



Review article

A review of current fumigation practices in Thailand

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Abstract

Importance of the work: Fumigation, as a pest management tool, plays an important role in reducing post-harvest losses and maintaining food and bio securities.

Objectives: To discuss the current state of fumigation practices in Thailand and some of the challenges faced by fumigation practitioners.

Materials & Methods: A typical fumigation job can be divided into three main steps: 1) the fumigation enclosure is constructed; 2) the fumigant is released and held within the enclosure for a certain period, called the exposure time; and 3) when the desired exposure time has elapsed, the enclosure is aerated.

Results: Phosphine in the form of aluminum phosphide tablets is the most-used fumigant. PH₃ generators are used to apply these tablets, thus releasing PH₃ gas more effectively. In addition, phosphine formulations in cylinders are used in niche applications. However, insects with strong resistance to phosphine are present in many areas of the country. Although methyl bromide was banned in Thailand in 2014, its use is necessary and still allowed in quarantine and pre-shipment applications. Carbon dioxide is used in the treatment of organic commodities; however, carbon dioxide fumigation is more costly and requires more gas-tight enclosures and a longer exposure time.

Main finding: To achieve successful fumigation, it is necessary to understand the advantages and limitations of these fumigants.

Introduction

Fumigation is one of the most important tools in pest management as it is often utilized, for example in disinfestation of import/export goods, stored agricultural commodities,

plantation soil, commercial and residential structures and food processing facilities (Bell, 2000; Hopkins and Johnson, 2022). For Thailand, the importance of fumigation can be reflected in the amounts of fumigants imported as the country does not produce them domestically, except for carbon dioxide (CO₂). Table 1 summarizes the amounts of fumigants imported each year for the last 10 years (Office of Agricultural Regulation, 2021b).

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Clearly, Thailand's fumigation practitioners have been relying exclusively on methyl bromide (MB) and phosphine (PH₃). The MB is imported in gas cylinders with either 99.4% purity or 98% MB + 2% chloropicrin. The PH₃ gas fumigant can be in either solid metal phosphide form or in gas cylinders. Aluminum phosphide (ALP) in the tablet form is by far the most used fumigant but magnesium phosphide (MgP) tablets and plates are still used in certain applications. The cylinderized gas mixture of 2% PH₃ and 98% CO₂ (Cytec Industries Inc., 2011; Solvay S.A., 2021a) has been used in Thailand since 2012. Although not yet in widespread usage, it is consistently used in sizeable volumes every year. While a small amount of 99.3% cylinderized PH₃ gas (Cytec Industries Inc., 2013; Solvay S.A., 2021b) was imported in 2017 (presumably for registration trial purposes), at the time of writing this review, it has never been used commercially in Thailand. Sulfuryl fluoride (SF) was first registered in Thailand in 2011 and re-registered in 2020 (Office of Agricultural Regulation, 2021a). However, it has never been commercially used.

Because MB is an ozone depleting substance according to the Montreal Protocol (United Nations Environment Programme, 2000), by the end of 2014 Thailand, as a developing country, was required to stop using MB, except for quarantine and pre-shipment (QPS) applications. This was achieved by the end of 2012, accelerated by the National Methyl Bromide Phase-out Plan Project (The World Bank, 2010). Currently, the production, importation or possession of the fumigants shown in Table 1 are closely regulated by the Hazardous Substances Act B.E. 2535 (1992) (Office of the Council of State, 1992). In addition, fumigators are required to report any usage amount of MB to the Department of Agriculture (DOA), Ministry of Agriculture and Cooperatives (Schafer, 1999). The objective of the current review article was to highlight the current state of fumigation practices in Thailand and to identify some of the challenges fumigation practitioners are facing.

Overall state of current fumigation practices in Thailand

Fumigation in Thailand can be classified into three major types: 1) QPS application; 2) post-harvest application; and 3) structural fumigation (The World Bank, 2010). Since the ban of MB in non-QPS applications, PH₃ has been the only alternative fumigant in Thailand. In many cases pest disinfection could not be performed based on structural fumigation in food or feed processing facilities. Phosphine has not been widely adopted in structural fumigation due to its required long exposure time and corrosive properties. The objective of QPS fumigation is to ensure that import and export goods are free of pests. In post-harvest application, the primary purpose is to maintain low levels of post-harvest pests where fumigation could be performed in silos, warehouses, bag stacks or other types of storage. Structural fumigation is typically conducted, aiming to eradicate pest infestation in commercial and residential buildings or to disinfest buildings or storage structures in food or feed processing facilities. In Thailand, fumigation in commercial and residential buildings is rare. Furthermore, Thai farmers and plant growers do not use soil fumigation when preparing land for crop rotation. At the core, fumigation is the process in which poisonous gas is released into an enclosure in order to kill any pests, such as rodents and micro-organism infesting the volume of the product in the enclosure. The fumigation is considered successful when a lethal concentration is maintained for a sufficient period of time. Thus, the dosage of a fumigant required to achieve 100% mortality of the pests is sometimes described as the concentration × time (Ct) product (Muthu et al., 1975; Gandy and Chanter, 1976; Bell, 1992; Annis, 1999; Thoms and Busacca, 2016). The Ct product is essentially the area under the fumigant concentration curve plotted over elapsed exposure time (Chayaprasert and Maier, 2010; International

Table 1 Amounts in kilograms of fumigants annually imported by Thailand 2011–2020

Year	Methyl bromide	Aluminum phosphide	Magnesium phosphide	Phosphine		Sulfuryl fluoride
				2% in 98% CO ₂	99.3%	
2020	156,100	461,579	3,078	14,871	-	-
2019	156,100	566,913	2,979	14,871	-	-
2018	188,100	687,588	1,980	14,871	-	57
2017	188,100	862,899	5,274	43,663	22	-
2016	157,400	1,151,453	3,359	19,220	-	-
2015	162,700	1,190,531	1,404	29,760	-	-
2014	61,700	1,404,875	4,464	9,920	-	-
2013	121,400	1,113,201	-	14,880	-	-
2012	321,900	615,277	-	8,184	-	-
2011	-	726,057	6,873	-	-	-

Source: Office of Agricultural Regulation (2021b)

Plant Protection Convention, 2010; Uniphos Envirotronic Inc., 2013). However, in practice Thai fumigation practitioners typically do not calculate such Ct product-areas. Although there are differences in certain details among the three fumigation types, their fundamental procedures are the same. The main steps are: 1) the fumigation enclosure is constructed; 2) the fumigant is released and held within the enclosure for a certain period of time, called the exposure time; and 3) when the desired exposure time has elapsed, the enclosure is ventilated.

To create a gas-tight envelope, thorough sealing of the enclosure is done either permanently or temporarily. This includes: 1) closing and sealing all doors, windows, hatches, manholes, slide gates, air vents, ducts, seams, loading equipment, conveyors, aeration fans etc. with plastic sheets, adhesive tapes or sealants or combinations of these; 2) covering bag, stacks or piles of the fumigated materials with tarpaulin sheets and sealing the edges with “sand snakes” or taping them to the floor; and 3) filling any small gaps with sealants or expandable spray foam or both.

Fumigators are usually preferred to permanent sealing if the former can be done effectively and without interfering with other normal usages of the structure. The methods for constructing and sealing enclosures have been described in more detail by several authors (Bond, 1984; Noyes et al., 1999; Graver, 2004; Office of Agricultural Regulation, 2008; Hopkins and Johnson, 2022; Jones et al., 2017). Along with the sealing step, fumigant introduction locations, circulation fan placement, and concentration monitoring points are prepared. How fumigants are released into enclosures depends on their formulations. Wireless fumigant sensors have not been available to Thai fumigators; instead, they have measured gas concentrations at different spots by placing plastic tubing with one end at the measuring point and the other outside the enclosure. Typically, these gas monitoring tubes are made from polyethylene or nylon with an inner diameter of 4 mm and lengths in the range 5–50 m, depending on the size of the enclosure. Insect bioassays are rarely placed during commercial fumigations. Pressure testing the enclosure is the recommended method to determine and ensure gas-tightness (Reichmuth, 1993; Navarro, 1999; Navarro and Zettler, 2001; Graver, 2004; Grains Research and Development Corporation, 2014) where the internal pressure is increased or decreased to a certain level and allowed to decay naturally (Sharp, 1982; Annis and Graver, 1991). The pressure decay time is measured and used as the gas-tightness indicator. However, pressure testing is usually not performed for any type of commercial fumigations in Thailand (except for CO₂ fumigation or some

QPS applications). Once the fumigant release has finished and the exposure period starts, the fumigant concentration inside the enclosure is monitored to ensure the fumigation efficacy. There are some commercial automatic monitoring systems available from overseas manufacturers (Spectros Instruments Inc., 2022; Uniphos Envirotronic Pvt. Ltd., 2022). After the initial setup, the systems are capable of automatically measuring and recording fumigant concentrations without additional human involvement. However, currently, such systems are not used in Thailand. The fumigation operators still manually measure and record gas concentrations. Equipment for measuring fumigant concentration can be classified based on the underlying sensing principles, such as colorimetry, electrochemistry, thermal conductivity, photoionization, optical interferometry or near-infrared spectroscopy. During the exposure time, fumigant concentrations are measured at certain time intervals, typically varying from a few hours to 3 d, depending on the circumstances. In case the concentration falls below the fumigant-specific lethal level, more fumigant could be added or the exposure time could be extended. Once the target exposure time is reached, all temporary seals are removed or opened to aerate the fumigant. Aeration, namely degassing, can be done naturally or assisted by electric fans. Despite having the same fundamental procedure, the three primary fumigants available to Thai fumigators (PH₃, MB and CO₂) have their own sets of unique advantages and limitations. The following subsections describe the practices and challenges specific to these fumigants.

Phosphine

As can be seen in [Table 1](#), the Thai fumigation industry heavily relies on PH₃ in all three formulations (tablets, plates or gas cylinders). Regardless of the formulation, one important issue that fumigators have been combating is insect resistance to PH₃. Research has identified PH₃ resistance with various levels of severity all over the globe, including Australia (Wallbank et al., 1998), Brazil (Athié and Mills, 2005), China (Ling, 1999), Greece (Agrafioti et al., 2019), India (Rajendran, 1999), Morocco (Benhalima et al., 2004), Pakistan (Ahmedani et al., 2007), South Korea (Kim et al., 2019), Turkey (Kocak et al., 2018), the USA (Konemann et al., 2017), Vietnam (Nhung and Tu, 2004) and many other countries in Africa and Asia (Taylor and Halliday, 1986; Taylor, 2002). Typically, the level of PH₃ resistance is expressed in terms of a resistance ratio, which is the dose of PH₃ that is required for 100% mortality of the test population divided by the discriminating dose. [Table 2](#)

summarizes the PH3 resistance ratios of some insect affecting stored products in Thailand during the past 20 years or so by several authors, mostly from the Postharvest and Processing Research and Development Division, DOA. These studies used the resistance evaluation method developed by the Food and Agriculture Organization (Anonymous, 1975). Table 2 clearly shows that the insects in stored products throughout the country have various levels of resistance and that the levels of resistance have been growing. For example, Phromsatit et al. (1998) did not find PH3 resistance in *Tribolium castaneum* from 14 sampled locations in 13 provinces; however, a later study by Uraichuen and Pengkum (2015) reported that this insect species sampled from 125 rice mills in 45 provinces was 23.55–62.63 times more resistant to PH3 compared to the susceptible laboratory population (resistance ratios in the range 23.55–62.63 folds). Among the species reported, *Cryptolestes* spp. was clearly the most resistant. Notably, Pengkum et al. (2018) found *Cryptolestes* spp. from two locations that showed resistance ratios of more than 13,577 folds. Similarly, researchers in other countries found *Cryptolestes* spp. to be one of the most common PH3-resistant insects (Reichmuth et al., 2004; Yuchi et al., 2008; Nayak et al., 2013; Konemann et al., 2017).

Ineffective fumigation where the PH3 concentration or the exposure time or both were not sufficient resulted in survival of the insect pests and the development of PH3 resistance (Friendship et al., 1986). Thus, to prevent this resistance development, it is important that fumigators utilize sufficient doses and exposure times for all fumigation jobs. The resistance ratio discussed earlier is an effective tool for quantitatively comparing resistance levels among insect populations. However, it does not provide an obvious recommendation on the sufficient dose or concentration and the corresponding

exposure time. For PH3, insect mortality is not well correlated directly with the Ct product (the area under the concentration curve), because with the same Ct product a longer exposure time is much more effective in achieving control than a shorter one (Winks, 1984, 1985; World Health Organization, 1988; Tiongsong, 1992). In other words, the Ct product required for a particular level of mortality decreased as the exposure time was extended (Hole et al., 1976). Consequently, a proper dosage for a PH3 fumigation is given typically as a minimum concentration for a given minimum exposure time. Several research articles have provided insight in terms of the sufficient dose and exposure time for the population of stored-product insects in Thailand. With a minimum phosphine concentration of about 750 parts per million (ppm) at day 7, Suthisut et al. (2020) showed that a dose of 2–3 AIP tablets per tonne of milled rice with an exposure time of 7 d could kill all life stages of resistant strains of *Oryzaephilus surinamensis* found in Thailand. Notably, in general, one AIP tablet contains approximately 1 g of PH3 equating to 720 ppm when an AIP tablet is placed in a volume of 1 cubic meter (United Phosphorus Inc., 2010). Kengkanpanich et al. (2010) recommended fumigation with three AIP tablets per tonne for 7 d to for control *Rhyzopertha dominica* and *T. castaneum* in stored maize. However, at four AIP tablets per tonne of rice seed with a 14 d exposure time and two tablets per tonne with a 7 d exposure time (concentration data not available), Kaewnango and Thong-ake (2021) found that small percentages of most life stages of *R. dominica* and *S. zeamais*, respectively, survived their experimental fumigations. Pengkum et al. (2018) conducted a fumigation experiment in which each enclosure contained 1 t of milled rice. For moderately resistant strains of *Cryptolestes* spp., they obtained 100% mortality of all life stages at doses of two AIP tablets per tonne of milled rice with a 14 d exposure time

Table 2 Summary of resistance ratios of some insects to PH3 affecting stored products in Thailand

Insect species	Author	Number of sampled locations (in number of provinces)	Discriminating dose	Resistance ratio
<i>Cryptolestes</i> spp.	Kengkanpanich et al. (2019)	28 (22)	0.06 mg/L at 20 h	2→81
	Pengkum et al. (2018)	15 (10)	0.06 mg/L at 20 h	1.54→13,577
	Pengkum et al. (2015b)	47 (22)	0.06 mg/L at 20 h	2→19
<i>Oryzaephilus surinamensis</i>	Suthisut et al. (2020)	43 (25)	0.05 mg/L at 20 h	2→22
	Suthisut et al. (2014)	50 (32)	0.05 mg/L at 20 h	1→9
<i>Tribolium castaneum</i>	Uraichuen and Pengkum (2015)	125 (45)	0.04 mg/L at 20 h	23.55–62.63
	Jittanun and Chongrattanameteekul (2014)	2 (2)	0.04 mg/L at 20 h	1.45–25.8
	Phromsatit et al. (1998)	14 (13)	0.04 mg/L at 20 h	1
<i>Rhyzopertha dominica</i>	Chotimanothum (2000)	15 (15)	0.03 mg/L at 20 h	1→3
	Phromsatit et al. (1998)	23 (21)	0.03 mg/L at 20 h	1→2
<i>Lasioderma serricorne</i>	Kengkanpanich et al. (2017)	16 (6)	0.03 mg/L at 24 h	2→60
<i>Sitophilus zeamais</i>	Phromsatit et al. (1998)	7 (7)	0.04 mg/L at 20 h	1

(average concentration of 343 ppm at day 14) or of three tablets per tonne with a 7 d exposure time (average concentration of 1,221 ppm at day 7). For highly resistant strains, 100% mortality levels were achieved at a dose of five tablets per tonne with a 7 d exposure time (average concentration of 1,991 ppm at day 7). Pengkum et al. (2015a) performed fumigation trials in a 3,800 t maize silo at doses of 4 and 5 AIP tablets per cubic meter with 7 d and 10 d exposure times (concentration data not available). Phosphine gas distribution during the trials was assisted using a recirculation system. Bioassays of *Cryptolestes* spp. prepared by the researchers were placed in the headspace of the silo. For all of trials, the researchers found complete mortality of all life stages of the bioassay insects. However, live insects were found emerging from random samples of the grain in the silo after all the trials had been completed. Kengkanpanich et al. (2013) sampled five storage insect species from grain storages throughout Thailand and conducted laboratory-scale PH3 fumigation trials on these insects. In terms of sufficient phosphine concentrations and exposure times, these researchers were able to kill all life stages of *R. dominica*, *S. zeamais*, *T. castaneum*, *O. surinamensis* and *Lasioderma serricorne* by exposing them to PH3 for 5 d at 450 ppm, 200 ppm, 250 ppm, 75 ppm and 100 ppm, respectively. When the exposure time was increased to 7 d, the concentrations required to achieve 100% mortalities were 300 ppm, 50 ppm, 100 ppm, 50 ppm and 75 ppm, respectively. Thai fumigation practitioners typically use the doses and exposure times suggested by the above-mentioned articles. However, they prefer to use the lower limits of 2–3 tablets per cubic meter for 5–7 days. Some fumigation service providers do follow the longer exposure time recommendation (10–14 d), with the goal of achieving at least 300 ppm PH3 concentration at the end of the fumigation. In some cases where the enclosure is relatively leaky, the dose might be increased to 5–6 six tablets per cubic meter. This practice is also consistent with the recommendations in many AIP tablet product manuals (United Phosphorus Inc., 2010; United Phosphorus Ltd., 2011; D & D Holdings Inc., 2017). However, notably, this is still below dosages that can control *C. ferrugineus* with strong PH3 resistance, as stated in the literature (Table 3).

Table 3 Recommended dosage for effective control of *Cryptolestes* spp

Author	Recommended dosage
Li and Yan (2008)	200 ppm for 28 d
Wang et al. (2008)	300–500 ppm for 16–25 d
Collins (2009)	400 ppm for 14 d or 200 ppm for 25 d
Nayak et al. (2010)	720 ppm for 24 d or 360 ppm for 30 d
Kaur and Nayak (2015)	720 ppm for 15 d or 1,440 ppm for 6 d

ppm = parts per million

When conducting PH3 fumigation there are several different techniques used by Thai fumigators to utilize PH3 effectively. Typically, PH3 fumigation is done under fumigation tarpaulins (sheeted piles or bag-stacks, as shown in Fig. 1A) or in storage structures (silos, as shown in Fig. 1B). The typical tarpaulin used for PH3 fumigation is polyvinyl chloride (PVC) sheets with 0.05 mm or 0.1 mm thickness (Kengkanpanich et al., 2015). Gas tightness of the enclosure is checked by visual inspection before fumigation or measuring PH3 concentrations around the enclosure's perimeter during fumigation. Whenever the situation permits, fumigators will install a gas recirculation system to assist with fumigant distribution. Jones et al. (2017) outlined the process for designing such a recirculation system in a grain silo. This so-called closed-loop fumigation system included a centrifugal fan and ducting, as shown in Fig. 1B. The fan was equipped with an electric motor (375–1,500 W) and installed at ground level. The ducting forms an airflow path from the headspace to the base of the silo.

Traditionally, fumigators place the AIP tablets in breathable fabric bags that facilitate gas exchange. Then, these bags are placed on the surface of the grain mass (Fig. 1). For sheeted fumigation, after the grain pile is covered with PVC tarpaulins, AIP tablets are left to react with the moisture in the air to generate PH3 gas which then naturally permeates the pile. With a silo, after the last opening on the silo is sealed, the recirculation fan is turned on, with the length of operation depending on several factors, often based on the past experience of the fumigator. Generally, the fan is not turned on for the entire exposure period because it increases the gas leakage rate.

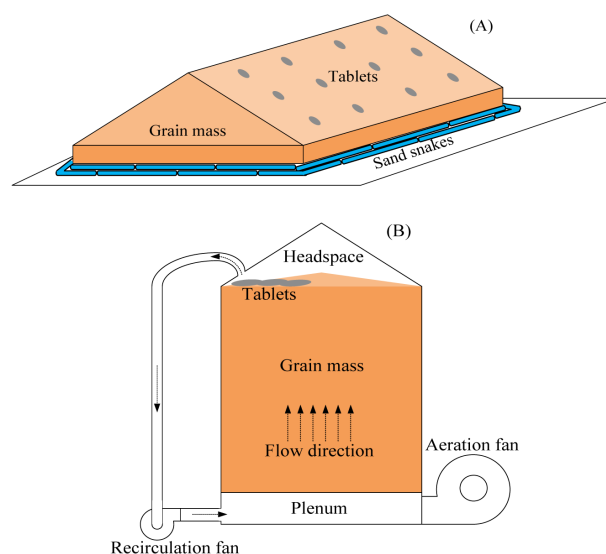


Fig. 1 Two types of fumigation enclosures: (A) sheeted grain pile; (B) grain storage structure with a gas recirculation system

Xianchang (1994) demonstrated that under favorable conditions (30°C and 90% relative humidity) an AIP tablet takes at least 35 h to react and release most of its PH₃ content. This long reaction time is one downside of the traditional method of applying AIP tablets while waiting for the PH₃ gas to be effective. To reduce this gas build-up time, Thai fumigation service providers have utilized two types of PH₃ generators: wet or dry. One particular model of the wet type used is manufactured by Beijing Liangmao Technology Development Co. Ltd., China, for which the operation and the results of fumigation trials were described in detail by Zhao (2010), Ryan et al. (2010) and Ganesh (2018). Fig. 2A illustrates the basic working principle of the wet-type PH₃ generator, consisting of a reactor tank, filter tank, tablet container and CO₂ tank. The reactor and filter tanks are filled with water. Simultaneously, AIP tablets and CO₂ gas are dropped and injected, respectively, into the reactor tank, with the tablets reacting with water generating PH₃ gas and the CO₂ acting as a carrier gas. The PH₃-CO₂ mixture flows from the reactor tank to and from the filter tank. From the filter tank, the PH₃-CO₂ stream is fed into the recirculation system (Fig. 2B). There are other PH₃ generator models that accelerate the reaction via the use of water, such as those made by Detia Degesch GmbH, Germany (Steuerwald et al., 2006) and by UPL Limited, India (Waterford et al., 2004; Asher, 2008) which use specialized formulations of magnesium and aluminum phosphide granules, respectively (D & D Holdings Inc., 2006; United Phosphorus Inc., 2008). However, these generators have never been used in Thailand. By accelerating the reaction rate with liquid water, the entire required amount of PH₃ gas should be released within 4–10 h, depending on the size of the enclosure. However, one drawback is that the generator uses a considerable amount of CO₂ and needs thorough cleaning after each use.

In principle, the dry-type PH₃ generator is a chamber containing AIP tablets. This chamber is installed in series in the recirculation flow circuit typically at ground level (Fig. 3). The recirculation fan pushes moist air from the headspace through the chamber and the AIP tablets reacts with the water vapor in the flowing air, generating PH₃ gas. Then, the PH₃ gas enters the silo at the bottom and flows through the grain mass. This working principle of the dry-type generator is used by the so-called Speedbox (Kostyukovsky et al., 2015; Degesh America Inc., 2022) and the Kotzur Phosphine Fumigation Box (Warrick, 2011; Kotzur Pty. Ltd., 2021). Notably, the Speedbox uses magnesium phosphide plates. One of the application methods for mixture formulation of a particulate phosphide and a water-immiscible compound described by Waterford and

Winks (2002) was via a dry-type PH₃ generator. The benefits of using the dry-type generator are that tablets can be applied at ground level, there is less risk of having to work in confined spaces and it is easier to collect residue dust. However, as PH₃ can self-ignite at 18,000 ppm concentration (United Phosphorus Inc., 2010), placing a lot of AIP tablets in such a small volume presents a severe explosion hazard. However, while the recirculation fan is still running, the concentration in the chamber can be maintained below the self-ignition level. Nonetheless, a substantial risk of explosion occurs in circumstances when the fan's operation is interrupted, such as with an electricity power outage.

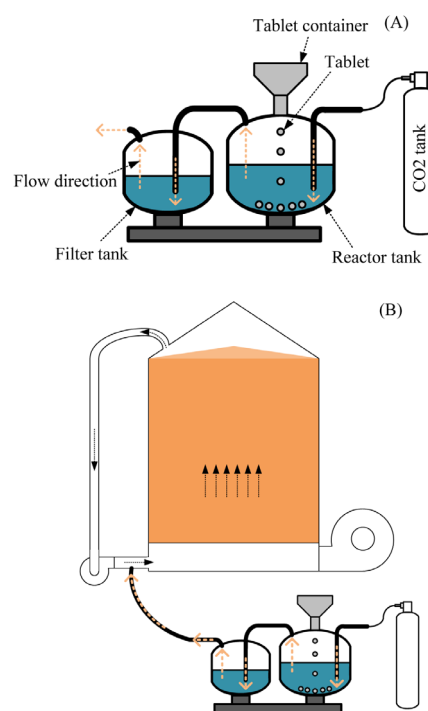


Fig. 2 Schematics of fumigation using wet-type PH₃ generator: (A) PH₃ generator; (B) gas flow direction

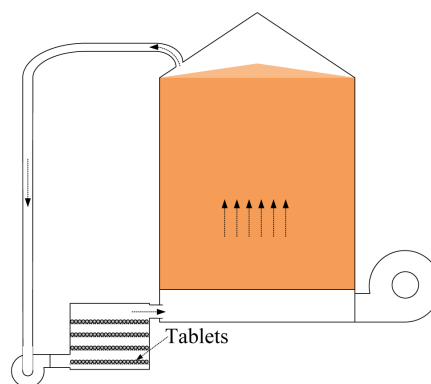


Fig. 3 Schematics of fumigation using a dry-type PH₃ generator

In terms of cylinderized PH3 formulations, Thai fumigators have been using the 2% PH3 in 98% CO₂ formulation almost exclusively (Table 1). Compared to solid metal phosphide formulations, this cylinderized PH₃_{2%}-CO₂_{98%} fumigant is much easier to apply and also no residue dust needs to be collected, resulting in lower risk of fumigators being exposed to PH3. With the high proportion of CO₂ in the mixture, self-ignition of PH3 is unlikely. In addition, unlike solid metal phosphide formulations, no reaction time (typically 48–72 h) is required to achieve the PH3 lethal concentration. However, the cost of the cylinderized PH₃_{2%}-CO₂_{98%} fumigant is much higher than that of AIP tablets. Quite a few studies on the efficacy of this fumigant against stored product insects have been conducted by Thai researchers. For example, in fumigation trials by Pengkum et al. (2015a), enclosures each containing 8 t of maize in jumbo bags were fumigated with the PH₃_{2%}-CO₂_{98%} fumigant at: 1) a dose of 25 g/m³ for 3 d, 4 d and 5 d; 2) a dose of 50 g/m³ for 2 d, 3 d and 4 d; and 3) a dose of 70 g/m³ for 1 d, 2 d and 3 d. The doses were equivalent to PH3 concentrations of 350 ppm, 700 ppm and 1,000 ppm, respectively. All the dose-exposure time combinations resulted in 100% mortality rates of bioassays consisting of all life stages of *S. zeamais* and *T. castaneum*. Kengkanpanich et al. (2018) used the PH₃_{2%}-CO₂_{98%} formulation to fumigate milled rice in bag stacks and a jumbo bag with stack sizes of about 50 m³ and 300–400 m³, respectively. The exposure times were either 2 d or 3 d, while the PH3 concentrations were maintained at above 800 ppm for all treatment conditions. With mixed-age cultures of *S. zeamais*, *T. castaneum* and *O. surinamensis* as the bioassays, the fumigation trials resulted in 100% mortality in all trials. In addition, this fumigant was effective against *Callosobruchus maculatus* and *C. chinensis*. Potikan et al. (2019) showed that all life stages of these two insect species were completely killed at a PH3 concentration of 1,250 ppm in combination with exposure for 24 h. Potikan et al. (2020) reported on the fumigation of *Cryptolestes* spp. with the PH₃_{2%}-CO₂_{98%} fumigant for 24 h at PH3 concentrations in the range 0–1,250 ppm, with 99% mortality of eggs, larva, pupa and adults at PH3 concentrations of 975.22 ppm, 227.30 ppm, 261.91 ppm and 159.92 ppm, respectively. However, these results were in contrast to most established findings from many studies (Table 3). In addition, when *Cryptolestes* spp. had PH3 resistance ratios of greater than 11 folds, Kengkanpanich et al. (2019) found that PH₃_{2%}-CO₂_{98%} doses of 25 g/m³, 50 g/m³ and 70 g/m³ (equivalent to PH3 concentrations of 350 ppm, 700 ppm and 1,000 ppm, respectively) in combination with exposure times of 5 d, 4 d and 3 d, respectively, did not produce 100% mortality in all life stages. Even with doses of 50 g/m³ and 70 g/m³ and

exposure times of 14 d and 10 d, respectively, these researchers still found a small number of survivors. Notably, Nayak et al. (2013) classified *Cryptolestes ferrugineus* with resistance ratios of 7.3–11.4 folds as weakly resistant. Based on the results of these studies, it could be argued that regardless of the source of PH3 gas (either cylinderized or solid formulations), the problem of insect resistance persisted. Although the cylinderized ready-to-use formulation cuts down the reaction time, when the target insect is a resistant species, it still requires a long exposure time for the PH3 gas to take effect. This information is important for Thai fumigation practitioners.

Another PH3 formulation that the Thai fumigation community has been made aware of is cylinderized PH3 gas with 99.3% purity (Solvay S.A., 2021b). To prevent PH3 self-ignition, this type of fumigant has to be diluted on-site either with air or other inert gases using specially designed equipment (Cytec Industries Inc., 2013). Various models of diluting equipment have been developed, one of which is the Horn Diluphos System® (Horn and Horn, 2006; Fosfoquim, 2022). In addition to many benefits similar to those of the PH₃_{2%}-CO₂_{98%} variant, (including no residue dust, lower risk of worker exposure and no delay for the reaction time), implementation of the cylinderized PH3 formulation involves a smaller number of heavy steel cylinders and provides more precise PH3 concentration control. On the other hand, it requires more skilled operators and a sizable amount of capital investment for the equipment. However, this cylinderized PH3 fumigant has never been commercially used in Thailand.

For monitoring the efficacy of PH3 fumigation, colorimetric tubes or electronic devices, such as electrochemical sensors, are commonly used in Thailand. Several manufacturers provide such equipment, such as Drägerwerk AG & Co. KGaA. (2022) or GasTech Australia Pty. Ltd. (2022), respectively. PH3 near-infrared (NIR) PH3 sensors and photoionization detectors (PID) can be purchased overseas (GazDetect, 2022; Spectros Instruments Inc., 2022) but are not yet widely used in Thailand. When selecting the monitoring device of choice, fumigators generally consider the price, accuracy, life span, durability and maintenance requirements. For example, the price of a colorimetric tube and an accompanying hand pump is lower than that of most electronic sensors and does not require regular calibration, while electronic sensors often need recalibration every 6 mth. On the other hand, colorimetric tubes are intended for one-time use only, while electronic sensors can be repeatedly used with an expected life span of about 1–2 yr. Fumigant concentrations are measured by drawing a gas sample through the tubing placed during the construction of the enclosure into the monitoring device. Concentration measurements are done once every 1–3 d.

Regardless of the enclosure type and whether aeration is done naturally or assisted using electric fans, the PH3 fumigant has to be vented from the enclosure until its concentration decreases below the threshold limit value (TLV) of 0.3 ppm (Graver, 2004; Office of Agricultural Regulation, 2008; United Phosphorus Inc., 2010) before the fumigated goods or structure can be safely accessed by workers. Thus, during aeration, fumigators usually check the TLV concentration using colorimetric tubes or electrochemical sensors. Hot-wire semiconductor detectors are also used, such as those described by Riken Keiki Co. Ltd. (2019). Aeration ceases when the concentration subsides below the TLV level. Notably, PH3 residue in milled rice must not be above the maximum residue limit (MRL) of 0.1 mg of PH3 per 1 kg of milled rice, as mandated by the Thai Agricultural Standard: TAS 9002-2013 (National Bureau of Agricultural Commodity and Food Standard, 2013). When fumigating wheat and corn at a dose of 2 g of PH3 per cubic meter for 7 d, after 5 d of ventilation and more than 2 d of holding, Thabit and Elgeddawy (2018) reported PH3 residues in the ranges 0.00770–0.00985 mg/kg and 0.00730–0.00903 mg/kg, respectively. At doses of up to 10 g of PH3 per cubic meter and a 14 d exposure period, Marie-Carolin and Gerhard (2018) reported levels of PH3 residues of less than 0.05 mg/kg in cereal-grain samples taken directly after the end of aeration.

Methyl bromide

As MB is exclusively used for QPS applications, MB fumigation is mostly performed in shipping containers that can be either sheeted or un-sheeted, purpose-built fumigation

chambers or sheeted enclosures. Many Thai fumigation service providers participate in the Australian Fumigation Accreditation Scheme (AFAS) (Department of Agriculture, Water and the Environment, 2020, 2021) and when constructing sheeted enclosures for MB fumigation, they often consider the methodology given by AFAS (Department of Agriculture, Water and the Environment, 2018b) as a benchmark, regardless of the import or export country. In terms of purpose-built MB fumigation chambers, the chambers have to be certified every 2 yr by the DOA (Department of Agriculture, 2008). Agricultural commodities fumigated in an uncertified chamber cannot receive phytosanitary certification. Although DOA's certification does not have any criteria regarding pressure testing, AFAS requires MB fumigation chambers to be pressure tested every 6 mth by raising the gauge pressure in the chamber to about 250 Pa and measure the time required for the pressure to decay from 200 Pa to 100 Pa (Graver, 2004). The chamber is considered appropriate for MB fumigation only if this pressure decay time is more than 10 s (Department of Agriculture, Water and the Environment, 2018b).

The required doses and exposure times differ by destination country and several agricultural commodities are listed in the Training Manual on Pests, Regulations and Phytosanitary Requirements of Import Countries (Office of Agricultural Regulation, 2017). Some examples are listed in Table 4. It can be seen that the required dose and exposure time typically vary in the ranges 24–48 g/m³ and 2–24 h, respectively, depending on the type of commodity and the country. Notably, 1 g of MB in a volume of 1 cubic meter is approximately equal to 250 ppm (Glassey, 2018).

Table 4 Examples of methyl bromide (MB) doses and exposure times required by different destination countries and commodities

Destination country	Commodity	MB dose (g/m ³)	Exposure time (h)	Temperature (°C)
Australia	Pineapple	32	2	> 21
Brunei Darussalam	Ornamental plants	32	2	-
	Ornamental plants (growing medium)	32	4	-
	Groundnut	32	2	-
	Red bean	32	2	-
European Union	Orchid cut flowers	20–24	1.5	-
Iran	Orchid cut flowers	24	1.5	> 21
	Pineapple	32	6	> 21
Israel	Ribbon dracaena	32	3	> 21
Malaysia	Rice and flour	32	24	-
New Zealand	Rice	48	24	10–15
	Orchid cut flowers	32	2	> 21
South Korea	Mangosteen	32	2	> 21
Taiwan	Betel nut	32	4	> 21
United States of America	Asparagus shoot	24	2	> 27
		32	2	21–26
	Yam	40	4	> 32
		48	4	27–31.6

Source: Office of Agricultural Regulation, Department of Agriculture, Thailand (Office of Agricultural Regulation, 2017)

With wood packaging, for a wood temperature of at least 21°C, International Standards for Phytosanitary Measures (ISPM) No.15 specifies minimum achieved Ct products of 650 g-h/m³ after 24 h exposure (International Plant Protection Convention, 2009). This translates to an initial dose of 48 g/m³ with a minimum final concentration of 24 g/m³ after 24 h. In rare cases when *Trogoderma granarium* is the target pest, for example in imported wheat (Matichon online, 2018), an MB dose of 80 g/m³ for a minimum exposure time of 48 h was used, adhering to the requirement of Australia's Department of Agriculture, Water and the Environment (2022).

To ensure that the required dose is accurately applied, either the gas cylinder is placed on a digital scale while releasing MB or the target amount of MB is pre-filled in a dispenser. Complete vaporization of MB is achieved by using a vaporizer that acts as a heat exchanger, in which MB is directed through piping that is submerged in boiling water before being released into the enclosure (Department of Agriculture, Water and the Environment, 2018a). Uniform distribution of MB is assisted by electric fans placed inside the enclosure. After releasing the fumigant, a halide lamp is used to check for excessive gas leakage around the perimeter of the enclosure. The color of the flame changes from green to blue as it comes in contact with an increasing MB concentration (Department of Agriculture, Water and the Environment, 2018a).

MB concentrations are usually measured at three locations inside the enclosure: a top corner, in the middle and in the bottom corner diagonally opposite the measured top corner (Department of Agriculture, Water and the Environment, 2018b). In addition to colorimetric tubes, MB concentration monitoring equipment can be found in forms of thermal conductivity (Key Chemical & Equipment Co., 2022), NIR (Spectros Instruments Inc., 2022) or optical interferometric sensors (RKI Instruments Inc., 2002). The thermal conductivity monitor can often be seen in use in Thailand. In addition to specifying the minimum dose and exposure time, AFAS also mandates that the MB concentration must not fall below certain minimum limits during the entire exposure period (Department of Agriculture, Water and the Environment, 2018b). For example, with an initial dose of 32 g/m³, the concentration at 4 h, 12 h, 24 h and 48 h must remain above 16 g/m³, 11.2 g/m³, 9.6 g/m³ and 8 g/m³, respectively, in order for the fumigation to be considered acceptable. When the concentration is likely to fall below these limits, the fumigator can release additional MB (topping-up). At the end of the exposure period, the enclosure must be aerated until the MB concentration is ≤5 ppm before re-entry is allowed; thus, the TLV of MB is 5 ppm (Graver,

2004; United States Environmental Protection Agency, 2010) and the fumigated area is not accessible until a 5 ppm TLV has been achieved.

Table 5 summarizes the MRL values of MB in milled rice as mandated by the Thai Agricultural Standard: TAS 9002-2013 (National Bureau of Agricultural Commodity and Food Standard, 2013). Notably, when fumigating white rice at an MB dose of 40 g/m³ for about 24 h (Ct product of about 1,000 g-h/m³) at 20°C, Norman (2000) found MB residues of 0.007 mg/kg at 14 d after the fumigation. When the dose was reduced to 9 g/m³ (Ct product of about 200 g-h/m³), the residues found 7 d after the fumigation were below 0.005 mg/kg. Thus, with the proper dosage and sufficient elapsed time, MB residues should have already declined below the mandated MRL by the time the fumigated rice reaches retail stores.

Table 5 Maximum residue limits (MRL) of methyl bromide in milled rice as mandated by Thai Agricultural Standard: TAS 9002-2013

Analyzed substance	mg/kg	Remarks
Methyl bromide	1	Rice has been freely exposed to air for at least 24 hr
	0.01	at point of retail sale
Bromide ion	50	-

Carbon dioxide

Navarro (2006) describes controlled atmosphere (CA) as a treatment where the gaseous composition of the atmosphere inside the treated enclosure is controlled or maintained at a level lethal to insects. The composition can be modified artificially by additionally generating the desired gases or by further purging the storage using these gases. CO₂ treatment is a form of CA treatment. However, in the present review, CA treatment with CO₂ gas will be referred to as CO₂ fumigation. CO₂ fumigation is considered a residue-free treatment that can be used on organic commodities (Graver, 2003; National Bureau of Agricultural Commodity and Food Standard, 2010; Grieshop et al., 2012; Department of Agriculture, Water and the Environment, 2016). Thus, a majority of commercial CO₂ fumigation jobs are carried out for exported organic rice in sheeted bag-stack enclosures. The cost of CO₂ fumigation is generally more than for PH3 and MB fumigations (Table 6). At the time of writing this review paper, the author sought fumigation service pricing from a Thai fumigation company (Table 6) for comparative purposes. Notably, the costs listed here do not include travel expenses to the fumigation site.

Table 6 Cost comparisons of PH₃, methyl bromide and CO₂ fumigations

Fumigant	Cost (THB)	
	2010	2022
PH ₃	15–22 THB/m ³ *	15–24 THB/m ³ ***
MB	25–30 THB/m ³ *	45–135 THB/m ³ ***
CO ₂	357 THB/m ³ **	575 THB***
	12,500 THB/21 t *	

*Pest Management Plan on Thailand Methyl Bromide Phase-out Project (The World Bank, 2010); **Conversion by the author; ***Acquired from a Thai fumigation company in 2022

Fig. 4 illustrates an example of typical CO₂ fumigation enclosures. The enclosures are normally made of PVC sheets with thickness between 0.3 mm and 0.5 mm. In PH₃ and MB fumigations, the bag stack is placed directly on the floor surface and the fumigation tarpaulin covering the stack is weighed down by placing sand snakes around the perimeter of the stack. In many cases, the edges of the cover tarpaulin are taped to the floor. Unlike PH₃ and MB fumigations, in CO₂ fumigation the fumigator has to first lay a floor sheet and then the bag stack is constructed on it. Occasionally, corrugated card boards are placed on top of the floor sheet before constructing the stack. A gas introduction port made of a 1–2 m long, 10–15 mm diameter PVC pipe is laid on the floor sheet in the middle of

the stack. The PVC pipe is drilled along its length to aid gas distribution. Three gas sampling tubes are fitted at a top corner of the stack, in the middle and at the bottom corner diagonally opposite the top corner. The cover sheet is usually prefabricated into a rectangular box shape, without the bottom side. After the cover sheet is put in place on the stack, its edges are heat-sealed to the floor sheet. At four defined spots, PVC solvent glue is used for sealing. These steps for constructing enclosures are identical to the instructions given by Annis and Graver (1991).

With CO₂ fumigation, Thai fumigators always pressure test enclosures to verify the gas tightness. When performing a pressure test, the fumigator generates negative pressure inside the enclosure using a vacuum cleaner. The pressure difference between the inside and outside of the enclosure is measured using a water filled U-tube manometer. An often-used criterion for sufficient gas tightness as recommended by Annis and Graver (1991) is that the time taken for a negative pressure of 500 Pa (5 cm of water gauge) to fall to 250 Pa (2.5 cm of water gauge) should not be shorter than 10 minutes. Often, this time is referred to as the pressure half-life. Notably, for rigid structures, such as sealed steel silos, a positive pressure is applied and a minimum pressure half-life of 5 min is required according to the Australian Standard AS2628-2010 (Standards Australia, 2010). The larger the structure, the longer the pressure half-life that is recommended (Navarro, 1999).

Pressurized CO₂ cylinders each containing 20–25 kg of CO₂ are commonly used as the CO₂ source. When releasing CO₂ into the enclosure, the cylinder is either inverted or laid on its side. Sometimes the CO₂ flow is routed through an evaporator or electric heater to avoid freezing the PVC tarpaulin and thus preventing it from cracking. The minimum required concentration and exposure time for CO₂ fumigation are 35% and 15 d, respectively (Annis and Graver, 1991; Navarro, 2006; Food and Fertilizer Technology Center, 2015). In practice, fumigators maintain CO₂ concentrations of at least 50% for 15 d. Notably, for CO₂, the Ct product model does not very well explain insect mortality. This implies that a lack of concentration cannot be compensated for by increasing the exposure time or *vice versa* (Annis and Graver, 1991; Rameshbabu et al., 1991; Mann, 1998). A variety of CO₂ meters/sensors is available, most of which operate based on the NIR principle (AFC International Inc., 2022; CO2Meter Inc., 2022; E-Z Systems Inc., 2022). After the 15 d exposure time has passed, the enclosure is opened. Workers can re-enter the treated area once the CO₂ concentration decreases below 5,000 ppm or 0.5% (TLV = 5,000 ppm) (United States Environmental Protection Agency, 2011).

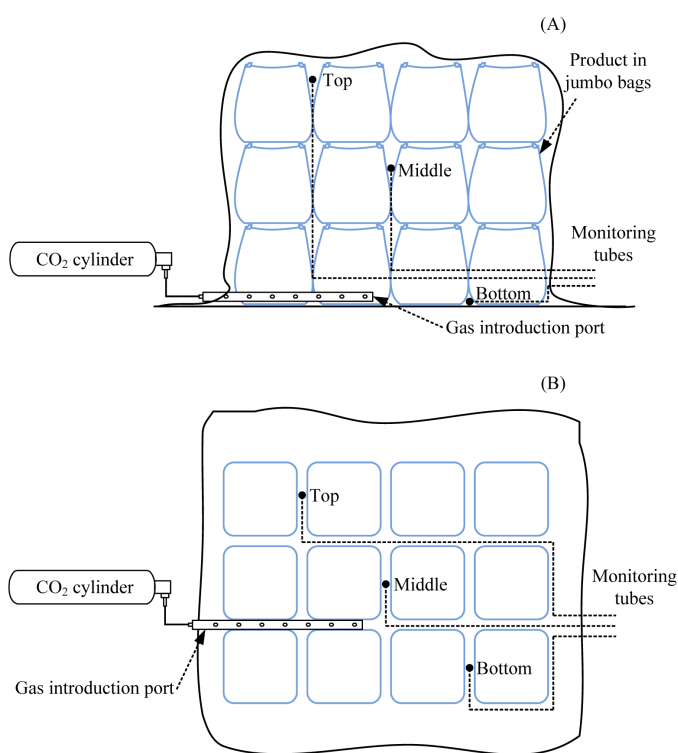


Fig. 4 Examples of typical CO₂ fumigation enclosures: (A) Side view; (B) Top view

In addition to a PVC tarpaulin, different types of multi-layer plastic films are available (Intergro Co., Ltd., 2022). Such films generally consist of at least one CO₂ barrier layer and can be fabricated into bags or rectangular enclosures of different sizes of a few liters to more than 300 m³ (GrainPro Inc., Ltd., 2021). They are being explored by Thai fumigators in terms of ease of handling, gas retention effectiveness and cost competitiveness.

Conclusions

The current practices of fumigation with PH₃, MB and CO₂ in Thailand indicated that each fumigant has its own advantages and limitations. With its low cost, PH₃ in the form of AIP tablets remains the most-used fumigant in Thailand. The use of these tablets requires PH₃ generators, thus releasing PH₃ gas more effectively. The cylinderized PH₃_{2%}-CO₂_{98%} formulation is used in niche applications. However, severe cases of insect resistance to PH₃ can be found in many areas of the country, prompting fumigators to be extra careful when selecting the dose and exposure period. MB still plays an important role in QPS applications despite being heavily regulated and having limited availability. The protocol for MB fumigation from setting up an enclosure to finishing aeration is well established and routinely followed. Organic products can be treated with CO₂ that, in general, is safer to handle than PH₃ and MB. However, besides being more costly, CO₂ fumigation requires more gas-tight enclosures and a longer exposure time. Both PH₃ and MB in all formulations and the necessary equipment, such as gas monitors, must be imported. These limitations present challenges to Thai fumigation practitioners. Therefore, it is necessary to explore alternative fumigants, other types of treatments and associated technologies to overcome these challenges.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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