed 19 December 2012. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Hilton, H. W. & W. H. Robison. 1972. Fate of zinc phosphide and phosphine in the soil-water environment. J. Agric. Food chem., 20 (6): 1209-1213.

IPCS. 1997. International Chemical Safety Card for Phosphine. ICSC #0694. Resource document. Accessed 28 December 2012. http://www.inchem.org/documents/icsc/icsc/eics0694.htm

Klimmer, O.R. 1969. Contribution to the study of action of phosphine. Archiv fur Toxikologie, 24(23): 164-187.

Meister, R.T. (Ed.). 1992. Farm Chemicals Handbook '92, Meister Publishing Co., Willoughby, OH.

Pratt, S. & J. Desmarchelier. 1998. Residues of phosphine and aluminum phosphide in wheat after fumigation by admixture. Australian Postharvest Technology Conference, Stored grain research laboratory, CSIRO Entomology, Canberra ACT.

Sato, K. & M. Suwanai. 1974. Absorption of hydrogen phosphide to cereal products. Appl. Entomol. Zool., 9 (3): 127-132.

Singh, K. N., B. P. Srivastava & G. Nath. 1983. Phosphine residues and its effects on germination of stored pulses. Indian J. Entomol., 45 (1): 71-80.

TAC Identification & Control Act, Cal. Food & Agric. Code §§ 14021-14027 (West 2012).

Thorn (Jr), T. G., E. M. Chodyniecki, K. W. Ingold, G. A. Lone, C. D. Miller, E. A. Robinson, F. Cowan & R. L. Thomas. 2002. Continuous real-time monitoring of phosphine concentrations in air using electrochemical detectors interfaced by radio telemetry. Environ. Sci. Technol. 36, 2048-2053.

US EPA. 1985. Aluminum phosphide/magnesium phosphide: tolerances for residues. Code Fed. Reg., 40: 180, 225, 291-292, 333, 375.

US EPA. 1998a. Reregistration Eligibility Decision Al and Mg Phosphide. Office of Prevention, Pesticides and Toxic Substances, Office of Pesticide Programs, US Government Printing Office: Washington, DC. Resource document. Accessed 11 January 2013. http://www.epa.gov/oppsrrd1/REDs/0025red.pdf.

US EPA. 1998b. Reregistration Eligibility Decision Zinc Phosphide. Office of Prevention, Pesticides and Toxic Substances, Office of Pesticide Programs, US Government Printing Office: Washington, DC. Resource document. Accessed 7 December 2012. http://www.epa.gov/oppsrrd1/REDs/0026red.pdf.

US EPA. 1999. Pesticide fact sheet: Phosphine. Office of Prevention, Pesticides and Toxic Substances. Washington, DC. Resource Document. Accessed 28 December 2012. http://www.epa.gov/opprd001/factsheets/phosphine.pdf.

US EPA. 2000. Memorandum of agreement between the US EPA and signatory registrants of phosphine based fumigants. Special Review and Reregistration Division, Office of Prevention, Pesticides and Toxic Substances. Washington, DC. Resource document. Accessed 28 December 2012. http://www.epa.gov/oppsrrd1/REDs/phosphine_agree.pdf

US EPA. 2004. Memorandum of agreement amending aluminum and magnesium phosphide RED: Status update. Special Review and Reregistration Division, Office of Prevention, Pesticides and Toxic Substances. Washington, DC. Resource document. Accessed 28 December 2012. http://www.epa.gov/oppsrrd1/REDs/factsheets/phosphine-moa-fs-Dec02.htm

USDA. 2011. National Program 308: Methyl bromide alternatives Accomplishment Report 2006-2011. ARS.

Vidrio, E., Wofford, P., Segawa, R., and Schreider, J. 2012. Air monitoring network results for 2011: Volume 1. DPR, Cal/EPA, Sacramento, CA. Resource document. Accessed 11 January 2013. http://www.cdpr.ca.gov/docs/emon/airinit/amn_draft_vol1.pdf

Warmerdam, M-A. 2007. Proposed toxic air contaminant monitoring for 2007. Memo dated January 29, 2007 to Catherine Witherspoon, ARB. DPR, Cal/EPA, Sacramento, CA. Resource document. Accessed 28 December 2012.
http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/reqst_07.pdf

Warmerdam, M-A. 2008. Proposed toxic air contaminant monitoring for 2008. Memo dated January 4, 2008 to James Goldstene, ARB. DPR, Cal/EPA, Sacramento, CA. Resource document. http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/reqst_08.pdf Accessed 7 December 2012.

WebElements.com. (2012) Phosphorus compounds: phosphine. Resource document. Accessed 5 December 2012. http://www.webelements.com/compounds/phosphorus/phosphine.html.

WHO. 1988. Phosphine and selected metal phosphides. Environmental Health Criteria 73:1-77. Geneva. Resource document. Accessed 11 January 2013.
http://www.inchem.org/documents/ehc/ehc/ehc73.htm.