The relation between phosphine sorption and terminal gas concentrations in successful fumigation of food commodities

Palvai Vanitha Reddy, Yellappa Rajashekar, Khamrunissa Begum, Bhadravathi Chandrappa Leelaja and Somiahnadar Rajendran*
Food Protectants and Infestation Control Department, Central Food Technological Research Institute, Mysore 570 020, India

Abstract: Owing to increased tolerance and the development of resistance in stored product insects to the fumigant phosphine, in recent years there has been a shift in the target terminal concentration from 100 ppm (100 mL m^{-3}) to a higher level of 1000 ppm to achieve 100% insect mortality in 7 day commodity treatments. Therefore, there is a need to investigate whether the revised target concentration could be achieved for food commodities fumigated with phosphine at the standard dose of 2 g m^{-3} for 7 days under airtight conditions at ≥25 °C. When different types of food commodity (total 74) were fumigated (300 g per replicate) with phosphine at 2 g m^{-3} for 7 days, the terminal gas concentrations in the free space of the commodities varied from 0 to >2000 ppm. In chambers containing no substrate, a 1417 ppm concentration was recorded. Paddy rice, most of the oilseeds, shelled tree nuts, butter beans, cardamom, green gram splits, coriander powder, rice bran and cocoa powder were more sorptive (≥60%), such that the target concentration of 1000 ppm was not achieved at the end of 7 days. For these commodities, increased doses of 3–6 g m^{-3} were required to attain 1000 ppm. In-shell almonds, green cardamom, in-shell peanuts, leaf tea, tamarind pulp and sunflower seeds were exceptionally sorptive (>90%), so that 0, 41, 112, 168, 203 and 217 ppm respectively were noted at the end of 7 days; the dose must exceed 6 g m^{-3} for effective fumigation of these commodities.

Keywords: phosphine; food commodities; sorption; target concentration; effective dose

1 INTRODUCTION

Fumigation is a vital tool for insect pest control in stored agricultural products including food commodities. The success of fumigation depends on the maintenance of a certain minimum gas concentration in the free space of the commodity under treatment during the entire fumigation period. During fumigation, the gas concentration within the enclosure depletes, mainly owing to sorption of the fumigant by the commodity and leakage. As the sorptive capacities of food commodities vary, commodity sorption can be a major factor in determining whether a lethal concentration of fumigant is achieved under sufficiently airtight conditions.[1,2] Sorption includes reversible or 'physisorption' and irreversible absorption or 'chemisorption'.[3,4] Sorption of fumigants is known to be influenced by a given commodity's previous fumigation history, moisture content, particle size and composition, exposure period and dose.[4,5]

In recommending fumigant doses, the following factors are generally considered: target pest, temperature and commodity. Typically, in methyl bromide fumigations, the dose regimes vary according to the type of commodity and treatment temperature.[6,7] With ethyl formate, the recommended dose varies from 50 to 400 g m^{-3} according to the sorptive nature of the commodity.[8] For phosphine, a widely used fumigant, dose schedules, however, have often considered only two variables, namely temperature and target insect. Commodity sorption was considered to be insignificant when compared with other factors, i.e. type of storage structure and gas-tightness.[9] Haseltine[10] suggested an application rate of 2–5 g phosphine tonne^{-1} of commodity, depending on pest species for sheeted bag-stack fumigations, whereas EPPO[11] recommends a dose of 1 g phosphine m^{-3} with a 4–16 days exposure period that depends on target pest and temperature conditions. In well-sealed structures, doses recommended by professional bodies and commercial companies vary from 0.3 to 2.5 g m^{-3} with 5–28 days of exposure at ≥25 °C.[12] In China, phosphine is applied at a rate of 3–6 g m^{-3} for space treatments and 6–9 g m^{-3} for grain bulks with 3–15 day exposures.[13] There are isolated reports indicating the need for allowance for commodity sorption while recommending doses.[14,15]

It has been noted that the target phosphine concentration for a successful treatment has increased over the years owing to better understanding of the response of stored product insects of field origin to phosphine.

* Correspondence to: Somiahnadar Rajendran, Food Protectants and Infestation Control Department, Central Food Technological Research Institute, Mysore 570 020, India
E-mail: somiah_r@yahoo.co.uk
(*Received 14 February 2006; revised version received 27 June 2006; accepted 5 July 2006*)
Published online 19 October 2006; DOI: 10.1002/ps.1298

Earlier, a target concentration of 100 ppm (100 mL m^{-3})[16] or 150 ppm[17] was suggested for treatments with phosphine for 7 days. Subsequently, studies with mixed-age cultures of stored product insects have established that it requires a minimum concentration of 1 g phosphine m^{-3} (about 720 ppm) throughout the 7 days of fumigation conducted at $\geq 20\,°C$ to obtain complete mortality of grain weevils (*Sitophilus* spp.) and other insects with low-level phosphine resistance. For highly resistant strains, particularly the lesser grain borer, *Rhyzopertha dominica* (Fabricius), and the flat grain beetles, *Cryptolestes* spp., still higher target levels are needed.[18] Annis[19] analysed published data on the mortality responses of stored product insects to phosphine and arrived at the following target concentrations to achieve a very high level of insect mortality (excluding resistant strains, psocids and diapausing moths and the dermestids, *Trogoderma* spp.) in fumigations at $> 15\,°C$: 10 000 ppm for 1.5 days, 1200 ppm for 2 days, 1000 ppm for 8 days, 200 ppm for 10 days, 35 ppm for 20 days and 10 ppm for 30 days. Insect mortality response data in field experiments with phosphine in India revealed that a terminal concentration of 1000 ppm and above is required for the extinction of population of phosphine-resistant *R. dominica*.[20] Furthermore, Nayak *et al.*[21] determined target phosphine concentrations of 1450 ppm with 6 days of exposure or 720 ppm over 11 days for controlling phosphine-resistant psocids occurring in stored grains. In the context of the revised target end-concentrations of phosphine against stored product insect pests, the sorption factor has gained significance. Therefore, it was considered important to examine the sorption of phosphine by various food commodities to fix commodity doses accordingly. There are a few reports concerning the sorption of phosphine by some food commodities.[15,22–24] In these reports the authors showed that commodities differ in their phosphine-holding capacity, but they did not discuss the target concentration (1000 ppm) which is critical for successful phosphine fumigation. The objective of the present experiment was to check whether, when using the standard dose of 2 g phosphine m^{-3} for 7 days, the revised target end-concentration of 1000 ppm could be achieved in the free space of the commodities under treatment, and, if not, to find alternative higher doses for effective fumigation.

2 MATERIALS AND METHODS

2.1 Fumigation

Different types of food commodity were purchased from the local market. The previous history of fumigation of these commodities was not known. The moisture content of the commodities was determined by hot air oven (cereals, cereal products, pulses and pulse products), toluene distillation (oilseeds, spices, spice products, nuts and dried fruits) or vacuum oven (sugar, jaggery and milk powder) method. The commodities were fumigated with phosphine at the standard dose of 2 g m^{-3} for 7 days in 0.74 L gas wash bottles that served as fumigation chambers. In the majority of cases, 300 g of a commodity was taken for treatment. However, for some commodities, i.e. chillies (100 g), rice bran (150 g), in-shell peanuts (180 g), white oats, coriander and macaroni (200 g) and cocoa powder, tea powder and leaf tea (250 g), lesser quantities were taken as they occupied larger volumes. The void volume of the individual chambers was determined by evacuating the chambers completely and subsequent air filling with a 500 mL airtight syringe.[15] The void volume of the reference chambers was 0.74 L, whereas the free space in commodity-filled chambers varied from 0.32 L (sunflower seeds) to 0.63 L (chillies) depending on the bulk densities of the commodities. Before dosing, the open ends of the stopper of the fumigation chambers were closed with rubber septa, which were sealed using instant adhesive ('Fevikwik').

Phosphine was generated in a gas burette from aluminium phosphide tablets.[25] A known volume of phosphine was drawn from the gas burette with an airtight syringe and injected into the fumigation chambers through the septa. Before injecting phosphine, an equivalent volume of air was drawn from the chambers to avoid development of any positive pressure inside. In each set of experiments, ten commodities were fumigated with four replicates per commodity, a further two chambers without a commodity serving as reference chambers. For each commodity, untreated controls in duplicate were maintained at the same time. The fumigated chambers and the untreated control chambers were held at controlled temperature conditions of $25 \pm 1\,°C$ for 7 days. A PortaSens II (ATi Technologies, UK) monitor provided with a phosphine sensor (1–2000 ppm range) was used to measure the phosphine concentrations in the experimental chambers at the end of 7 days. The gas monitor was fitted with 6 mm internal diameter nylon tubes for inlet as well as outlet. To measure phosphine, the inlet and outlet tubings were quickly connected to the side tubes of the fumigation chamber after removing the rubber septa. Concentrations were also checked in unfumigated control chambers to record readings due to any interfering volatiles emitted by the commodities. In unfumigated commodities, only sunflower and cocoa powder showed about 8 and 22 ppm gas concentration readings respectively. The terminal phosphine concentrations for these commodities were corrected for the readings in untreated control batches. In the case of green cardamom, additional tests were conducted with pericarp and seeds separately at 2 g m^{-3} dose, and terminal concentration was measured as described above.

The difference between the concentration of phosphine in the reference chambers and that in the commodity chambers at the end of 7 days was considered as an index of the sorption capacity of the commodities under test. Based on end-concentration data in the first experiment, food commodities with high sorption capacity were subsequently tested at higher doses of 3–6 g m^{-3} (four replicates for each commodity) to ascertain that the target concentration of 1000 ppm of phosphine could be achieved at the end of a 7 day exposure period. Reference chambers (four replicates for each dose) without the substrate were fumigated at 3, 4 and 6 g m^{-3} doses at the same time. Terminal phosphine concentrations were determined and corrected (for sunflower seeds and cocoa only) as described above.

2.2 Data analysis

In order to determine the percentage sorption of phosphine by individual commodities, the terminal phosphine concentrations in commodity chambers and in reference chambers were computed uniformly for 1 L of free space. The computed concentration data were used to determine percentage sorption of commodities using the following formula:

$$\text{Sorption (\%)} = [(A - B)/A] \times 100$$

where A is the computed value for the reference chamber and B is the computed value for the fumigated commodity.

3 RESULTS

The terminal concentrations of phosphine varied from 0 to >2000 ppm depending on the sorptive nature of the commodities; in the reference chambers without substrate an average concentration of 1417 ppm was observed (Table 1). Paddy rice among cereals, most of the oilseeds, in-shell commodities such as peanuts and almonds, tree nuts without shell, butter beans, green gram splits, coriander powder, rice bran, tamarind pulp and cocoa powder were more sorptive (≥60% sorption). In these commodities the target concentration of 1000 ppm was not achieved at the end of 7 days. High levels of sorption (80–90%) were observed in safflower seeds, tea powder and mustard seeds, such that the final phosphine concentrations achieved were 483, 285 and 296 ppm respectively. In-shell almonds (0 ppm), leaf tea (168 ppm), in-shell peanuts (112 ppm), tamarind pulp (203 ppm), sunflower seeds (217 ppm) and green cardamom (41 ppm) were also exceptionally sorptive (>90%). Low to moderate levels of phosphine sorption were noted in some of the cereal grains, whole pulses, spices, dried fruits and cereal products (21–60%). In these commodities, the terminal concentrations exceeded 1000 ppm. Phosphine sorption was very low or negligible (≤20%) in wheat, parboiled rice, pearl barley, most of the dried fruits, vermicelli, refined wheat flour, macaroni, semolina, milk powder, jaggery, white sugar, coffee seeds and sago.

The particle size of wheat did not influence phosphine sorption and the resulting free space concentration. In whole wheat the terminal concentration was 1804 ppm, while in wheat products such as semolina and refined wheat flour (white flour) the end-concentrations were high at 1860 and >2000 ppm respectively. Processed foods such as vermicelli (>2000 ppm), macaroni (1747 ppm) and noodles (1393 ppm) similarly showed low sorption of the fumigant. Milk powder (skimmed or unskimmed), irrespective of the particle size, also showed very low phosphine sorption and gave a terminal concentration that exceeded 2000 ppm following a dose of 2 g m^{-3}.

The terminal gas concentration data (Table 1) indicated the need to adjust phosphine dose regimes for food commodities according to their phosphine-holding capacity. For most of the sorptive commodities, when the doses were increased to 3–6 g m^{-3}, the desired concentration of 1000 ppm was achieved at the end of 7 days (Table 2). In reference chambers dosed at 3, 4 and 6 g m^{-3}, phosphine concentrations at the end of 7 days exceeded 2000 ppm in all three treatments. For shelled tree nuts, black gram splits, chickpea flour and rice bran a dose of 3 g m^{-3} was adequate to reach the 1000 ppm end-concentration. However, green gram splits, paddy rice, safflower seeds, copra, and tea powder required 4 g m^{-3} doses to achieve the target concentration. With exceptionally sorptive commodities (e.g. green cardamom, in-shell almonds, in-shell peanuts, tamarind pulp, sunflower seeds and leaf tea) the terminal concentrations were less than 1000 ppm even at 6 g m^{-3}. Based on the degree of sorption observed and the terminal concentrations achieved at 2–6 g m^{-3}, phosphine doses for the food commodities at 25 °C and above for 7 days have been determined (Table 3).

4 DISCUSSION

In about 31% of the food commodities (total 74) treated at the standard dose of 2 g m^{-3} at 25 ± 1 °C, the target concentration of 1000 ppm was not achieved after 7 days. In paddy rice, the terminal concentration was low (578 ppm) owing to 72% sorption of the fumigant. Other workers in laboratory tests,[24,26,27] as well as in field experiments,[28] have reported high-level phosphine sorption in paddy rice. Higher sorption has been attributed to the siliceous husk which contributes about 20% of the total weight of the grain. It has been shown in electron microscopy studies that paddy husk has a peculiar sinuous structure.[29] Annis[30] suggested that doses as high as 10 g phosphine m^{-3} may be required for paddy rice in view of its high phosphine-holding capacity. Some workers have reported that sorghum also shows high phosphine sorption.[23,24,27] However, in the present experiments, low-level sorption (22%) was observed for sorghum (moisture content 10.6%) and the terminal phosphine concentration at 1869 ppm was high. To confirm the low-level sorption of the commodity, a second sorghum variety (10.4% moisture content) was fumigated at the same dose and gave an average concentration of 1618 ppm (33% sorption) at the end

Pest Manag Sci **63**:96–103 (2007)
DOI: 10.1002/ps

Table 1. Terminal phosphine concentrations in the free space of 300 g food commodities dosed at 2 g phosphine m^{-3} for 7 days at 25 ± 1 °C

Commodity	Moisture content (%)	Phosphine concentration at end of 7 days (ppm) (±SD)[a]	Concentration computed for 1 L free space (ppm) (±SD)	Sorption (%)
Reference chambers (without commodity)	–	1417 (±107.1)	1049 (±79.2)	–
Cereals				
Sorghum	10.6	1869 (±77)	815 (±41)	22.3
Wheat	10.1	1804 (±35)	850 (±37)	19.0
Barley (pearl)	11.5	1778 (±29)	856 (±29)	18.4
Milled rice, parboiled	10.8	1746 (±149)	857 (±69)	18.3
Maize	10.3	1684 (±70)	791 (±40)	24.6
Pearl millet	11.3	1629 (±21)	745 (±27)	29.0
Dehusked rice, raw	13.0	1603 (±47)	749 (±16)	28.6
White oats (200 g)	6.8	1409 (±44)	702 (±57)	33.1
Milled rice, raw	12.4	1407 (±99)	656 (±50)	37.5
Paddy rice	12.3	578 (±4)	290 (±9)	72.3
Pulses				
Peas	11.8	1738 (±59)	786 (±41)	25.1
French beans	11.4	1618 (±65)	720 (±39)	31.4
Green gram	11.4	1495 (±8)	697 (±20)	33.5
Field beans	10.4	1401 (±69)	653 (±23)	37.7
White gram	10.0	1367 (±105)	620 (±54)	40.1
Cowpea	9.7	1105 (±96)	516 (±46)	50.8
Chickpea	11.0	1056 (±25)	533 (±10)	49.1
Butter beans	10.9	717 (±35)	363 (±21)	65.5
Oilseeds				
Soybean	7.5	1623 (±129)	712 (±62)	32.1
Peanuts, shelled	6.0	1135 (±24)	440 (±22)	58.0
Sesame seeds	5.6	1063 (±76)	442 (±30)	57.9
Copra	5.3	633 (±43)	256 (±22)	75.6
Safflower seeds	7.0	483 (±32)	188 (±24)	82.1
Mustard	8.3	296 (±35)	134 (±13)	87.2
Sunflower seeds	5.8	217 (±13)	77 (±4)	92.6
In-shell peanuts (180 g)	5.9	112 (±11)	47 (±6)	95.5
Spices				
Cumin	6.6	1751 (±40)	785 (±49)	25.2
Poppy seeds	6.2	1578 (±94)	641 (±33)	38.9
Turmeric fingers	10.2	1550 (±27)	777 (±13)	25.9
Coriander (200 g)	8.8	1487 (±56)	724 (±31)	30.9
Fennel	8.1	1425 (±98)	598 (±30)	43.1
Chillies (100 g)	11.0	1210 (±93)	736 (±52)	29.8
Dried ginger	10.2	1126 (±24)	481 (±23)	54.1
Large cardamom	10.0	1101 (±25)	509 (±27)	51.4
Tamarind pulp	19.5	203 (±17)	79 (±6)	92.5
Cardamom, green	5.6	41 (±4)	17 (±1)	98.4
Dried fruits and tree nuts				
Figs	11.0	1852 (±9)	898 (±38)	14.4
Raisins	13.2	1728 (±37)	872 (±25)	16.9
Sultanas	9.8	1784 (±60)	845 (±27)	19.4
Dried dates	9.3	1571 (±108)	686 (±71)	34.6
Dates (edible)	15.3	1537 (±105)	713 (±57)	32.0
Walnuts, shelled	3.6	825 (±40)	345 (±18)	67.1
Pistachio nuts, shelled	4.6	798 (±24)	309 (±6)	70.4
Cashew nuts, shelled	4.1	793 (±39)	343 (±19)	67.3
Almonds, shelled	6.0	784 (±33)	341 (±18)	67.5
In-shell almonds	10.6	0	0	100
Beverage crops				
Coffee seeds (Robusta cherry)	10.5	1924 (±121)	839 (±44)	20.0
Cocoa powder (250 g)	5.0	813 (±37)	393 (±18)	62.5
Tea powder (250 g)	6.9	285 (±4)	146 (±3)	86.1
Leaf tea (250 g)	7.2	168 (±10)	88 (±6)	91.6

Table 1. Continued

Commodity	Moisture content (%)	Phosphine concentration at end of 7 days (ppm) (±SD)[a]	Concentration computed for 1 L free space (ppm) (±SD)	Sorption (%)
Cereal products				
Refined wheat flour	13.5	>2000 (±0)	>957 (±26)	<8.8
Vermicelli	10.7	>2000 (±0)	>917 (±38)	<12.6
Semolina	14.3	1860 (±22)	834 (±72)	20.5
Macaroni (200 g)	9.9	1747 (±136)	935 (±44)	10.9
Whole wheat flour	9.6	1466 (±71)	666 (±11)	36.5
Noodles	8.2	1393 (±114)	696 (±58)	33.6
Pulse products				
Lentil splits	11.2	1442 (±29)	675 (±21)	35.6
Field bean splits	11.0	1229 (±38)	605 (±22)	42.3
Red gram splits	9.6	1176 (±108)	523 (±24)	50.1
Chickpea splits	9.8	1102 (±32)	531 (±42)	49.4
Chickpea flour	8.4	908 (±34)	456 (±12)	56.5
Black gram splits	11.0	857 (±48)	431 (±21)	58.9
Green gram splits	10.4	619 (±32)	306 (±21)	70.8
Spice products				
Asafoetida powder, compounded	12.0	1613 (±54)	801 (±41)	23.6
Turmeric powder	7.0	1322 (±74)	620 (±67)	40.9
Curry powder	4.5	1018 (±10)	412 (±31)	60.7
Chilli powder	5.0	942 (±33)	425 (±9)	59.5
Coriander powder	6.0	724 (±80)	309 (±26)	70.5
Others				
White sugar	0.4	>2000 (±0)	>990 (±29)	<5.6
Milk powder, skimmed	9.1	>2000 (±0)	>880 (±16)	<16.1
Milk powder, unskimmed	3.3	>2000 (±0)	>980 (±22)	<6.6
Jaggery	11.5	>2000 (±0)	>982 (±26)	<6.4
Sago	12.8	>2000 (±0)	>935 (±39)	<10.9
Rice bran (150 g)	11.2	744 (±128)	422 (±70)	59.8

[a] Four replicates for each commodity and 14 replicates for reference chambers.

of 7 days. This would therefore indicate the potential for differences in sorption between sorghum varieties.

Phosphine sorption was high, with in-shell peanuts, copra, safflower, sunflower and mustard seeds giving end-concentrations of phosphine that varied from 633 to 112 ppm. High levels of phosphine sorption by oilseeds such as safflower[1,23] and peanuts[1,27,31] have similarly been reported elsewhere. Banks[1] reported 72% phosphine sorption in canola in a 5 day treatment, but Li and Jin[27] observed only 26% sorption in rapeseed in phosphine fumigation for 21 days. Among spices, tamarind pulp and green cardamom were exceptionally sorptive. Higher moisture content (19.5%) may be one of the contributing factors for higher sorption in tamarind pulp. Phosphine was largely sorbed by the fibrous and tough pericarp, which constitutes about 25% of green cardamom, such that the end-concentrations for whole cardamom and for the pericarp alone were almost similar (41 and 59 ppm respectively). Beyond the data presented here, there is a lack of published data on phosphine sorption by green cardamom and tamarind pulp. Phosphine sorption was low in all dried fruits, whereas in-shell tree nuts as well as shelled nuts were notably sorptive. Leesch[32] also observed high levels of phosphine sorption for in-shell pecans and walnuts, while Somay *et al.*[23] noted that cashew nuts were moderately sorptive to phosphine when treated at 2 g m^{-3} for 6 days at 16 °C.

Gas concentration data for whole wheat and wheat products (semolina, white flour and vermicelli) reveal that milling or processing does not always result in increased phosphine sorption. However, in whole-wheat flour as well as in noodles the terminal concentrations were less than that of wheat grain. Rangaswamy and Gunasekaran[15] noted that milled wheat products such as semolina, whole-wheat flour and white flour sorbed relatively more phosphine than whole-wheat grain when treated at 6 g phosphine $tonne^{-1}$ for 7 days. Differences in moisture contents and varieties of wheat might be the factors responsible for varied results on sorption of milled/processed wheat products. On the other hand, Sato and Suwanai[33] observed that in broken white rice the particle size strongly influenced the quantity of phosphine sorbed. In the present work, rice bran treated at 2 g phosphine m^{-3} showed 60% sorption, which may be due to oil content and the presence of hull in rice bran. In green gram as well as black gram splits and chickpea flour, terminal concentrations were less

Table 2. Terminal phosphine concentrations in the free space of 300 g food commodities treated at higher doses for 7 days at 25 ± 1 °C

Commodity[a]	Phosphine concentration at end of 7 days (ppm) (±SD)[b]	Concentration computed for 1 L free space (ppm) (±SD)
Dose 3 g m^{-3}		
Reference chambers	>2000 (±0)	>1488 (±0)
Rice bran (150 g)	1644 (±57)	918 (±16)
Chickpea flour	1408 (±77)	620 (±50)
Black gram splits	1320 (±114)	577 (±69)
Butter beans	1192 (±155)	478 (±84)
Cashew nuts, shelled	1101 (±107)	441 (±60)
Walnuts, shelled	1092 (±45)	455 (±11)
Pistachio nuts, shelled	1047 (±141)	454 (±79)
Almonds, shelled	1091 (±59)	412 (±43)
Coriander powder	975 (±111)	412 (±43)
Green gram splits	733 (±15)	359 (±10)
Dose 4 g m^{-3}		
Reference chambers	>2000 (±0)	>1488 (±0)
Paddy rice	1746 (±60)	807 (±25)
Green gram splits	1238 (±31)	469 (±29)
Copra	1230 (±87)	469 (±66)
Tea powder (250 g)	1072 (±42)	565 (±56)
Safflower seeds	997 (±29)	373 (±29)
Mustard seeds	698 (±58)	317 (±27)
Dose 6 g m^{-3}		
Reference chambers	>2000 (±0)	>1488 (±0)
Mustard seeds	1571 (±39)	609 (±36)
Leaf tea	893 (±35)	389 (±48)
In-shell peanuts (180 g)	872 (±57)	387 (±37)
Tamarind pulp	778 (±39)	319 (±15)
Sunflower seeds	604 (±33)	205 (±16)
In-shell almonds	237 (±40)	103 (±19)
Cardamom, green	78 (±10)	32 (±4)

[a] Moisture content of the commodities as in Table 1.
[b] Four replicates for each commodity and four for reference chambers for each dose.

than 1000 ppm. Rangaswamy and Gunasekaran[15] also observed high-level phosphine sorption in split pulses (field beans, green gram and chickpea), resulting in low terminal concentrations in 7 day treatments. Muthu[22] noted 87% sorption in chickpea splits fumigated with phosphine at 1.5 g tonne^{-1} for 7 days. Muthu[22] mentioned that sago was exceptionally sorptive (97% sorption) when treated at 1.5 g phosphine tonne^{-1} for 8 days. In contrast, in the present work, sago was noted to be least sorptive (16.7%), so that the end-concentration exceeded 2000 ppm.

It must be noted that the terminal concentration data for the tested commodities and their corresponding computed value for 1 L free space do not always match. This may be due to variations in the volume of free space of the commodities, depending on their particle size. For example, in chickpea and sesame seeds, the actual terminal concentrations were 1056 and 1063 ppm respectively, whereas the computed values were 533 and 442 ppm. As the percentage sorption was calculated on the basis of computed values, sorption levels were different for the commodities (49 and 58% respectively). For some of the commodities, less than 300 g was used in the experiments (e.g. white oats, in-shell peanuts, rice bran, etc.), and end-concentrations for these commodities would have been lower if 300 g per replicate had been used uniformly.

In untreated control commodity samples, only sunflower and cocoa powder produced false readings. This may have been due to cross-sensitivity of the sensor to certain volatiles emitted from the commodities. The hydride sensor fixed to the instrument has been claimed to show very low-level cross-sensitivity to the presence of hydrogen, acetylene, dimethyl ether and ethanol in air samples.

This investigation has shown the trend with regard to phosphine sorption by different categories of food commodities. Levels of phosphine sorption in a particular commodity are likely to be affected by other parameters such as moisture content (paddy rice), oil content (sunflower seeds), variety and previous fumigation history.[14] Follow-up studies are therefore needed on highly sorptive commodities. The present study has highlighted the importance of considering commodity type when planning a phosphine treatment schedule at temperatures of ≥25 °C. The terminal concentration data indicate that for certain commodities (e.g. milk powder, refined wheat flour, vermicelli, white sugar and sago) the phosphine dose could be less than 2 g m^{-3}, whereas for sorptive commodities it has to be increased to 3–6 g m^{-3}. For exceptionally sorptive commodities

Table 3. Recommended phosphine doses for food commodities based on their sorptive capacities for treatments at ≥25 °C for 7 days

Phosphine dose (g m^{-3})	Commodities
≤2	Barley (pearl), dehusked rice, maize, milled rice (raw and parboiled), pearl millet, sorghum, wheat, white oats.
	Chickpea, cowpea, field beans, French beans, green gram, peas, white gram.
	Peanuts (shelled), sesame seeds, soybean.
	Asafoetida powder, chillies, coriander, cumin, dried ginger, fennel seeds, large cardamom, poppy seeds, turmeric fingers.
	Dates (edible), dried dates, figs, raisins, sultanas.
	Coffee seeds.
	Macaroni, noodles, refined wheat flour, semolina, vermicelli. Whole-wheat flour.
	Chickpea splits, lentil splits, red gram splits.
	Curry powder, turmeric powder.
	Jaggery, milk powder, sago, white sugar
3	Almonds (shelled), black gram splits, butter beans, cashew nuts, chickpea flour, pistachio nuts (shelled), rice bran, walnuts (shelled)
4	Copra, coriander powder, green gram splits, paddy rice, safflower seeds, tea powder
≥6	Cardamom green, leaf tea, mustard seeds, in-shell peanuts, in-shell almonds, sunflower seeds, tamarind pulp

the dose must exceed 6 g m^{-3} to achieve 1000 ppm end-concentration.

Laboratory studies have demonstrated that phosphine is much more effective against insect pests at lower concentrations over longer exposure periods than at higher concentrations for a shorter period.[34] At higher phosphine concentrations, adults of stored product insects are narcotised, and the narcotised insects are likely to survive the treatment.[35] Winks[36] stated that there are two approaches for effective phosphine fumigation: (1) apply a low phosphine dose in order to achieve a low concentration over a longer exposure period until the tolerant eggs and pupae reach susceptible stages, and (2) apply a higher dose that yields gas concentrations sufficiently high to kill eggs and pupae. In practical situations, especially for bag-stack treatments with phosphine, 5–7 day exposure periods are commonly practised. In that case, it is important that the revised target concentration (1000 ppm) is achieved for a successful treatment. In addition to cost, application of higher doses, however, may result in unacceptable levels of phosphine residues (0.1 mg kg^{-1} in whole grains and 0.01 mg kg^{-1} in milled products) in treated commodities. Therefore, commodities treated at higher doses may require a longer aeration period. In view of the implications of using high doses of phosphine, alternative approaches such as multiple applications of low doses with an extended exposure period and continuous application systems using low doses from cylinderised phosphine formulations or on-site generators must be considered for management of sorption in the context of insect resistance to phosphine.

ACKNOWLEDGEMENT

The authors thank the Director, Central Food Technological Research Institute, Mysore, for encouragement and support.

REFERENCES

1 Banks HJ, Uptake and release of fumigants by grain: sorption/desorption phenomena, in *Proceedings of International Conference on Controlled Atmosphere and Fumigation in Grain Storages, Winnipeg, Canada*, ed. by Navarro S and Donohaye E. Caspit Press Ltd, Jerusalem, pp. 241–260 (1993).

2 Sinclair WB and Lindgren DL, Factors affecting the fumigation of food commodities for insect control. *J Econ Entomol* **51**:891–900 (1958).

3 Banks HJ, Sorption and desorption of fumigants on grains: mathematical descriptions, in *Pesticides and Humid Tropical Grain Storage Systems: Proceedings of International Seminar, Manila, Philippines*, ed. by Champ BR and Highley E. Australian Centre for International Agricultural Research, Canberra, Proceedings No. 14, pp. 179–193 (1986).

4 Berck B, Sorption of phosphine by cereal products. *J Agric Food Chem* **16**:419–425 (1968).

5 Dhaliwal GS, Analysis of some important factors affecting sorption of fumigants by food commodities. *J Food Sci Technol* **12**:1–5 (1975).

6 EPPO, EPPO Recommendations on Fumigation Standards, Standard 13, Methyl bromide fumigation of stored products. *EPPO Bull* **12**:30–31 (1982).

7 Rajendran S and Muthu M, A laboratory study on the minimum dosage requirements for effective methyl bromide fumigation of food commodities. *Internat Pest Control* **20**:5–9 (1978).

8 Muthu M, Rajendran S, Krishnamurthy TS, Narasimhan KS, Rangaswamy JR, Jayaram M *et al*, Ethyl formate as a safe general fumigant, in *Controlled Atmosphere and Fumigation in Grain Storages, Proceedings of International Symposium on Practical Aspects of Controlled Atmosphere and Fumigation on Grain Storages, Perth, Western Australia*, ed. by Ripp BE. Elsevier, Amsterdam, pp. 369–393 (1984).

9 Leesch JG, Cuperus G, Criswell J, Sargent J and Mueller J, Practical fumigation considerations, in *Stored Product Management*. Cooperative Extension Service, USDA, APHIS, Circular No. E-912, pp. 139–152 (1995).

10 Heseltine HK, A guide to fumigation with phosphine in the tropics. *Trop Stored Prod Inf* **24**:25–36 (1973).

11 EPPO, EPPO Recommendations on Fumigation Standards, Standard 18, Phosphine fumigation of stored products. *EPPO Bull* **14**:589–599 (1984).

12 Navarro S and Donahaye E, Generation and application of modified atmospheres and fumigants for the control of storage insects, in *Fumigation and Controlled Atmosphere Storage of Grain, Proceedings of International Conference, Singapore*, ed. by Champ BR, Highley E and Banks HJ. Australian Centre for International Agricultural Research, Canberra, Proceedings No. 25, pp. 152–169 (1990).

13 Jin Zuxun, *Summary on Research Progress in Grain Storage Science During Nearly Forty Years in China*. Booklet presented at the 7th International Working Conference on Stored Product Protection, 7th IWCSPP Secretariat, Beijing, China (1998).

14 Banks HJ, Behaviour of gases in grain storages, in *Fumigation and Controlled Atmosphere Storage of Grain, Proceedings of International Conference, Singapore*, ed. by Champ BR, Highley E and Banks HJ. Australian Centre for International Agricultural Research, Canberra, Proceedings No. 25, pp. 96–107 (1990).

15 Rangaswamy JR and Gunasekaran N, Free phosphine in the void space of food commodities during phosphine fumigation. *J Food Sci Technol* **26**:447–449 (1993).

16 Van S Graver JE and Annis PC, *Suggested Recommendations for the Fumigation of Grain in the ASEAN Region. Part 3. Phosphine Fumigation of Bag Stacks in Plastic Enclosures: an Operations Manual*. ASEAN Food Handling Bureau, Kuala Lumpur/Australian Centre for International Agricultural Research, Canberra (1994).

17 Friendship R, Fumigation with phosphine under gas-proof sheets. Overseas Development Natural Resources Institute Bulletin No 26 (1989).

18 Winks RG and Hyne EA, The use of mixed-age cultures in the measurement of response to phosphine, in *Proceedings of International Conference on Controlled Atmospheres and Fumigation in Stored Products, Nicosia, Cyprus*, ed. by Donahaye EJ, Navarro S and Varnava A. Printco Ltd, Nicosia, pp. 3–15 (1997).

19 Annis PC, Phosphine dosage regimes required for high mortality: a database approach, in *Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products, Fresno, CA*, ed. by Donahaye EJ, Navarro S and Leesch JG. Executive Printing Services, Clovis, CA, USA, pp. 45–55 (2001).

20 Rajendran S, Insect resistance to phosphine – challenges and strategies. *Internat Pest Control* **43**:118–123 (2001).

21 Nayak MK, Collins PJ and Pavic H, Resistance to phosphine in psocids: challenges ahead! in *Stored Grain in Australia 2000: Proceedings of Australian Postharvest Technical Conference, Adelaide*, ed. by Wright EJ, Banks HJ and Highley E. CSIRO Stored Grain Research Laboratory, Canberra, pp. 113–118 (2002).

22 Muthu M, Some aspects of phosphine as a fumigant, in *Fumigation and Gaseous Pasteurization*, ed. by Majumder SK and Venugopal JS. Academy of Pest Control Sciences, Mysore, India, pp. 23–36 (1973).

23 Somay Y, Kishino H and Akagawa T, Sorption of phosphine in cereal grains and beans. *Research Bulletin of the Plant Protection Service, Japan* **32**:47–50 (1996).

24 Tan Xianchang, Control of stored grain insects and mites in China, in *Grain Storage in China*. Pamphlet presented at the 7th International Working Conference on Stored Product Protection, 7th IWCSPP Secretariat, Beijing, China, pp. 30–42 (1998).

25 FAO, Recommended methods for the detection and measurement of resistance of agricultural pests to pesticides. Tentative method for adults of some major pest species of stored cereals, with methyl bromide and phosphine. FAO method No.16. *FAO Plant Prot Bull* **23**:12–25 (1975).

26 Ren Yonglin and Banks HJ, Studies on phosphine absorption in paddy. *J Zhenzhuo Grain College* **4**:47–50 (1987).

27 Li Lungshu and Jin Zuxun, The great achievement of grain storage scientific research in China, in *Stored Product Protection, Proceedings of the 7th International Working Conference on Stored Product Protection, Beijing, China*, ed. by Jin Zuxun, Liang Yongsheng, Tan Xianchang and Guan Lianghua. Sichuan Publishing House of Science and Technology, Chengdu, China, pp. 40–49 (1999).

28 Rajendran S and Muralidharan N, Performance of phosphine in fumigation of bagged paddy rice in indoor and outdoor stores. *J Stored Prod Res* **37**:351–358 (2001).

29 Houston DF, Rice hulls, in *Rice Chemistry and Technology,* ed. by Houston DF. American Association of Cereal Chemists, St Paul, MN, pp. 301–352 (1972).

30 Annis PC, Sealed storage of bag stacks: status of the technology, in *Fumigation and Controlled Atmosphere Storage of Grain: Proceedings of International Conference, Singapore*, ed. by Champ BR, Highley E and Banks HJ. Australian Centre for International Agricultural Research, Canberra, Proceedings No. 25, pp. 203–210 (1990).

31 Leesch JG, Gillenwater HB, Davis R and Wilson R Jr, Phosphine and methyl bromide fumigation of shelled peanuts. *Peanut Sci* **6**:18–26 (1979).

32 Leesch JG, The sorption of phosphine by whole walnuts, in *Postharvest IPM Research Summaries: April 2002.* Postharvest Technology Research Information Center, Davis, USA. [Online]. Available: http://postharvest.ucdavis.edu/Ipm/objectives_2002.shtml [26 July 2005].

33 Sato K and Suwanai M, Adsorption of hydrogen phosphide to cereal products. *Appl Entomol Zool* **9**:127–132 (1974).

34 Hole B, Bell CH, Mills KA and Goodship G, The toxicity of phosphine to all developmental stages of thirteen species of stored product beetles. *J Stored Prod Res* **12**:235–244 (1976).

35 Winks RG, The toxicity of phosphine to adults of *Tribolium castaneum* (Herbst): phosphine-induced narcosis. *J Stored Prod Res* **21**:25–29 (1985).

36 Winks RG, Strategies for effective use of phosphine as a grain fumigant and the implications of resistance, in *Proceedings of the 4th International Working Conference on Stored Product Protection, Tel Aviv, Israel,* ed. by Donahaye E and Navarro S. Caspit Press Ltd, Jerusalem, pp. 335–344 (1987).