Staff Report

USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT PHOSPHINE

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USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT PHOSPHINE

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties and the historical use of phosphine gas and phosphine gas generating metallic phosphides in agricultural and industrial pest control, mainly through fumigation. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Phosphine

Phosphine is presented in the marketplace as a pure phosphine gas and as a mix with other gases in canisters under pressure, or as metallic phosphides that release phosphine gas upon exposure to moisture in air. Table 1 summarizes some of the physical-chemical properties of phosphine gas and commonly used metallic phosphides and Figure 1 depicts its chemical structure.

Phosphine is a colorless gas at ambient temperature and pressure. It has been described, by various observers, to have a similar odor to that of garlic, rotting fish or stale urine. The odor is due to impurities, particularly diphosphine. Phosphine gas is reactive and is reported to react with OH^- radicals in air (World Health Organization (WHO), 1988). This WHO report states that the reaction of phosphine gas with OH radicals in air is independent of the phosphine concentration and is very rapid with a reaction rate constant at room temperature of about 1.5×10^{-11} cm^3/mol / sec. Direct reactions with ozone are quantitatively unimportant, since reaction with OH radical occurs before the PH_3 can reach the ozone rich upper atmosphere. With the usual concentrations of hydroxyl radicals, the half-life of phosphine in air is about 28 h. Sunshine increases the hydroxyl radical concentration and may reduce the half-life to less that 5 h. The eventual oxidation product of phosphine will be phosphorus oxyacids and inorganic phosphate, which will be deposited and contribute to the nutritive environment of soils and surface waters.

Phosphine reacts with metals, especially with copper or copper-containing alloys, which causes severe corrosion. This reaction is enhanced in the presence of ammonia, which may be generated with phosphine during the decomposition of some fumigation tablets or pellets (WHO, 1988). Phosphine dissolves in water to form a neutral solution. Solubility is little affected by the pH. Dissolved phosphine reacts with hydrogen ions to form the phosphonium ion – $(PH_4)^+$. Phosphine shows varying degree of solubility in different solvents, and at 17 ^{0}C and normal atmospheric pressure, the solubility in water is 26 (ml/100 ml) (International Program on Chemical Safety (ICSC), 1997). Because of its high vapor pressure (41.3 atm at 20 ^{0}C) (ICSC, 1997) and moderate Henry's law constant (2.44

x 10^{-2} atm m^3/mol at 25 ^{0}C) (Hazardous Substances Data Bank (HSDB), 2001), phosphine at the soil surface is expected to rapidly dissipate into the atmosphere.

The two common metallic phosphides, aluminum phosphide and magnesium phosphide are used as fumigants and as pesticides. The third, zinc phosphide is not a preferred fumigant. The phosphine gas is the active ingredient generated when aluminum and magnesium phosphides react with moisture in the air.

Figure 1: Structure of phosphine gas.

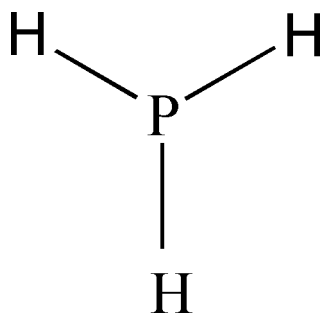


Table 1: Some Physical-Chemical Properties of Phosphine and Metallic Phosphides that generate Phosphine.

	Phosphine	Aluminum phosphide	Magnesium phosphide	Zinc phosphide
Common name	Phosphine Phosphorus trihydrite	Aluminum phosphide Phostoxin	Magnesium phosphide Magtoxin	Zinc phosphide
Some trade names	$ECO_2FUME^{®}$ $VAPORPH_3OS$™	Phoxtoxin Phosphume Phostek Gastoxin ect.	Magtoxin Fumi-Cell Magnaphos	Arrex, Commando, Denkarin Grains, Gopha-Rid, Phosvin, Pollux, Ridall, Ratol etc.
Physical state	gas[2]	solid	solid	solid
Color	none	grey/yellow	grey	grey
Odor	Garlic, decomposing fish[2]	Not available	Not available	Not available
CAS number[1]	7803-51-2	20859-73-8	12057-74-8	1314-84-7
Empirical formula	PH_3	Al P	Mg_3P_2	Zn_3P_2
Molecular weight	34.00[3, 9]	57.96[4, 8]	134.9[3]	258.1[6, 7]
Boiling Point	-87.7 ^{0}C[3, 9]	Not available	>1000 ^{0}C[9]	1,100 ^{0}C[6]
Melting point	-133 ^{0}C[3]	1000 ^{0}C[5, 8]	>750 ^{0}C[3]	>420 ^{0}C[6, 7]
Relative density (water:1)	0.8 g/cm^3, [3]	2.9 g/cm^3, [3]	2.1 g/cm^3, [9]	4.6 g/cm^3, [3]
Solubility in water, ml/100 ml at 17 ^{0}C	26[3]	Insoluble, reactive with water to form PH_3, [3, 8]	Reaction [3, 9]	None[3, 7]
Vapor pressure kPa at 20 ^{0}C or atm	4186[3] 41.3	Negligible @ 25 ^{0}C[3, 8]	0mm Hg[9]	Negligible[7]
Relative vapor density (air = 1)	1.17[3, 9]	Not available	Not available	Not available
Flash point	Flammable gas	Not available	Not available	Not available
Auto-ignition temperature	38 ^{0}C[3]	Not available	Not available	Not available
Explosive limits, vol % in air	1.8[3]	Not available	Not available	Not available

[1] = CDPR 2008a,b [2]=Voltaic, Inc, 2001 [3]=Phosphine (ICSC), 1997
[4]= US EPA, 1998 [5]=DEGESCH America Inc, 1988 [6]=HSDB, 2001 [7]=EXTOXNET, 1996a
[8]=EXTOXNET, 1996b [9]=Degesch America Inc, 2004

B. CHEMICAL USES

Phosphine gas and metallic phosphides

As of August 2008 there are only two phosphine products registered with the State of California (CDPR, 2008a and 2008b). $ECO_2FUME^{®}$ Fumigant Gas, EPA Registration number 68387-7-AA, is a fumigant with phosphine gas at a concentration of 2%. VAPORPH3OS™ Phosphine Fumigant, EPA Registration number 68387-8-AA, is the other fumigant where the phosphine concentration is at 99.3% (CDPR, 2008a and 2008b). There are at least three metallic phosphides used in California as pesticides. Aluminum phosphide has 22 registered products in DPR's Pesticide Registration database. Four pesticides with magnesium phosphide and 23 pesticides with zinc phosphide are also registered with the Sate of California as of August 2008 (CDPR, 2008a and 2008b). All phosphine-generating products discussed here are Restricted Use Pesticides (CDPR, 2008a and 2008b).

Zinc phosphide is commonly used as a rodenticide and a fumigant because of its reaction with acid to release phosphine. As a rodenticide, stomach acid causes the hydrolysis. For fumigation the acid has to be supplied. Since they hydrolyze in neutral moist conditions, aluminum and magnesium phosphides are preferred as fumigants. Zinc phosphide is available in bulk, typically to a specification of at least 80% Zn_3P_2, and containing 0.5% to 2% for use as a rodenticide by mixing in bait or approximately 5 to 10% in pastes (EXTOXNET PIP, 1996a). Aluminum and magnesium phosphides are available in different commercial formulations. Aluminum phosphide formulations usually contain approximately 57% active ingredient, and those of magnesium phosphide have 34% active ingredient.

Aluminum phosphide reacts with water to release phosphine. This reaction may be incomplete, possibly owing to the formation of a protective layer of aluminum hydroxide on the surface. Aluminum phosphide has been used as a rodenticide and a fumigant. Magnesium phosphide is used as a pesticide and a fumigant. Phostoxin (strips) formulations are designed to produce a controlled release of phosphine to achieve efficient fumigation with low operator risks. Some products include other ingredients designed to reduce fire hazards. Depending on the storage conditions, the composition of metal phosphides and their formulations may change over time by hydrolysis and oxidation. The recommended rates of phosphine vary widely, and commercial preparation, target pest, produce/product type and container, and other environmental factors affect the use.

Phosphine gas

Given below is the dosage guide for VAPORPH3OS™ Phosphine Fumigant. Cardinal Professional Products (2003), give product manuals including the VAPORPH3OS™ Fumigant Gas product manual.

Table 2. Dosage guide for VAPORPH3OS™

Temperature	**Phosphine Concentration maintained**	**Duration**
Below 32 ^{0}F (0 ^{0}C)	Do not Fumigate	Do not Fumigate
32-39 ^{0}F (0-4 ^{0}C)	200-500* ppm	6-14 days
40 – 53 ^{0}F (5 – 12 ^{0}C)	200-500 ppm	4-10 days
54 –59 ^{0}F (12 –15 ^{0}C)	200 –500 ppm	3-5 days
60 ^{0}F & above**	200-500 ppm	2-3 days

* Phosphine may ignite spontaneously at levels above its Lower Flammability Limit (LFL) of 1.8 % v/v (18,000 ppm) in air.
** Exposure to temperatures above 130 ^{0}F may cause bursting.

The precise concentration of phosphine can be calculated once it is decided how to blend pure phosphine with CO_2, air, or N_2, or to use an already blended "ready-to-use" preparation.

The instructions in VAPORPH3OS™ Phosphine Fumigant user manual states the following: "The amount VAPORPH3OS™ Phosphine Fumigant and CO_2 required to perform a fumigation will depend on the tightness of the space to be treated, and the tendency for the space to lose fumigant through the duration of the fumigation. The initial dose of VAPORPH3OS™ Phosphine Fumigant and CO_2/forced air is used to establish a pesticidal atmosphere in the fumigation space. Through active monitoring of the phosphine concentrations, additional VAPORPH3OS™ Phosphine Fumigant and CO_2/forced air added as required to maintain the target concentration for the prescribed period of time.

The initial dose of fumigant is based on the total volume of the space to be fumigated and the target phosphine concentration desired. When blending VAPORPH3OS™ Phosphine Fumigant with CO_2 and forced air, it is sometimes easier to speak in terms of the amounts of phosphine required rather than the amount of blended gas required. The maximum concentration of VAPORPH3OS™ Phosphine Fumigant used per fumigation should not exceed 500 ppm of Phosphine. **One gram of Phosphine (PH_3) will produce a concentration of 25 parts per million (ppm) in a volume of 1000 cubic feet (ft^3).** This volume refers to the container space where the produce being fumigated. This is the fundamental conversion used when calculating the amount of VAPORPH3OS™ Phosphine Fumigant needed to dose a space."

1 gram PH_3 = 25 ppm PH_3 / 1000 ft^3
1 pound of VAPORPH3OS™ Phosphine Fumigant = 454 grams of PH_3

To calculate the total amount of Phosphine or VAPORPH3OS™Phosphine Fumigant required to dose a space:

grams of PH_3 = (Target Conc. X Volume) / 25,000
"Target" is the desired Phosphine concentration in parts per million (ppm)
"Volume" is the empty volume of the space to be fumigated in cubic feet (ft^3)

To calculate the amount of Phosphine or VAPORPH3OS™ Phosphine Fumigant to be added to a space to re-establish the target concentration:

grams of PH_3 = (Target Conc. – Actual) X Volume) / 25,000 “ Actual” is the measured Phosphine concentration in parts per million (ppm) “Target” is the desired Phosphine concentration in parts per million (ppm) “Volume” is the empty volume of the space to be fumigated in cubic feet (ft^3)

There is a similar instructions manual for $ECO_2FUME^®$ Fumigant Gas, EPA Registration number 68387-7-AA (Cardinal Professional Products, 2003). This manual lists all relevant “How To” and the Dosage guide, among other related information. The temperature given below is not the ambient temperature during fumigation, but the actual temperature and also the concentration range of PH_3 near the insect pests.

Table 3: RECOMMENDED PHOSPHINE DOSAGE GUIDE FOR $ECO_2FUME^®$

Temperature	PH_3 Concentration Maintained	Rate of $ECO_2FUME^®$/1,000 cu.ft	Minimum Duration
Below 32 ^{0}F (0 ^{0}C)	Do not fumigate	Do not fumigate	Do not fumigate
32-39 ^{0}F (0-4 ^{0}C)	200-1,000 ppm	0.88 – 4.41 lbs	6 days
40-53 ^{0}F (5-12 ^{0}C)	200-1,000 ppm	0.88 – 4.41 lbs	4 days
54-59 ^{0}F (12-15 ^{0}C)	200-1,000 ppm	0.88 – 4.41 lbs	3 days
60-79 ^{0}F (16-25 ^{0}C)	200-1,000 ppm	0.88 – 4.41 lbs	2 days
80 ^{0}F & Above (=26 ^{0}C)	200-1,000 ppm	0.88 – 4.41 lbs	36 hours
80 ^{0}F & Above (=26 ^{0}C)	500-1,000 ppm	2.20 – 4.41 lbs	24 hours

All PH_3 fumigations whether by use of direct gas or through metallic phosphides generating PH_3 gas require a Fumigation Management Plan. $ECO_2FUME^®$ Fumigant Gas (2% PH_3) manual gives a simple plan. This is useful to fumigators to achieve maximum efficiency with minimum risk. However, VAPORPH3OS™ Phosphine Fumigant (99.3% PH_3) manual does not give a similar plan, and it will be diluted with air and/or CO_2 during fumigation and the manual is requiring appropriate blending equipment and training as part of the use requirements since this is a Restricted Use Pesticide. It is a good practice to follow the Fumigation Management Plan of ECO2FUME® Fumigant Gas as a routine and make adjustments to suite the specific commercial product. One important fact to remember is that under no circumstance the PH_3 in a fumigation enclosure should exceed its lower flammability limit of 1.8% v/v (18,000 ppm) since it may ignite spontaneously and may cause harm. Exposure to temperatures above 130 ^{0}F (54.4 ^{0}C) may cause bursting. Do not use or store near heat or open flame. Do not puncture or incinerate when in a pressurized container.

Metallic Phosphides

When metallic phosphides are used, the release of PH_3 happens over time. Both aluminum phosphide and magnesium phosphide react with moisture in air to generate phosphine.

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

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

Furthermore, the metallic hydroxides thus produced will react with CO_2 present to form respective carbonates.

Aluminum phosphide

There were at least 22 registered aluminum phosphide pesticide products recorded in DPR's pesticide Registration database as of August 2008. The formulation may be tablet, pellet, granule, rope or strip. One registrant, DEGESCH America, Inc., manufactures PHOSTOXIN® tablets and pellets (DEGESCH America Inc., 1988). The active ingredient is at 55% aluminum phosphide and is recommended as a source of commodity fumigation (Cardinal Professional Products, 2003). The tablet releases 1 gram of phosphine gas, and a pellet releases 0.2 grams of phosphine gas. The dosages vary depending on the type of fumigation, and DEGESCH PHOSTOXIN® User Manual identifies 15 types. Following dosage ranges are recommended for bulk (per 1000 bushels) and space (per 1000 cu. ft.) fumigations. One PHOSTOXIN® tablet or five PHOSTOXIN® pellets will produce a concentration of 25 ppm of PH_3 gas in a volume of 1000 cu.ft (1 gm of PH_3/1000 cu.ft. is equivalent to 25 ppm).

Maximum Allowable Dosage Guidelines for Fumigation with PHOSTOXIN®

Product	Per 1000 cu.ft.*	Per 1000 bu.*
Pellets	725	900
Tablets	145	180

*****Note: Maximum dosage for dates, nuts & dried fruits is (200 pellets. 40 tablets)/1000 cu.ft; (250 pellets, 50 tablets)/1000 bu.

The manual gives details of the dosage for the 15 types of fumigations described. Manual also describes the types of Personal Protective Equipment (PPE) required and when and where they are needed.

Magnesium phosphide

DEGESCH America, Inc., also manufactures MAGTOXIN® granules (EPA Registration number 72959-11) (DEGESCH America Inc., 2004). The active ingredient is magnesium phosphide at 94.6%. They are packed in stoppered 1100 cc aluminum flasks containing 850 grams of product. Each flask will produce 405 grams of phosphine gas, almost 1 gram of phosphine per 2 grams of MAGTOXIN® granules. The maximum allowable dosage for fumigation with MAGTOXIN® granules is 304 grams per 1000 cu.ft. The dosage ranges for various types of fumigations are given in the manual.

Table 4: Use of phosphine generating products from 2002 to 2007 (CDPR, 2008c).

Three main phosphine generating commercial products and their use							
Product Name	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Product Total**
Top twenty five aluminum phosphide products							
FUMITOXIN TABLETS	12,331	22,584	32,550	36,985	43,005	37,364	184,818
FUMITOXIN PELLETS	10,454	5,826	14,006	14,466	18,107	18,727	81,587
FUMITOXIN NEW COATED TABLETS-R	13,111	10,385	11,005	9,721	9,498	7,996	61,716
DEGESCH PHOSTOXIN TABLETS-R	4,168	6,974	22,069	12,269	9,454	4,465	59,399
PHOSTOXIN NEW COATED TABLETS	13,322	7,639	14,331	10,195	6,714	3,027	55,228
DEGESCH PHOSTOXIN PELLETS	5,185	9,955	6,913	7,880	10,827	6,438	47,198
WEEVIL-CIDE TABLETS	1,724	7,010	5,040	8,270	15,081	9,967	47,093
DEGESCH PHOSTOXIN COATED PELLETS	11,699	17,386	3,822	3,494	2,076	2,157	40,632
PHOSTOXIN COATED PELLETS	6,447	4,036	3,713	16,285	4,417	3,143	38,041
DEGESCH PHOSTOXIN NEW COATED TABLETS	12,186	5,659	5,627	4,427	5,332	1,266	34,497
GASTOXIN FUMIGATION TABLETS	15,738	5,478	3,015	3,404	1,870	2,150	31,654
DEGESCH PHOSTOXIN TABLETS	27,184	881	532	417	188	669	29,872
DETIA FUMEX	23,587	3,808	26		63	238	27,722
GASTOXIN FUMIGATION PELLETS	705	1,630	554	487	16,644	542	20,562
DEGESCH PHOSTOXIN TABLET PREPAC	1,694	2,361	3,928	2,333	4,054	2,743	17,112
FUMIPHOS 60% ALUMINUM PHOSPHIDE FUMIGANT TABLETS	2,622	1,682	1,458	1,770	424	284	8,241
DEGESCH PHOSTOXIN PREPAC ROPE	527	2,036	422	129	1,240	987	5,341
FUMITOXIN COATED PELLETS	2,491	1,424	530	261	210	320	5,237
DEGESCH PHOSTOXIN COATED PELLETS-PREPAC	1,195	1,932	780	365	8		4,281
DETIA PHOS TABLETS	1,286	141	23	635	468	83	2,636
WEEVIL-CIDE PELLETS	105	212	109	237	173	1,396	2,232
ALUMINUM PHOSPHIDE TABLETS	4	16	381	132	65	62	659
FUMITOXIN ALUMINUM PHOSPHIDE BAGS	61	16	136	184	139		536
DETIA GAS-EX-B	367	62					428
FUMIPHOS 60% ALUMINUM PHOSPHIDE FUMIGANT PELLETS	232	19	73	37	3	5	370
Magnesium phosphide products							
DEGESCH FUMI-CEL	187	819	949	1,885	3,053	3,431	10,324
DEGESCH FUMI-CEL PLATES	4,109	1,333	1,019	574	253	266	7,553
DEGESCH FUMI-STRIP	29	66	254	576	406	1,172	2,502
DEGESCH MAGTOXIN PELLETS-PREPAC	424	369	1	1			796
DEGESCH MAGTOXIN PREPAC SPOT FUMIGANT	3	117	142	94	175	113	644
DEGESCH MAGTOXIN PELLETS	72	136	251	14	44		518
Phosphine gas products							
ECO2FUME	900	1,139	1,285	1,692	2,080	2,574	9,670
VAPORPH3OS PHOSPHINE FUMIGANT			379	993	694	2,686	4,752

Pesticide Use Summary

In 1990, DPR implemented pesticide use reporting where all pesticide uses in California, defined as agricultural use and restricted use pesticides in structural pest control must be reported, and is entered into a Pesticide Use Report database (CDPR, 2008c). The information included in these monitoring recommendations reflects the use of phosphine gas in agricultural and industrial fumigations and use of aluminum and magnesium phosphide for similar purposes. As can be seen from Table 4, aluminum phosphide is the most commonly used phosphine generating commercial product and was over 90% of the total phosphine use. The use of magnesium phosphide and phosphine gas is small relative to aluminum phosphide use, but increasing. The commercial product, Fumitoxin Tablets is by far the most commonly used, followed by Fumitoxin Pellets. Therefore, the focus of use data will be on total phosphine use and aluminum phosphide use.

Table 5 and Figure 2 below give the average use of all phosphine sources by county and by month in California from 2002 to 2007. Of the top 10 counties with phosphine use, Fresno County accounted for approximately 21,000 pounds of active ingredient (a.i.) followed by Los Angeles County (approximately 15,000) and Kern County (approximately 11,000). Fresno County shows higher use in February, July, and December. A closer look at the data revealed a few suspect applications reported in 2002, which should be considered only for trend information. For these six years, the State monthly use totals of all phosphine sources ranged approximately from 9,300 to 18,800 pounds of a.i. These figures are smaller relative to other fumigants but have the potential to go up if phosphine is accepted as a candidate to replace some methyl bromide use, particularly in commodity fumigation.

Table 6 gives information on use of all phosphine sources by the top 20 Sites by year. Figure 3 gives only the top 10 Sites. The top three application sites are landscape maintenance followed by commodity fumigation and almonds. Landscape maintenance accounted for approximately 25% of the total phosphine used, followed by commodity fumigation, which used about 18%.

Table 7 presents the data on use of phosphine from all sources in top twenty counties for the period from 2002 to 2007. Figure 4 plots the same data for top ten counties. Fresno had the highest use, followed by Los Angeles and Merced Counties. The use pattern is somewhat steady, except for 2007, which shows a reduction in use that is similar to the use in 2003.

Tables 8 through 11 and Figures 5 through 8 give the use information for aluminum phosphide. The data in Table 8 show aluminum phosphide use by county by month. Similar to total phosphine use, Fresno, Los Angeles, Kern, and Merced Counties are the leading aluminum phosphide users, in that order. Fresno County on the average (2002-2007) used 1,634 pounds a.i. per month followed by Los Angeles County at 1,239 pounds a.i per month. The month of October had the largest annual average use of 17,737 and November, and September are the other leading user months respectively.

The Table 9 gives the data of aluminum phosphide use in the top twenty counties by year for the period from 2002 to 2007. The Figure 5 presents this data graphically for the top ten counties. Similar to aluminum phosphine use by county by month discussed above (Table 8

and Figure 5), the leading aluminum phosphide use by year is in Fresno, Los Angeles, Kern, Merced, and San Joaquin Counties. Fresno County used about 14% of the total State's use in this 6-year period. The most active months were from September to December, and the leading use month was October. The annual use has shown some fluctuation, from a high total use of over 169,000 pounds a.i in 2002 to some 104,000 pounds a.i in 2007. The mean for this 6-year period was 135,160 pounds a.i, with a relatively high standard deviation of 22,747 pounds a.i.

Table 10 gives the data on the monthly average use of aluminum phosphide in the top twenty application sites by month, from 2002 to 2007. The Figure 7 is a plot of the same data for top ten Sites. The month of October was the biggest user month with an average use of over 17,500 pounds a.i. The commodity fumigations accounted for closer to 5,500 pounds a.i, for this month. October, September, and November are the three leading user months, in that order.

Table 11 presents the aluminum phosphide use data for top twenty Sites by year, and Figure 8 plots the same data for the top ten sites. This table and plot follow the pattern of Table 10 and Figure 7, since they are the totals of twelve months of that respective year. Table 11 also shows that about 26% of the total aluminum phosphide used during 2002-2007 period was for landscape maintenance, followed by about 17% in commodity fumigation. Almond was the third highest user.

The use data point to the facts that: Landscape Maintenance and Commodity Fumigation were the leading Sites, Fresno, followed by Los Angeles was the leading user county and the month of October followed by September was the leading user month.

Table 5: All sources of phosphine use by county by month (CDPR, 2008c)

Average phosphine use (pounds a.i.) from all commercial formulations by all sites in top ten counties of California for years 2002 to 2007.														
County	**JAN**	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	**County Total**	**County average**
FRESNO	3,132	1,490	1,630	1,120	1,551	1,239	1,207	1,707	2,781	2,622	1,405	1,123	21,032	**1,753**
LOS ANGELES	1,730	730	1,339	747	726	681	3,495	710	1,219	2,203	749	797	15,126	**1,260**
KERN	443	369	318	1,212	733	773	728	1,189	2,241	2,188	828	559	11,582	**965**
MERCED	297	2,957	248	229	152	160	148	249	758	770	354	4,448	10,770	**897**
SAN JOAQUIN	376	242	286	322	695	532	418	494	390	3,227	2,105	416	9,503	**792**
YOLO	378	421	299	624	654	665	466	1,503	918	712	625	542	7,808	**651**
STANISLAUS	378	471	414	424	327	404	282	565	1,128	1,294	752	719	7,157	**596**
RIVERSIDE	348	302	442	412	414	633	302	307	309	603	778	361	5,212	**434**
SAN BERNARDINO	269	239	277	917	395	340	344	457	404	308	270	262	4,484	**374**
COLUSA	140	44	175	360	658	562	828	607	256	178	526	104	4,439	**370**
Top 10 total	7,492	7,264	5,428	6,369	6,304	5,990	8,218	7,789	10,404	14,105	8,391	9,332	97,112	
Top 10 as a % of State total	**78.6**	**70.9**	**58.3**	**61.6**	**64.4**	**54.7**	**66.5**	**67.2**	**71.7**	**74.8**	**63.7**	**80.0**	**68.2**	
State total	9,537	10,245	9,307	10,340	9,793	10,943	12,363	11,587	14,501	18,845	13,179	11,658	142,325	

Figure 2: The plot of month by top ten county data (CDPR, 2008c).

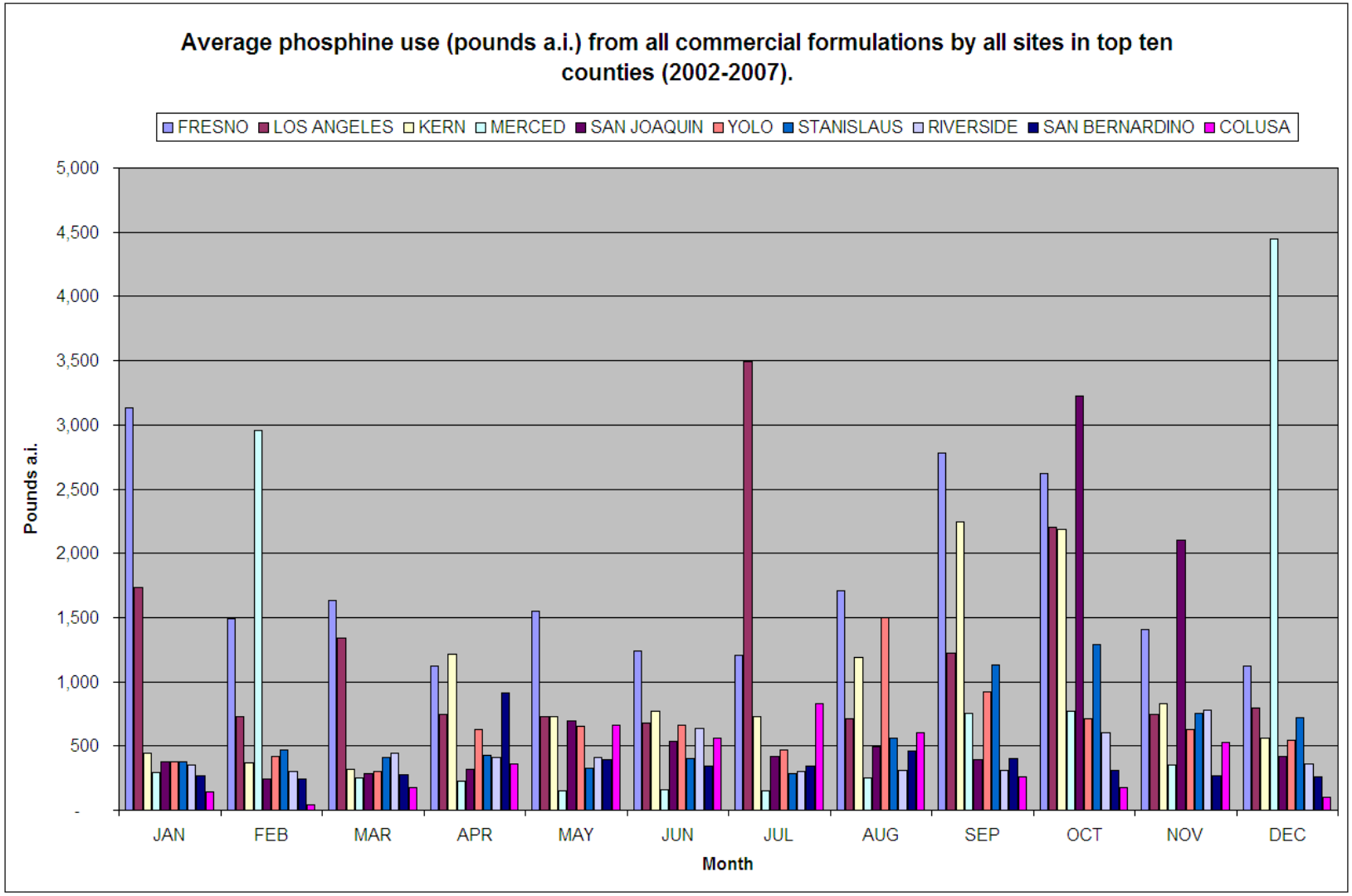


Table 6: Phosphine use in top 20 Sites (CDPR, 2008c).

Use of all phosphine sources (pounds a.I.) in top 20 Sites in California from 2002 to 2007.									
Site	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Site Total**	**Site average**	**Site as a % of total use**
LANDSCAPE MAINTENANCE	24,159	30,397	37,842	44,357	42,630	35,424	214,810	35,802	25.2
COMMODITY FUMIGATION	45,456	24,771	17,925	17,927	33,048	14,786	153,912	25,652	18.1
ALMOND	15,003	14,364	14,129	14,868	19,543	16,551	94,459	15,743	11.1
FUMIGATION, OTHER	32,811	9,934	8,345	6,635	8,840	5,953	72,518	12,086	8.5
STRUCTURAL PEST CONTROL	7,046	10,870	11,458	9,806	8,207	6,915	54,301	9,050	6.4
FRUITS (DRIED OR DEHYDRATED)	3,478	4,338	10,623	9,704	11,999	5,072	45,215	7,536	5.3
VERTEBRATE PEST CONTROL	6,025	5,301	8,060	7,623	11,554	2,600	41,163	6,860	4.8
RIGHTS OF WAY	17,172	2,354	2,698	4,431	2,973	6,042	35,670	5,945	4.2
GRAPES	11,284	8,922	4,086	2,320	2,353	3,687	32,652	5,442	3.8
PISTACHIO (PISTACHE NUT)	2,864	2,721	2,913	3,791	6,049	8,641	26,979	4,497	3.2
WHEAT, GENERAL	1,690	1,329	11,352	2,439	862	751	18,422	3,070	2.2
FIG				11,585	171	71	11,827	1,971	1.4
RICE (ALL OR UNSPEC)	2,711	195	848	562	3,047	1,597	8,961	1,494	1.1
GRAPES, WINE	1,155	757	734	682	2,328	856	6,513	1,085	0.8
WALNUT (E. WALNUT, P. WALNUT)	487	523	624	1,186	1,017	1,346	5,184	864	0.6
CORN, HUMAN CONSUMPTION	390	689	330	778	602	309	3,098	516	0.4
FOOD PROCESSING/HANDLING PLANT/AREA	554	401	436	554	401	436	2,783	464	0.3
PRUNE	572	96	248	420	618	704	2,658	443	0.3
ARTICHOKE (GLOBE) (ALL OR UNSPEC)				75	179	1,298	1,553	259	0.2
UNCULTIVATED NON-AG AREAS (ALL OR UNSPEC)	69	92	474	69	92	474	1,270	212	0.1
Top 20 Sites total for all phosphine use	172,926	118,055	133,123	139,816	156,515	113,514	833,949	138,991	97.8
Top 20 Sites total as a % of State total	98.1	94.8	97.4	98.7	98.9	98.6	97.8		
Grand Total	176,350	124,499	136,609	141,656	158,246	115,071	852,431	142,072	

Figure 3: Phosphine use in top 10 Sites (CDPR, 2008c).

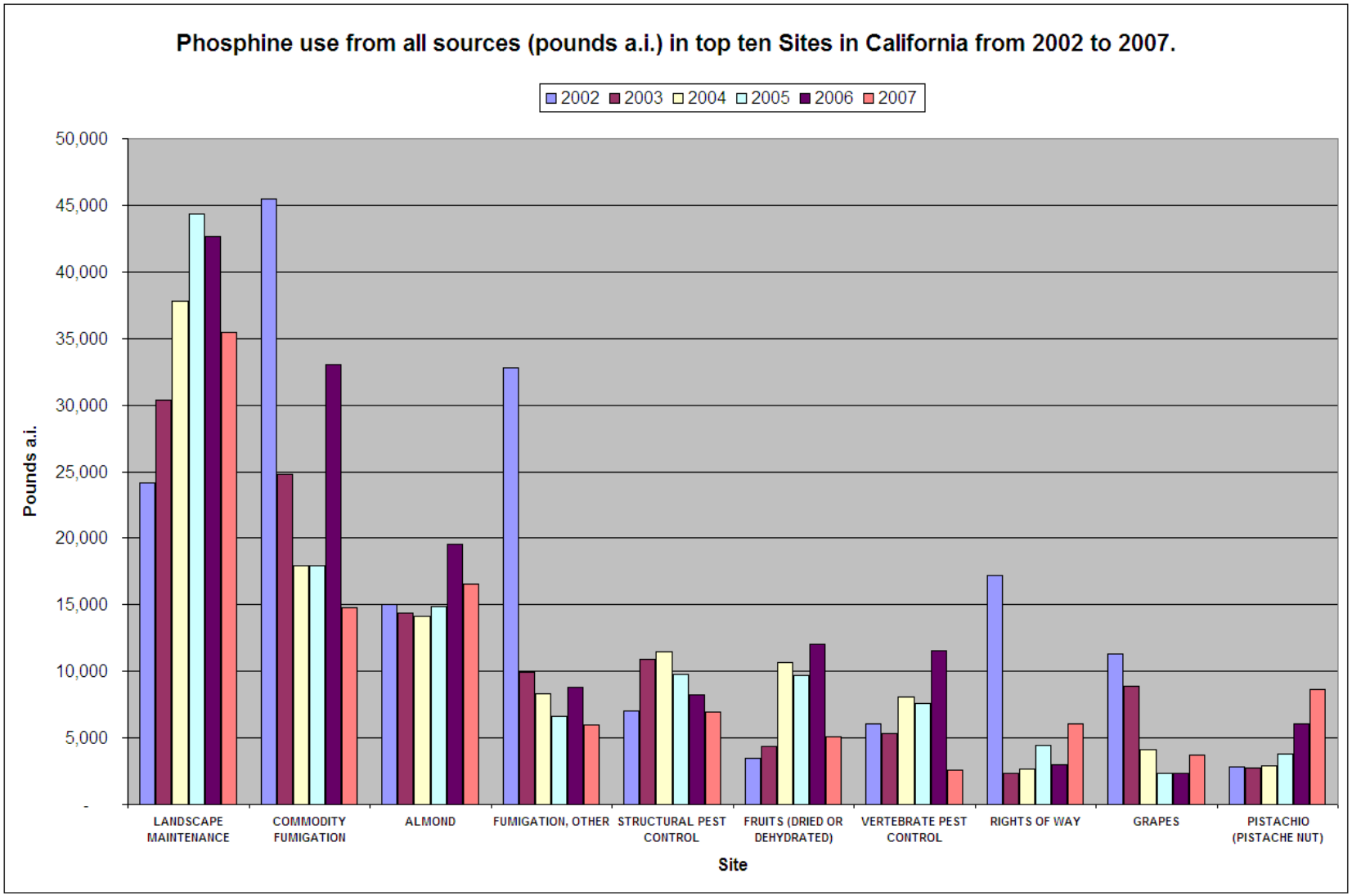


Table 7: All sources of phosphine use in top twenty counties by Year (CDPR, 2008c).

All phosphine use in top 20 counties from 2002 to 2007, pounds a.I.									
County	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Co.Total**	**Average**	**Co. use as a % of total**
FRESNO	20,707	15,744	21,578	32,374	23,062	13,661	127,125	21,187	14.8
LOS ANGELES	39,095	16,501	8,849	6,707	9,810	9,776	90,738	15,123	10.6
KERN	7,761	12,439	11,840	9,752	15,083	13,632	70,508	11,751	8.2
MERCED	45,532	3,301	3,573	3,872	4,047	4,731	65,057	10,843	7.6
SAN JOAQUIN	3,916	3,391	16,844	6,379	21,081	5,967	57,579	9,597	6.7
YOLO	7,636	9,787	7,039	7,088	7,845	7,456	46,850	7,808	5.5
STANISLAUS	7,211	8,381	4,818	7,628	8,030	7,325	43,393	7,232	5.0
RIVERSIDE	2,661	5,938	4,169	5,119	8,484	4,934	31,306	5,218	3.6
SAN BERNARDINO	2,684	2,437	3,852	2,767	9,789	5,376	26,905	4,484	3.1
COLUSA	3,657	4,558	4,820	5,368	3,480	4,751	26,634	4,439	3.1
ORANGE	3,322	2,927	3,890	8,136	3,979	4,377	26,630	4,438	3.1
SAN DIEGO	1,910	2,352	2,183	10,018	4,963	3,164	24,590	4,098	2.9
VENTURA	1,289	1,096	7,206	6,807	3,329	1,920	21,647	3,608	2.5
MADERA	3,967	3,507	3,403	3,234	3,460	4,056	21,627	3,604	2.5
SANTA CLARA	3,115	2,197	3,630	3,830	4,229	3,636	20,638	3,440	2.4
SUTTER	4,675	5,279	2,430	3,377	1,938	2,127	19,827	3,304	2.3
TULARE	1,271	2,912	4,314	3,715	3,662	2,575	18,449	3,075	2.1
SACRAMENTO	1,247	2,738	3,081	2,593	6,070	2,406	18,135	3,023	2.1
MONTEREY	2,830	2,278	4,278	1,732	3,669	3,138	17,925	2,988	2.1
SANTA BARBARA	613	4,605	3,711	1,047	1,620	731	12,327	2,054	1.4
KINGS	1,067	898	285	1,558	2,616	1,257	7,682	1,280	0.9
Total top 20 counties	166,165	113,267	125,795	133,102	150,246	106,997			
Top 20 Co. use as a % of total use	93	91	92	93	94	93			
State Total	178,348	124,867	137,204	143,824	159,446	115,623	859,313		

Figure 4: Use of phosphine from all sources in top ten counties from 2002 to 2007 (CDPR, 2008c).

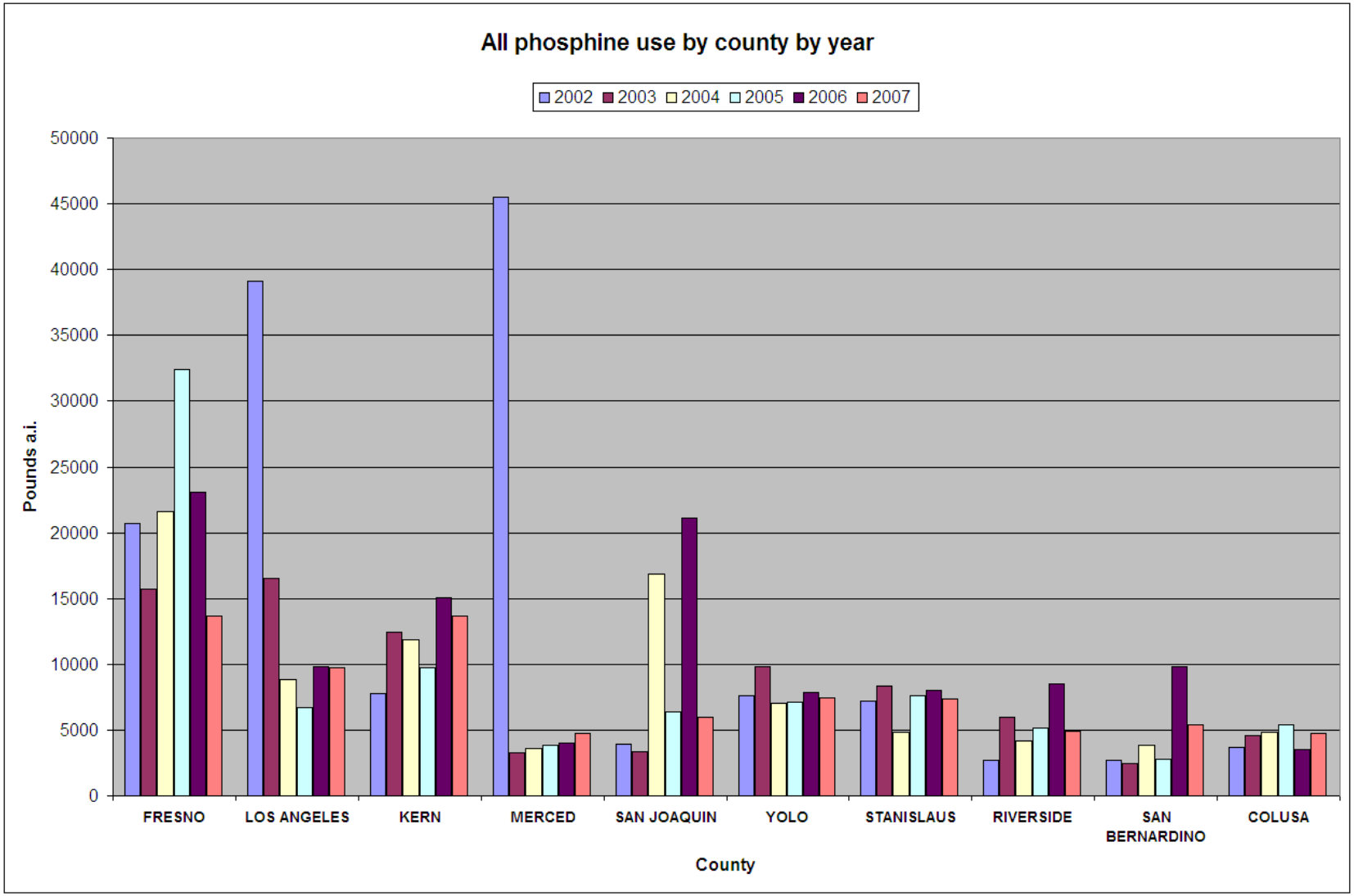


Table 8: Average monthly use of aluminum phosphide in top ten counties (CDPR, 2008c).

Average phosphine use (pounds a.i.) from aluminum phosphide sources in top ten counties of California for years 2002 to 2007														
County	**JAN**	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	**County Total**	**County average**
FRESNO	3,080	1,394	1,585	1,049	1,369	1,026	1,099	1,601	2,497	2,454	1,334	1,092	19,607	**1,634**
LOS ANGELES	1,721	725	1,333	735	692	659	3,458	685	1,181	2,173	721	790	14,872	**1,239**
KERN	428	358	310	1,205	716	759	715	1,130	2,150	2,141	788	541	11,241	**937**
MERCED	283	2,529	237	219	136	151	139	230	702	738	327	4,426	10,116	**843**
SAN JOAQUIN	341	206	268	307	669	498	388	441	327	3,004	1,904	361	8,716	**726**
YOLO	355	400	249	467	553	582	403	1,410	774	610	509	463	6,775	**565**
STANISLAUS	358	448	400	409	308	390	263	540	999	1,144	624	645	6,529	**544**
RIVERSIDE	347	302	442	408	409	619	283	298	308	602	777	361	5,156	**430**
SAN BERNARDINO	267	237	275	915	383	334	337	452	397	302	268	259	4,426	**369**
ORANGE	268	256	799	682	278	367	262	249	401	368	253	236	4,419	**368**
Top ten county total	7,449	6,855	5,898	6,397	5,512	5,384	7,347	7,036	9,736	13,538	7,505	9,173	91,857	**7,655**
Top ten as a % of State total	**80.4**	**71.9**	**65.4**	**64.3**	**59.4**	**51.6**	**61.5**	**63.5**	**72.3**	**76.3**	**61.3**	**81.9**	**68.0**	
State Total	9,260	9,531	9,023	9,952	9,276	10,426	11,949	11,075	13,474	17,737	12,233	11,198	135,160	11,263

Figure 5: Average monthly use of aluminum phosphide by top 10 counties by month (CDPR, 2008c).

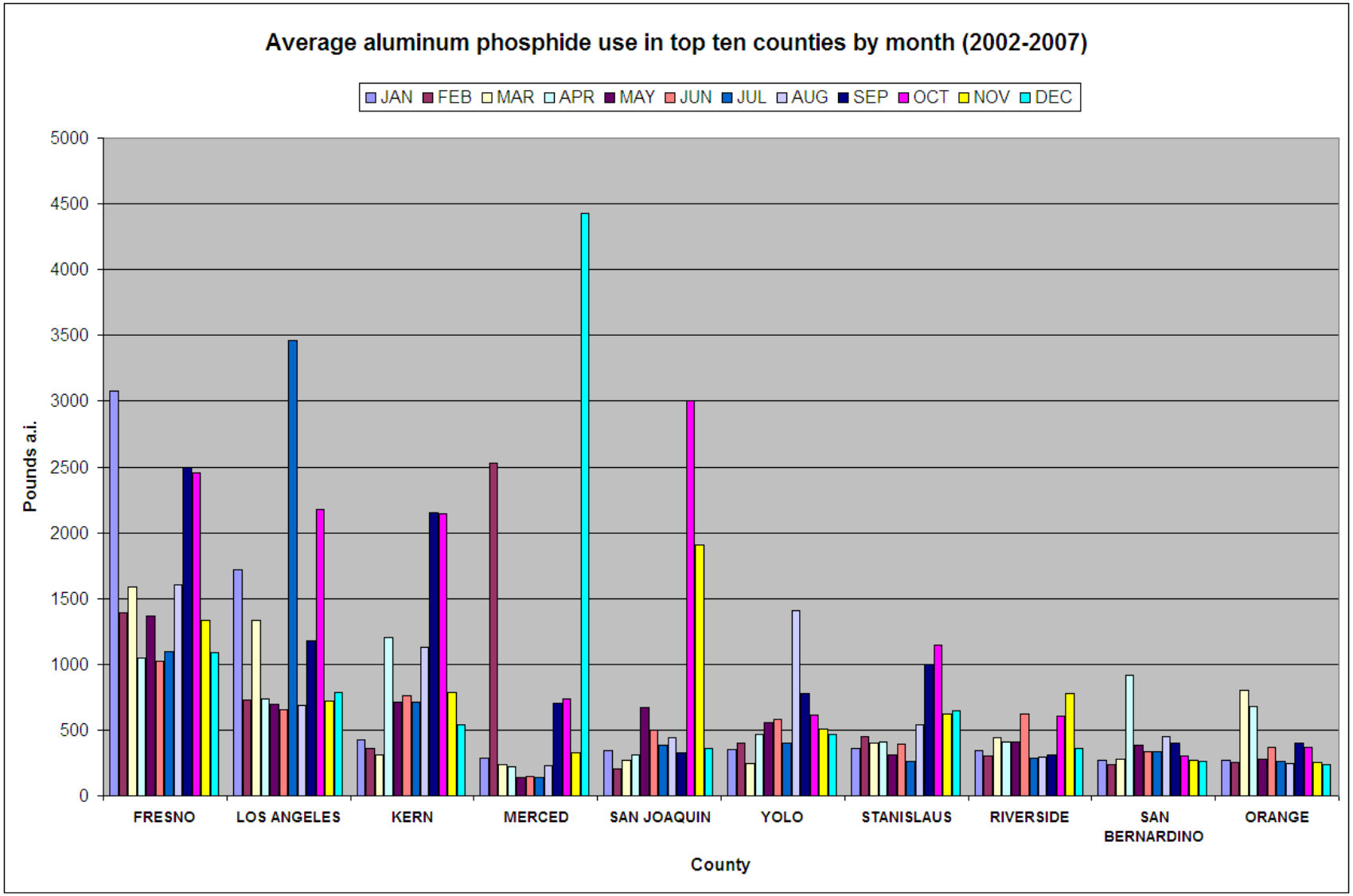


Table 9: Annual use of aluminum phosphide in top 20 counties by year (CDPR, 2008c).

Aluminum phosphide use (pounds a.I.) in top 20 counties, from 2002 to 2007								
County	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Co. total**	**Co. use as a % of total use**
FRESNO	19,314	14,322	20,154	30,332	21,418	13,032	118,571	14.5
LOS ANGELES	38,683	16,172	8,617	6,505	9,598	9,655	89,230	10.9
KERN	7,736	12,377	11,421	9,387	14,090	12,724	67,734	8.3
MERCED	42,875	3,195	3,390	3,676	3,758	4,243	61,138	7.5
SAN JOAQUIN	3,331	2,867	16,603	5,515	20,301	4,237	52,853	6.5
YOLO	7,214	8,762	6,131	6,036	6,949	5,563	40,654	5.0
STANISLAUS	6,883	8,135	4,456	7,290	7,711	5,106	39,580	4.9
RIVERSIDE	2,432	5,915	4,137	5,078	8,484	4,925	30,971	3.8
SAN BERNARDINO	2,499	2,371	3,809	2,745	9,782	5,350	26,556	3.3
ORANGE	3,263	2,922	3,884	8,129	3,964	4,353	26,516	3.3
COLUSA	3,370	4,324	4,560	5,124	3,334	4,511	25,223	3.1
SAN DIEGO	1,890	2,335	2,183	10,014	4,940	3,164	24,526	3.0
VENTURA	1,289	1,095	7,205	6,806	3,329	1,919	21,644	2.7
MADERA	3,967	3,507	3,400	3,129	3,360	4,032	21,395	2.6
SANTA CLARA	3,115	2,197	3,465	3,830	4,228	3,634	20,469	2.5
SUTTER	4,555	5,144	2,364	3,246	1,772	1,799	18,880	2.3
TULARE	1,242	2,873	4,309	3,666	3,615	2,536	18,242	2.2
MONTEREY	2,827	2,274	4,267	1,715	3,669	3,138	17,890	2.2
SACRAMENTO	1,247	2,738	3,081	2,388	4,653	1,817	15,924	2.0
SANTA BARBARA	613	4,605	3,711	1,046	1,620	731	12,326	1.5
Total top 20 counties	158,343	108,130	121,145	125,657	140,575	96,471	750,322	
As a % of State's total	93	90	92	92	93	92	92	
State Total	171,050	119,817	131,838	136,829	151,022	104,884	815,439	

Figure 6: Aluminum phosphide use in top ten counties by year (CDPR, 2008c).

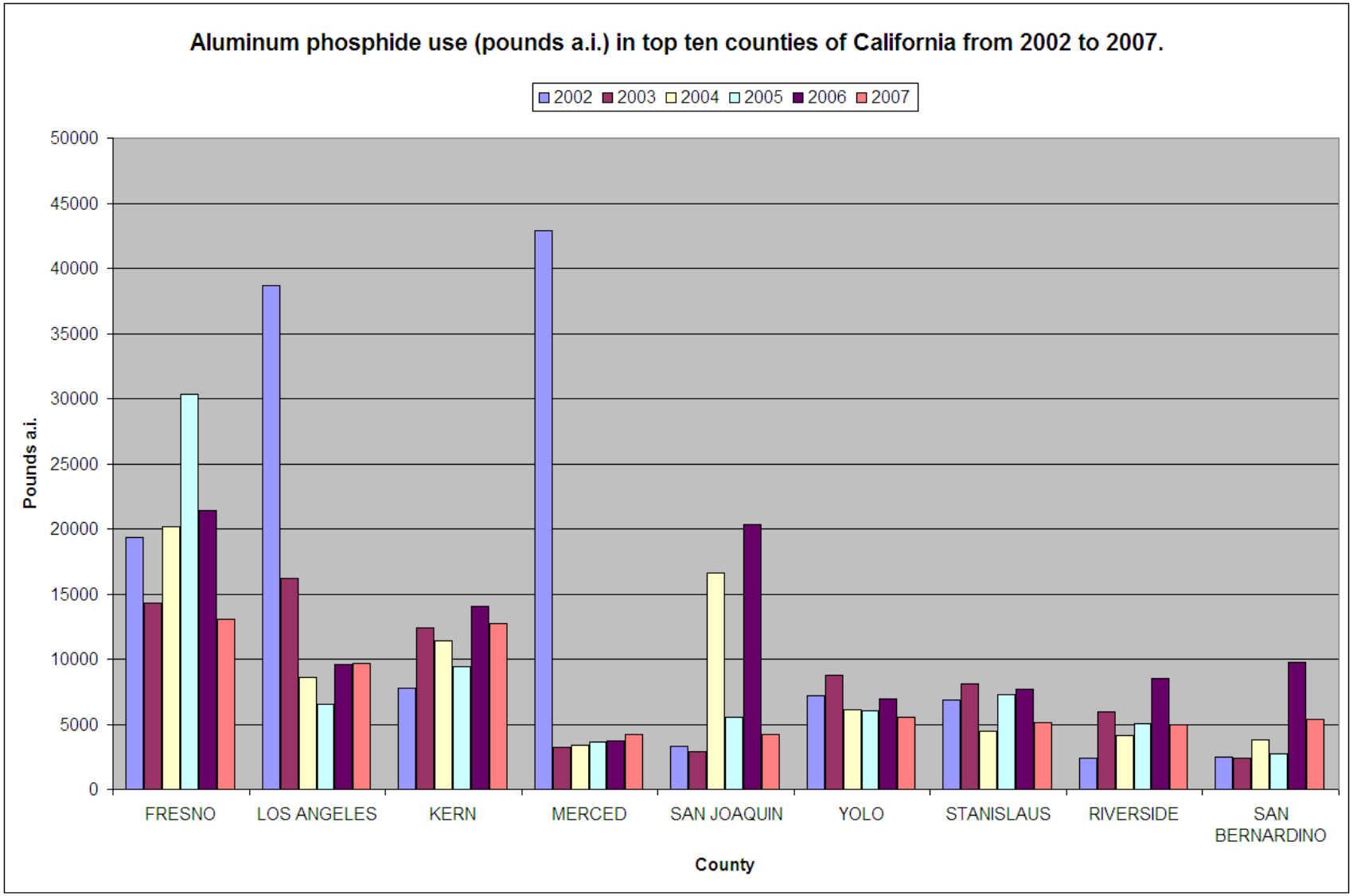


Table 10: Aluminum phosphide use on top 20 Sites by month (CDPR, 2008c).

Monthly average use of aluminum phosphide in top twenty Sites from 2002 to 2007.													
Site	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Site Total
LANDSCAPE MAINTENANCE	2,857	2,218	3,595	4,098	2,887	3,482	2,900	2,573	2,485	3,537	2,851	2,062	35,546
COMMODITY FUMIGATION	1,036	813	674	925	1,473	1,370	4,433	2,572	2,994	5,457	979	660	23,384
ALMOND	486	731	713	705	563	440	349	1,610	3,248	3,354	1,271	953	14,443
FUMIGATION, OTHER	229	248	206	308	346	644	499	988	886	1,103	1,032	4,564	11,055
STRUCTURAL PEST CONTROL	804	321	539	766	831	640	756	488	957	1,148	1,036	406	8,692
FRUITS (DRIED OR DEHYDRATED)	896	575	687	365	648	514	681	584	552	744	693	449	7,388
VERTEBRATE PEST CONTROL	487	815	782	1,240	460	470	447	576	219	224	722	417	6,859
GRAPES	338	665	429	526	459	313	321	456	382	647	474	420	5,431
RIGHTS OF WAY	204	2,450	510	258	150	302	237	195	164	117	197	394	5,178
PISTACHIO (PISTACHE NUT)	30	122	161	90	510	420	378	341	685	813	474	299	4,328
WHEAT, GENERAL	159	129	87	68	49	31	69	92	301	137	1,789	150	3,062
FIG	1,577	78	153	105	1	3	1	32	91	8	6	-	2,053
RICE (ALL OR UNSPEC)	2	5	97	93	87	321	297	207	79	56	186	24	1,454
GRAPES, WINE	28	155	125	146	117	143	85	18	15	5	232	18	1,085
REGULATORY PEST CONTROL	-	5	-	0	-	682	19	2	7	0	-	-	715
CORN, HUMAN CONSUMPTION	11	15	25	18	34	85	134	81	55	24	14	18	515
PRUNE	0	0	1	13	109	35	8	0	19	61	52	75	373
WALNUT (E. WALNUT, P. WALNUT)	4	13	29	37	56	31	32	22	43	27	41	9	344
ARTICHOKE (GLOBE/ UNSPEC)	0	-	1	1	49	171	58	12	7	16	1	2	317
AQUATIC ARE., Wt. ARE. /OR UNSPEC	-	-	-	-	-	156	-	-	80	78	-	-	313
Total Top 20 Sites	9,147	9,359	8,812	9,762	8,828	10,252	11,704	10,848	13,268	17,558	12,049	10,921	-
Top 20 Sites as a % of State Total	98.8	98.2	97.7	98.2	97.1	98.3	98.0	98.2	98.5	99.1	98.6	97.5	
Month Total	9,260	9,531	9,022	9,945	9,090	10,425	11,949	11,051	13,465	17,721	12,217	11,197	134,901

Figure 7: Monthly average use of aluminum phosphide in top ten sites (CDPR, 2008c).

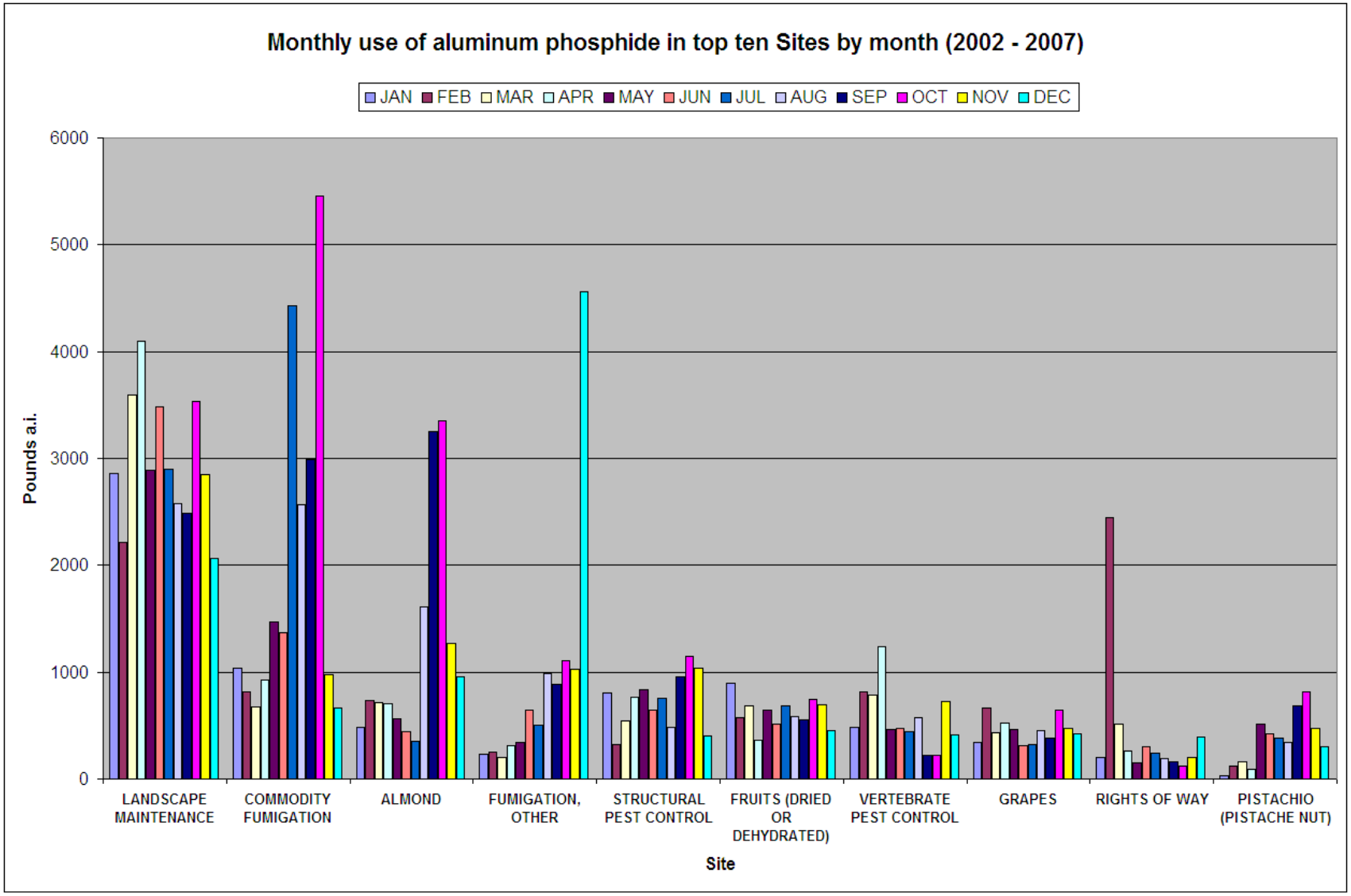
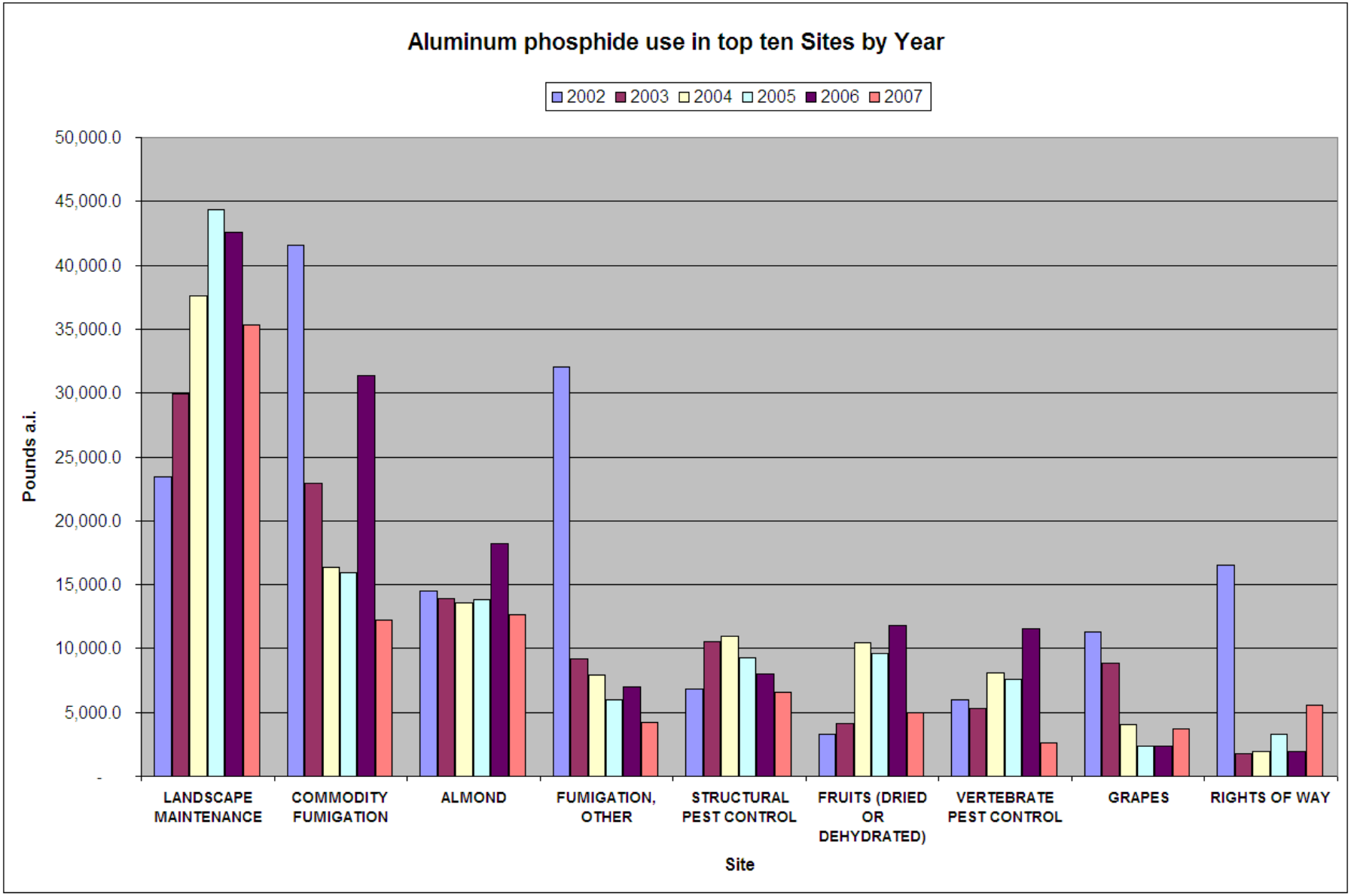


Table 11: Aluminum phosphide use in top 20 Sites from 2002 to 2007 (CDPR, 2008c).

Aluminum phosphide use in top twenty Sites by year								
Site	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Site Total**	**Site total as a % of State total**
LANDSCAPE MAINTENANCE	23,440	29,954	37,607	44,333	42,602	35,339	213,277	**26.3**
COMMODITY FUMIGATION	41,530	22,932	16,343	15,903	31,333	12,264	140,305	**17.3**
ALMOND	14,537	13,878	13,567	13,832	18,178	12,664	86,656	**10.7**
FUMIGATION, OTHER	32,080	9,191	7,925	5,996	6,959	4,180	66,331	**8.2**
STRUCTURAL PEST CONTROL	6,794	10,577	10,923	9,253	8,031	6,573	52,152	**6.4**
FRUITS (DRIED OR DEHYDRATED)	3,289	4,123	10,464	9,605	11,834	5,013	44,328	**5.5**
VERTEBRATE PEST CONTROL	6,025	5,301	8,060	7,623	11,546	2,600	41,155	**5.1**
GRAPES	11,284	8,870	4,070	2,320	2,353	3,687	32,584	**4.0**
RIGHTS OF WAY	16,512	1,773	1,945	3,277	1,980	5,582	31,069	**3.8**
PISTACHIO (PISTACHE NUT)	2,863	2,628	2,572	3,684	5,938	8,285	25,971	**3.2**
WHEAT, GENERAL	1,690	1,329	11,318	2,439	862	737	18,374	**2.3**
FIG	180	17	300	11,582	171	71	12,321	**1.5**
RICE (ALL OR UNSPEC)	2,705	195	842	562	2,904	1,513	8,722	**1.1**
GRAPES, WINE	1,155	757	734	682	2,328	853	6,510	**0.8**
REGULATORY PEST CONTROL		4,152		22	113	0	4,288	**0.5**
CORN, HUMAN CONSUMPTION	390	689	328	778	599	304	3,088	**0.4**
PRUNE	530	70	234	264	441	699	2,238	**0.3**
WALNUT (E. WALNUT, P. WALNUT)	444	407	210	188	252	565	2,066	**0.3**
ARTICHOKE (GLOBE/UNSPEC)	100	109	143	75	179	1,298	1,904	**0.2**
AQUA. AREAS, WATER ARE. / UNSPEC)			1,403	477			1,880	**0.2**
Use in top twenty Sites	165,548	116,953	128,987	132,897	148,604	102,228	795,217	
Use in top twenty Sites as % of total	**97.9**	**97.9**	**98.2**	**98.7**	**98.7**	**97.9**		
Year Total	169,081	119,451	131,295	134,605	150,539	104,434	809,404	

Figure 8: Aluminum use in top ten Sites by year (CDPR, 2008c).



The sampling should take place before application (four samples), during treatment (8 samples per period as a set), and during aeration (9 samples per period as a set). Quality control samples are additional to the above samples. Assuming the minimum duration of 2 days of holding of the fumigant above 20 ^{0}C is the plan, two sample sets; one at sunrise and the other at sunset should be collected for both days. Aeration is expected to continue at least for 48 hours. Once aeration is stopped, collect the final 24-hour post aeration sample set.

Sample period begins	**Sample duration**
Background (pre-application) Fumigation start 1 hour before sunset 1 hour after sunrise 1 hour before sunset 1 hour after sunrise Continue until Start of aeration Start of mechanical aeration 1 hour before sunset 1 hour after sunrise	24 hours From Start of fumigation until 1 hour before sunset [1]Overnight (until 1 hour after sunrise) Day time (until 1 hour before sunset) Overnight (until 1 hour after sunrise) Daytime Overnight/Daytime Overnight (until I hour after sunrise) Daytime: until end of aeration (when cleared), stop the sampling at that time and record the duration of last sampling. However, the aeration has to continue until the residue concentration is below the allowable limit.
End of Aeration (if before noon) End of Aeration (if after noon) As appropriate based on the time of aeration end: 1 hour before sunset or, 1 hour after sunrise	Until 1 hour before sunset Until 1 hour after sunrise Overnight (until 1 hour after sunrise) Daytime (1 hour before sunset)
24- hour post aeration	From the time that the concentration was detected to be below 0.3 ppm, another 24 hours of sampling (to ensure that the phosphine levels have stayed below 0.3 ppm) while aeration continued (to bring below the 0.01 ppm for processed food's acceptable residue level).

[1] All overnight samples must include the period from one hour before sunset to one hour after sunrise.

The Target Quantitation Limit is 10 ug/m^{3}.
DPR requests the following information be included in the monitoring report:

1) an accurate report of the application site, including topographic features.

2) an accurate record of the positions of the monitoring equipment with respect to the application site, including exact direction and distance of the samplers from the edge of the application site.

3) an accurate record of pesticide application, including application rate or quantity of the pesticide applied, application starting and ending time, and the method.

4) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles with respect to north (identified as either true or magnetic north).

5) if applicable, meteorological data collected at 1-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover.

The structure selected for monitoring must have enough clearance around it to place the samplers in two rings, the outer one approximately 60-70 feet from the fumigation chamber. Each ring comprises of four samplers and their arrangement is shown in Figure 1A. DPR proposes a different arrangement of samplers during aeration, which would have a higher probability of capturing phosphine in air during this period (Figure 1B). The placement of samplers during aeration is governed by the direction of wind just prior to aeration. Monitoring during aeration requires an un-obstructed path of 100 feet from the fumigation facility to two further-most samplers as shown in Figure 1B. In selecting the site, this requirement should be taken into account.

Monitoring of applications during conditions of rain and high winds should be avoided. Moderate wind up to about 10 miles per hour could be acceptable.

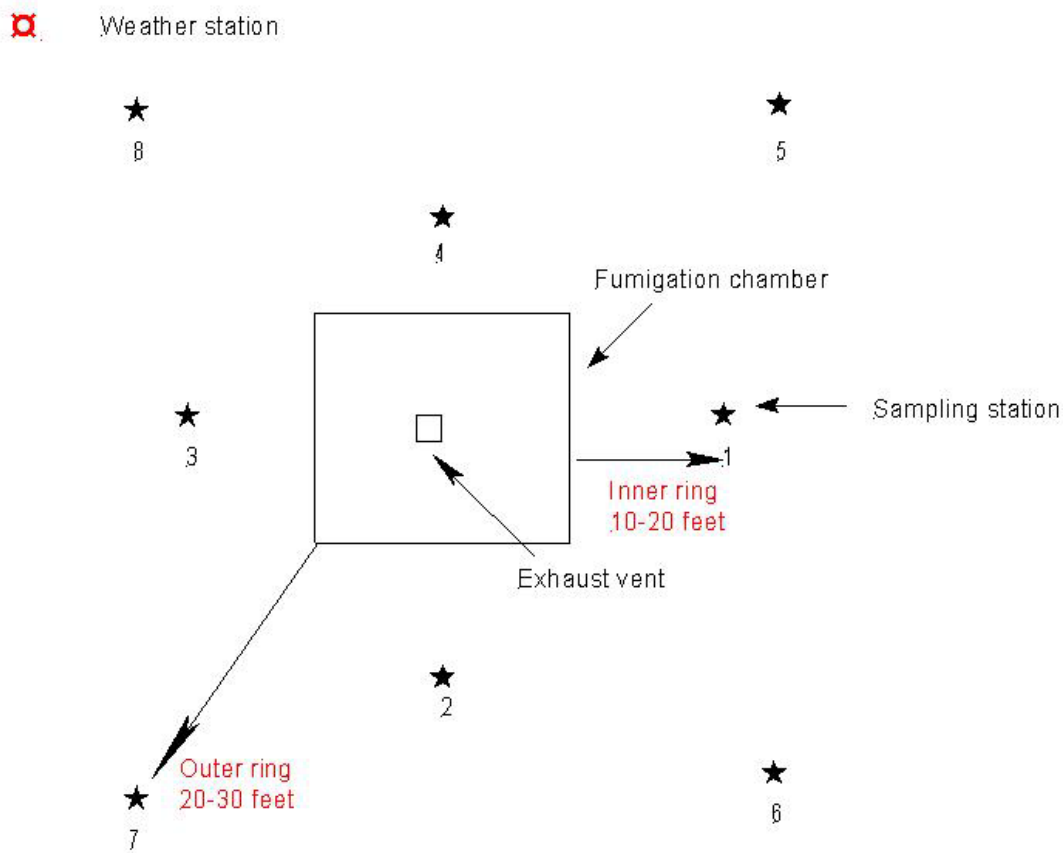


Figure 1A: Fumigation with phosphine - Monitoring arrangement during fumigation
(view from above)

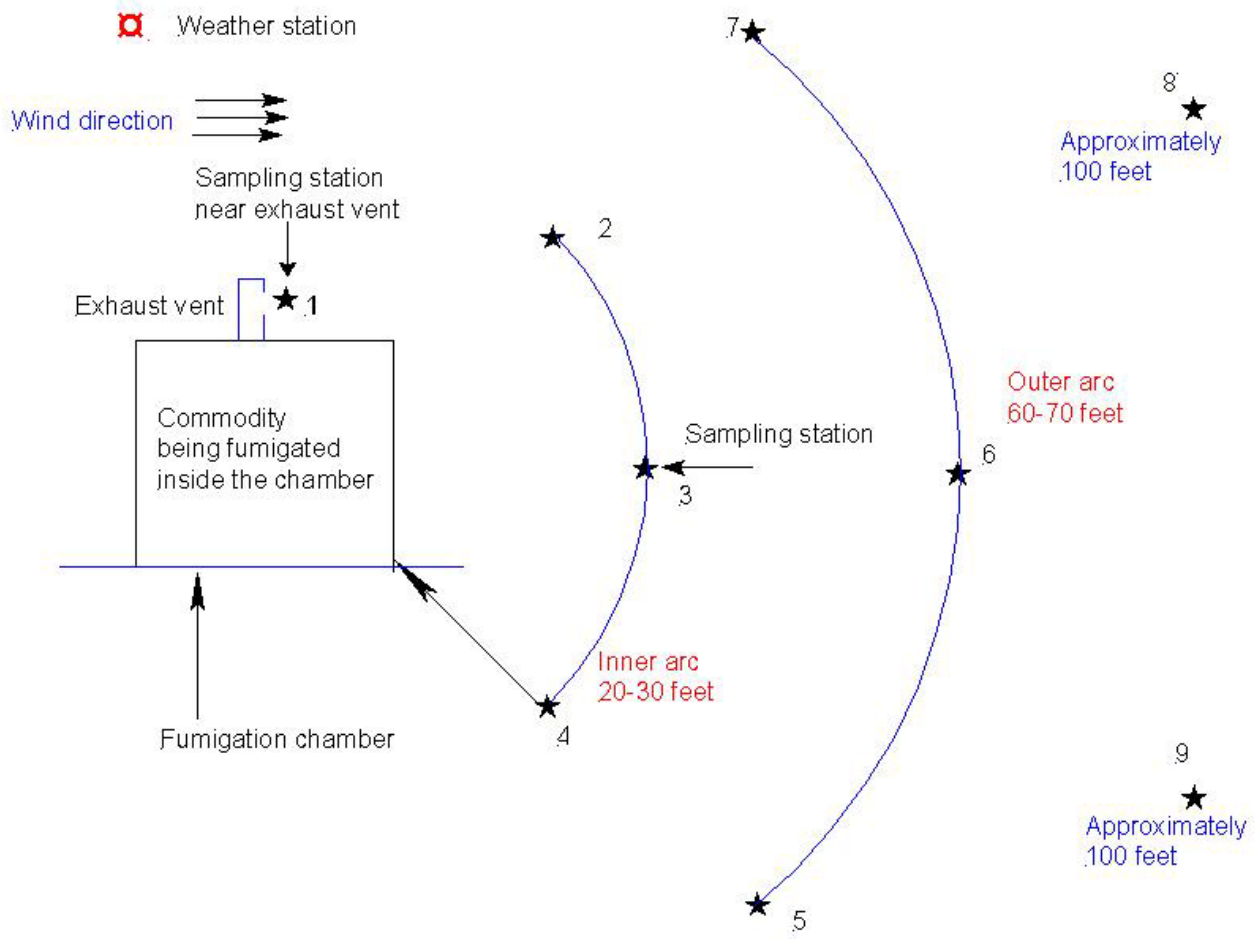


Figure 1B: Fumigation with phosphine - Monitoring arrangement during aeration (side view)

Tolerance for phosphine residues in animal feeds is 0.1 ppm and for processed foods is 0.01 ppm. The Occupational Health and Safety Administration's (OSHA, 2000) Permissible Exposure Limit (PEL) for General Industry: is 0.3 ppm, (0.4 mg/m^3) TWA (Time Weighted Average). Aluminum phosphide manual suggests a minimum of 48-hour aeration and testing concentration, before re-entry.

D. SAFETY RECOMMENDATIONS:

The applicator's manuals of ECO2FUME® Fumigant Gas**,** VAPORPH3OS™ Phosphine Fumigant and PHOSTOXIN® tablets and pellets give the details of safety measures to be followed with each product. The object of these recommendations is to prevent the sampling personnel being exposed to pesticide fumes. Therefore, most of these precautions are for reference only.

Product labels for the two fumigants and the metallic phosphides carry the "Danger" signal word. Inhalation of the vapors or ingestion of the phosphide product may be fatal or cause serious illness. Do not get in eyes, on skin or on clothing. If a garlic odor is detected you must monitor to determine whether phosphine gas is present above the acceptable exposure units (limits are given above). Mild exposure by inhalation causes malaise (indefinite feeling of sickness), ringing of ears, fatigue, nausea, and pressure in the chest, which is relieved by removal to fresh air. Moderate poisoning causes weakness, vomiting, pain just above the stomach, chest pain, diarrhea, and dyspnea (difficulty in breathing). Symptoms of severe poisoning may occur within a few hours to several days, resulting in pulmonary edema (fluid in lungs) and may lead to dizziness, cyanosis (blue or purple skin color), unconsciousness, and death. In all cases of overexposure get medical attention immediately. Follow the label recommended PPE when appropriate.

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