14 Fumigation

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Fumigation is the practice of using gaseous pesticides applied directly to commodities or to part or all of a structure, including vehicles used to store, handle, process, or transport raw commodities or finished food products. A fumigant is a toxic chemical or mixture of compounds that kills pests as a volatile gas within a range of temperatures. For purposes of this book we consider fumigant gases that are targeted at killing arthropod pests and rodents infesting grains, grain products, other durable stored foods, and stored seeds for planting. A highly toxic fumigant such as methyl bromide can be used to kill weed plants and seeds, fungi, snails, and nematodes in addition to arthropods in some use contexts. Because fumigants act in the gaseous stage, they are ideal for penetrating commodities and protected parts of buildings and food containers. These areas are inaccessible to contact by other pesticide formulations, including aerosols, which are actually fine mists of liquid materials.

Fumigants are the most effective control measures for stored product insect and mite pests. When properly applied, they deliver a high level of mortality and leave no chemical residue on grain or food to pose a health concern. In addition to being effective insecticides, fumigants are among the most dangerous to use for applicators, for human bystanders and for nontarget organisms. Of all insecticides, fumigants belong to the most dangerous group of pesticides, Category 1 U.S. EPA. Packages are marked with a skull-and-crossbones (Figure 1).

Almost every year one or more people die in the United States from misuse of registered fumigants or unauthorized entry into fumigated spaces. It is critical that applicators receive thorough training and certification from government regulatory agencies before using fumigants. Insecticides with residual toxicity — those that can be applied to a commodity or a surface in a building and kill insects on contact for several weeks or months following application — are covered in Chapter 9 of this book. More detailed and technical reviews of fumigation for stored products have been given in previous publications (e.g., Bond 1989, Walter 1991, Thoms and Phillips 2004). The objective of this chapter is to summarize the characteristics and application methods for the fumigants registered for use on stored products and associated structures and buildings in the United States.

Overview of Available Fumigants

Table 1 gives a summary of the physical and chemical properties of the five fumigant gases covered in this chapter. Despite what might seem an adequate number of fumigant insecticides to meet the needs of the pest control and food industries, each compound has particular characteristics or a regulatory status that make it more or less applicable to any given situation. For example, methyl bromide is highly effective at killing all life stages of most pest species in a short period of time, but it is currently being phased out and banned under the international Montreal Protocol and U.S. Clean Air legislation. Ethyl formate may be relatively safe and easy to use but its effectiveness as a toxin may be limited.

Table 1. *Physical and chemical properties of commonly used fumigants currently registered or proposed in the U.S. for stored products.**

Fumigant (chemical formula)	Molecular weight	Specific gravity air = 1	Boiling point (°F)	Flammability by volume in air (%)	Water solubility ppm	Odor as gas	Incompatibility	
							Liquid or solid	Gas
Methyl bromide (CH_3Br)	94.94	3.27 @32°F	38.5	Nonflammable	15,444 ppm	None (sweet odor in high concentrations)	Contact of liquid with aluminum, magnesium, zinc, and alkali metals may result in liberation of toxic gases, and possible fire and explosion. Liquid incompatible with plastics, like polyvinyl. Liquid may react with sulfur compounds to create malodors.	In high concentrations, gas may react with sulfur compounds to create malodors. Decomposes in flame, glowing filament to produce HBr.
Sulfuryl fluoride (SO_2F_2)	102	2.88	-67	Nonflammable	750 ppm @77°F	None (sulfur odor in high concentrations)	Contact of liquid with glass, metals	Decomposes in flame, glowing filament to produce HF
Phosphine (PH_3)	34.04	1.21 @39.2°F	-125	1.79% by volume of air	416 ppm @63°F	Garlic-like odor due to contaminant; ammonia in certain formulations	Solid metal phosphide formulations can spontaneously ignite if contacted by water, acids, or chemicals.	Can corrode copper, brass, copper alloys, and precious metals such as gold and silver. Can react with metallic salts on photographic film.
Carbon dioxide (CO_2)	44.01	1.53	-109.3	Nonflammable	88%	Odorless	None	Various elastomers
Propylene Oxide (C_3H_6O)	58.08	0.86	34.2°C	Extremely flammable	40.5%	Irritant	Aluminum, copper, brass, bronze	Anhydrous metal chlorides, acids, bases, clay-based materials
Ethyl Formate ($C_3H_6O_2$)	74.08	0.92	54°C	Flammable liquid	1,000 ppm	Sweet, fruity	Decomposes slowly in water	Generates flammable hydrogen when mixed with alkali metals or hydrides

* Excerpted from Walter 1991.

Readers who would like to learn more or who seek to become fumigant applicators can pursue training and education provided by universities, professional associations, and fumigant manufacturers and distributors. Because fumigants act to kill insects and rodents in the gaseous state, their mode of action is believed to begin with respiration. Arthropod life stages most susceptible to fumigants are those that are most physically active — the larvae/nymphs and adults that take in a lot of toxic gas through breathing. Less active life stages, such as pupae and embryos in eggs, are less susceptible to fumigants.

Methyl bromide

Methyl bromide (MeBr, CH_3Br) has a long history of use in the agricultural sector as a broad spectrum biocidal fumigant. It is applied primarily to control pest populations in soils, commodities, processing facilities, and commercial marketing channels. MeBr predominates in gaseous form at normal atmospheric temperatures and pressures. It diffuses homogeneously within the headspace or pore space of treated substrates (e.g., grain, nuts, etc.) to reach pests and achieve uniform exposure, a highly coveted characteristic. The gas is stored in, delivered in, and released from metal canisters and cylinders of various volumes at 100% concentration (Figure 1).

Figure 1. *The skull-and-crossbones symbol (top) is used on labels for Category 1 insecticides, the most dangerous category assigned by the USEPA. Methyl bromide (bottom) comes in containers of various sizes.*

MeBr was identified as a chemical that contributes to the depletion of stratospheric ozone, and its production and use are subject to regulation under the U.S. Clean Air Act. As one of the original signatories of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, the United States ratified the Protocol in 1988. Amendments to the Clean Air Act were enacted in 1990 to include Title VI on Stratospheric Ozone Protection to ensure that the United States would satisfy its obligations under the protocol. For developed countries including the United States, consumption was frozen at 1991 "baseline" levels until 1998, and then reduced incrementally until an intended 100% reduction, or phase-out, was reached by a target date of 2005. Before 1991, the United States used roughly 27,000 metric tons (MT) annually (Ragsdale and Vick 2001). Of this about 75% was used for soil fumigation, 11% for commodity treatments, and 6% for structural fumigation, with the remainder used as feedstock in industrial chemical production. In keeping with the schedule set by the Montreal Protocol and a commitment to a gradual reduction, MeBr usage in the United States has declined significantly (Figure 2, Johnson et al. 2012).

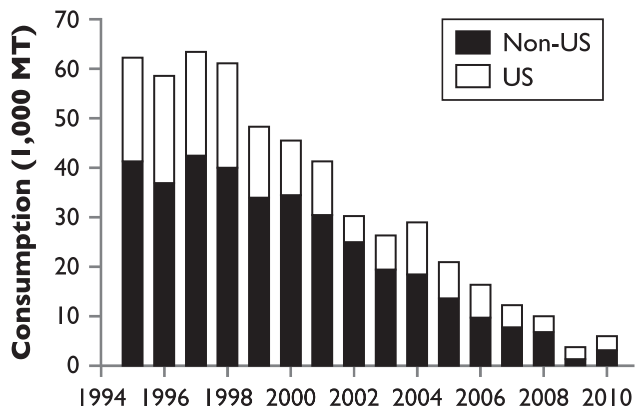

Figure 2. *World and United States consumption of methyl bromide 1995-2010. Quarantine and pre-shipment applications are not included (Source: Johnson et al. 2012).*

The Montreal Protocol and the U.S. Clean Air Act allow yearly requests for critical use exemptions for MeBr use in scenarios where no technical or economic alternatives are available (Table 2, USEPA 2011a). Since 2005, more than 90% of the critical use exemption allowance goes to preplant soil fumigations, with strawberries alone taking up 30 to 66%. Postharvest MeBr uses involve the direct treatment of commodities in marketing channels that are not subject to domestic and international quarantine

Table 2. *United States critical use exemptions for methyl bromide (MT)*.*

	2009	2010	2011	2012
Postharvest				
Mills and processors	291.4	173.0	135.3	74.5
NPMA food processing structures	54.6	37.8	17.4	0.2
Commodities	45.6	19.2	5.0	2.4
Dried cured pork	19.0	4.5	3.7	3.7
Total	410.6	234.5	161.4	80.9
Preplant				
Strawberries – field	1,269.3	1,007.5	812.7	678.0
Tomatoes – field	1,003.9	737.6	292.8	54.4
Peppers – field	549.0	463.3	206.2	28.4
Cucurbits	407.1	303.0	195.7	59.5
Orchard replant	292.8	215.8	183.2	18.3
Forest nursery seedlings	122.1	117.8	93.5	34.2
Ornamentals	107.1	84.6	64.3	48.2
Eggplant – field	48.7	32.8	19.7	6.9
Nursery stock – fruit, nut, rose	25.3	17.4	8.0	1.6
Sweet potato slips	18.1	14.5	11.6	8.7
Strawberry runners	7.9	4.7	6.0	3.8
Total	3,851.3	2,998.9	1,893.8	942.0
Grand total	4,262.0	3,233.5	2,055.2	1,022.8

* Values are those exemptions granted by the Parties to the Montreal Protocol (Source: USEPA 2011a).

requirements. Postharvest uses take less than 10% of the total critical use exemption allowance, with mills and processors receiving 71 to 92% of this. Postharvest critical use exemptions are not expected to continue for the United States past 2015.

Also exempt from the Montreal Protocol are quarantine and pre-shipment uses of MeBr as well as emergency uses, although the latter have not yet been granted. Quarantine and pre-shipment uses of MeBr refer to those required by regulatory entities to ensure pest-free commodities. The intent of quarantine and pre-shipment MeBr fumigation in the United States is to enhance the distribution and safety of commodities, promote and retain access of U.S. commodities to domestic and foreign markets, and protect the United States and its trading partners from the threat posed by pests. As the overall agricultural use of MeBr declines, quarantine and pre-shipment applications constitute a growing percentage of the total, and there is pressure to end the exemption under the Montreal Protocol. MeBr alternatives for quarantine and pre-shipment use must be consistent with international phytosanitary standards (IPPC 2011), generally requiring dose response data and confirmatory treatments that kill sufficient numbers of insects to provide the required security (usually Probit 9 or 99.9968% mortality) for each pest of quarantine concern (Couey and Chew 1986).

Unlike critical use exemptions, the amount of MeBr used for quarantine and pre-shipment is relatively difficult to track, as there is no single source for these data (Schneider and Vick 2002). Amounts used under USDA Animal and Plant Health Inspection Service (APHIS) supervision are given in Table 3, but additional MeBr is used by industry and supervised by state and local regulators with few records taken. Best estimates indicate U.S. imports require roughly twice the MeBr that exports do, with Chilean imports receiving more than 60%. Among the commodities treated, grapes receive the most MeBr for quarantine treatments, followed by logs.

The elimination of MeBr for quarantine and pre-shipment applications would require specific analyses of the technical efficacy and economic feasibility for each application scenario and alternative. Alternatives acceptable for one quarantine pest and commodity may not necessarily be applied to other applications without sufficient data to support the regulatory allowance. Gradual adoption of these alternatives (such as sulfuryl fluoride or phosphine) will help reduce the use of MeBr for quarantine and pre-shipment treatments, but issues of cost, product quality, and the acceptance by quarantine regulatory agencies must be addressed. Of particular concern is the treatment of domestic products or imports requiring fumigation upon arrival at port and inspection facilities. Because these quarantine and pre-shipment fumigations are generally time-sensitive and may involve large amounts of product to be treated, most MeBr alternatives are not currently acceptable.

Preventing the release of MeBr into the atmosphere following chamber fumigations may extend quarantine and pre-shipment use. Several commercial recapture systems are available, and research continues to develop commercially viable processes to contain, destroy, or reuse MeBr and alternative fumigants after use to reduce agricultural effects on air quality. To address this situation in a manner that minimizes nontarget effects on human and environmental health, the USDA has established research initiatives to reduce or eliminate the emission of fumigants and other agriculturally derived volatile organic compounds (VOCs) into the atmosphere (Civerolo et al. 1993).

Phosphine – hydrogen phosphide

Hydrogen phosphide gas has the chemical formula PH_3 and is commonly referred to as phosphine. Phosphine is by far the most commonly used fumigant for bulk-stored cereal grains, oil seeds, and other bulk dried commodities due to its low cost and relative ease of use. Phosphine can be purchased in various formulations that vary in method of application, rate, and efficiency of gas delivery to the target pest insect. Phosphine has a specific gravity of 1.21 (Table 1), similar in density to air, which allows it to spread and penetrate well through commodities and structures. The toxic mode of action of phos-

Table 3. *Quarantine use of methyl bromide in the United States.*

	2005	2006	2007	2008	2009	2010
Total MeBr Usage (metric tons)						
Export*	101.3	113.8	113.8	87.1	71.5	56.5
Import	213.5	245.1	233.7	248.9	251.1	252.4
Total	314.8	358.9	347.5	336.0	322.6	309.0
Commodity Type						
Fresh fruits and vegetables	190.8	216.7	210.1	215.8	224.7	210.3
Propagative plant material	1.0	0.9	0.5	0.8	0.8	0.6
Cut flowers and greenery	2.2	4.7	4.9	5.3	5.5	5.0
Other**	120.8	136.5	132.0	114.2	91.5	93.1
Total	314.8	358.9	347.5	336.0	322.6	309.0
Country of Origin (Import only)						
Chile	148.7	166.1	154.5	149.4	164.9	150.6
Peru	20.9	25.8	32.3	37.6	36.6	34.3
Costa Rica	9.4	11.0	12.6	16.3	9.6	10.9
Italy	9.1	7.1	6.8	10.1	8.5	11.2
China	4.5	9.3	9.7	9.8	7.7	7.8
All Others	20.9	25.8	17.8	25.8	23.8	25.8
Total	213.5	245.1	233.7	248.9	251.1	240.6

* Data from APHIS methyl bromide use database, includes only APHIS supervised treatments; amounts supervised at the state and county level are not included in the table.
** Includes tile, steel, and logs.

phine is not well understood but is generally believed to interfere with metabolism of oxygen at the cell membrane. Oxygen must be present for phosphine to be toxic. It is not recommended to use phosphine in combination with low oxygen controlled atmosphere treatments that would reduce the efficacy of the gas.

Phosphine fumigants are registered for more than 50 raw commodities, processed foods, and nonfood items in the United States, and can be used in one of several formulations or delivery methods. The most common formulations of phosphine are as metallic phosphide salts that react with moisture in the air to generate phosphine gas. Aluminum phosphide (AlP) and magnesium phosphide (MgP) react with water molecules according to the following chemical reactions.

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

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

Aluminum and magnesium phosphide can be purchased as pellets or tablets (Figure 3) that can be incorporated directly into the commodity to release gas throughout a grain mass, or the phosphide salt can be commercially formulated as a powder or granule in a ventilated linen "sachet" or pressed as a thin layer on a metal plate. As the reaction formulae indicate, one molecule of AlP reacts with three molecules of water to generate one molecule of phosphine, PH_3, but MgP generates twice as much phosphine in its reaction. Both reactions are limited in their rate by the ambient temperature and the water vapor available through humidity in the air.

Application labels for these formulations indicate that application should be done when the commodity air temperature is above 40˚F. The minimum ideal conditions for reaction of phosphide salts to yield phosphine gas are 80 to 90˚F and 70% RH or higher. With all conditions being equal more phosphine is generated at a higher rate from MgP compared to AlP. Applicators often choose MgP for commercial fumigations that require treatment to be done in one or two days, while treatment of bulk stored commodities for which treatment time is not critical will utilize AlP. The application label for phosphide salts will report a range of doses that can be effectively applied to a commodity or space. The effectiveness of phosphine fumigation, as with fumigants using other active ingredients, is determined by the con-

Figure 3. *Pellets (left) and tablets (right) of aluminum phosphide that generate 0.2 and 1.0 g, respectively, of phosphine each when fully reacted.*

centration of the gas, the temperature at which the fumigation is conducted, and the length of time the gas can be held on the target pest. Gas concentration is a function of gas-tightness of the structure or space being treated and the total amount of fumigant added to the structure or commodity. When consulting application instructions that recommend a range of treatment doses, it is recommended that the applicator use a higher number of pellets or tablets to maximize the total amount of phosphine gas that could be generated and counteract any loss of gas that may occur in a leaky structure.

Phosphine also can be delivered directly as a gas to a commodity or structure from a phosphine generator or from one of several formulations of hydrogen phosphide gas released from a pressurized gas cylinder. A phosphine generator requires that a phosphide salt be reacted with water in a highly controlled and contained reaction vessel from which the gas is released into the treatment area (Figure 4). Phosphine in cylinders may be composed of PH_3 dissolved at about 2% in carbon dioxide, all of which is released into the commodity or structure, or nearly pure phosphine gas from a cylinder can be precisely and rapidly mixed with air upon release from the tank and then delivered directly to the treated commodity or space (Figure 4). Phosphine gas concentrations of more than 18,000 ppm can spontaneously combust and explode in a normal atmosphere, so rapid dilution in air is essential during a treatment. Current USEPA registrations for cylinder-based phosphine are very specific and strict as to the method and instrumentation used for releasing the gas.

Phosphine fumigants have some drawbacks that may preclude their use in specific situations. Flammability or explosion of solid and gaseous formulations of phosphine products is a safety hazard, as discussed. Spontaneous ignition of phosphine gas, if the gas concentration exceeds 18,000 ppm, rarely happens but could occur if large numbers of phosphide pellets or tablets quickly generate gas in a small-volume space. Dangerous high concentration situations may be more likely when using cylinderized pure PH_3 gas that is not properly mixed with a diluting gas. Phosphide pellets and tablets are prone to smoldering. Ignition and fires can occur within buildings or grain masses when they are deposited in piles in which the pellets are touching each other or when standing water is present. As with spontaneous combustion under high concentration, fire hazard from “piling” can be avoided by proper application.

A common drawback of phosphine that dictates the places and structures that can be fumigated — though not a direct human safety concern — is that the gas is highly corrosive to certain metals that it contacts. These metals include gold, silver, and most importantly, copper. Electrical appliances, wiring,

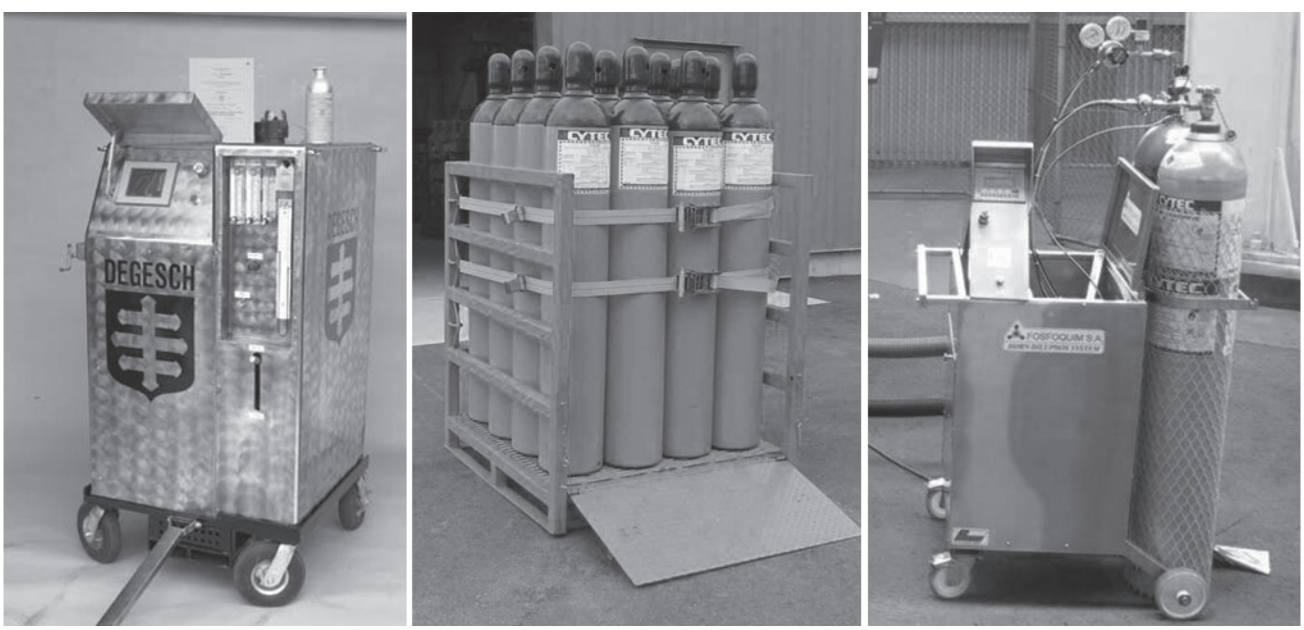

Figure 4. *A phosphine generator (left). Cylinder-based phosphine at 2% in carbon dioxide (center) and 100% PH_3 being diluted immediately in air (right).*

lighting, and especially electronic equipment with integrated circuits, computer chips, and similar devices with copper and other conductors of electricity are at risk of being damaged under phosphine fumigation and may not work properly after the fumigation. This corrosive factor, more than any other, is why phosphine fumigation is rarely applied to buildings such as flour mills, food plants, climate-controlled warehouses, and other buildings that have extensive electrical wiring, light fixtures, telephones, computers, and electrically powered and computer-processor controlled equipment that could be damaged by the gas. Grain bins, grain silos, bag stacks, barges, ship holds, and buildings with minimum electrical equipment are thus ideal for phosphine fumigation because the gas is relatively inexpensive and easy to apply.

Sulfuryl fluoride

Sulfuryl fluoride (SF) has been used for more than 50 years, under the trade name Vikane gas fumigant (Dow AgroSciences, Indianapolis, Ind.), for control of structure-infesting pests including drywood termites, other wood-destroying insects, and most recently, bedbugs. Vikane does not have food tolerances, so food must be removed or sealed in airtight containers before fumigation. Another SF product, trade name ProFume gas fumigant, registered in the United States in 2004, has EPA-approved food tolerances and is labeled for fumigation of more than 50 commodities, food processing and storage structures, stationary vehicles, and permanent and temporary (e.g., tarped stack) chambers. ProFume was developed by Dow AgroSciences at the request of the food processing industry as a postharvest fumigant replacement for MeBr, which is being phased out under the Montreal Protocol as an ozone-depleting substance.

Sulfuryl fluoride (ProFume) is formulated as 125 pounds of liquid (99.8% SO_2F_2) packaged under pressure in steel cylinders (Figure 5). SF is an inorganic molecule. It is nonflammable, nonexplosive, and as a gas is considered relatively inert and nonreactive. SF has been used for more than 50 years to fumigate more than 2 million buildings, including museums, research laboratories, medical facilities, and historical structures for control of structure-infesting pests. Similarly, extensive research to develop ProFume documented that SF does not impart odor or off-taste to commodities and does not alter the handling and baking characteristics of grain.

Figure 5. *Cylinder of ProFume gas fumigant (sulfuryl fluoride, Dow AgroSciences).*

Sulfuryl fluoride is a colorless, odorless gas at working concentrations. The mode of action involves breakdown of SF into fluoride anions, which in excessively high concentrations can interrupt processing of stored fats and carbohydrates required for normal metabolic functions. For these reasons, detailed procedures to ensure worker and public safety are included on ProFume labeling, and a comprehensive product stewardship program including mandatory training has been developed by Dow AgroSciences for fumigators who use ProFume (see safety section, this chapter).

A computer program called the Fumiguide (Dow AgroSciences) is used to calculate dosing for ProFume based on the pest species, exposure time, temperature, volume, and fumigant confinement (called half-loss time, HLT) (Figure 6). When ProFume concentrations are measured during fumigation, the program will use this information to calculate an actual HLT, accumulated and predicted dosage, and to update instructions on exposure time and if additional fumigant is required. In some commodity substrates, SF may form trace fluoride residues for which food tolerances have been established. The accumulated (concentration × time) dosage of ProFume should not exceed 1,500 oz-hours/1,000 ft^3 based on these food tolerances.

The SF is released through an introduction hose into the fumigated space, with the applicator and fumigant cylinder located outside the fumigated space. The high vapor pressure (15.2 times normal atmospheric pressure at 68˚F) and low boiling point (-67˚F) of SF result in the liquid fumigant expanding instantaneously to a gas upon release from the introduction hose. During this expansion, ambient air temperature is cooled. Moisture condensation and potential damage to surfaces can result if fans are not used to blend air in the fumigated space. Fans serve as heat exchangers when releasing SF. The length and inside diameter of the introduction hose control the release rate of SF and the fan capacity (cubic feet per minute, or CFM) controls the rate at which air is mixed throughout the fumigated space. The labeling for ProFume and the Fumiguide (Figure 6) provide directions on the required hose specifications to obtain the appropriate release rate of ProFume in relation to fan capacity; e.g., 1 pound of ProFume released per minute per 1,000 CFM fan capacity.

Fumigating tarped sacks of commodities may not have space for fan placement. In these conditions, SF should be introduced very slowly by using a long, narrow inside diameter hose to prevent condensation. Long introduction hoses, up to 500 feet, are commonly used when fumigating large structures with ProFume. During release of SF, the cylinder valve is fully opened by one complete turn to prevent flow restrictions that could cause frost damage to the valve and hose. In buildings, the introduction sites should be large, open spaces to provide a large reservoir of ambient air for temperature stabilization.

Carbon dioxide

Carbon dioxide (CO_2) is toxic to insects and many other pests when held at high concentrations for adequate time periods and suitable temperatures. CO_2 in normal air occurs at a fraction of a percent concentration, but concentrations of 20% or higher can be toxic to air-breathing animals through direct action on tissues. CO_2 as a fumigant for pest control must be applied on site and delivered into a gas-

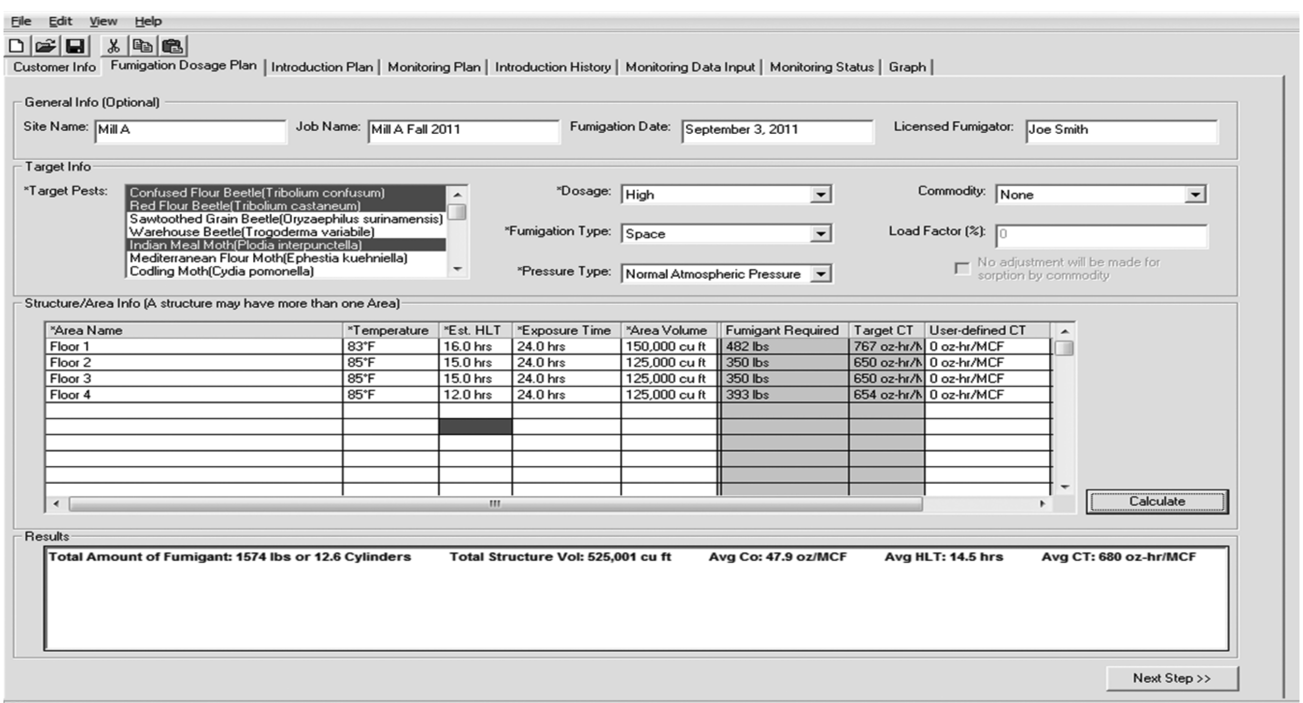

Figure 6. *Screenshot from the ProFume Fumiguide, a computer software tool for logging relevant information for a specific fumigation treatment and to calculate proper application dose of ProFume to a structure. The Fumiguide logs a record of past fumigations of the same structure for more precise fumigations of that structure in the future.*

tight structure where it can be held for several days. Because CO_2 is at low concentration in normal air, it cannot be easily concentrated from air for use, as nitrogen can be for low oxygen treatments (see Chapter 16). Instead, CO_2 must be manufactured or collected as a combustion product from some primary industrial activity, concentrated as a gas or liquid in large tanks, and then applied to the fumigation site. Because CO_2 used in pest control is mechanically or synthetically generated for this purpose, rather than simply extracted from existing air, it must meet regulatory standards as an insecticide.

Despite the initial perception of CO_2 being a "natural" fumigant, because it is an atmospheric gas, it has several chemical and practical features that limit its commercial use. Positive aspects include its effective toxicity when used properly, lack of harmful residues in commodities or structures, and immediate dilution and toxic neutralization when diluted in air during ventilation or aeration of a treated structure. Negative aspects include the relative high cost of performing an effective CO_2 treatment due to large quantities of gas needed to impart toxicity, long hold times relative to other fumigants, and the apparent environmental drawback of releasing quantities of a greenhouse gas into the atmosphere after use. Unless a CO_2 fumigation is specifically required, more practical and cost-effective fumigants are probably available.

Propylene oxide

Propylene oxide (PPO) is presently approved by the U.S. Food and Drug Administration (FDA) as a microbial sterilant for spices, cocoa powder, and processed nut meats (except peanuts), but it has yet to be registered as a fumigant insecticide. PPO has physicochemical characteristics that make it exist predominately in a liquid form at room temperatures and pressures. It is flammable at concentrations in normal air at or above 3%. To facilitate its safe and effective dispersal as a gas throughout commodities and structures, it is often delivered with the aid of a propellant, e.g., a 98% dilution in CO_2 (2% PPO + 98% CO_2), or it can be applied under low pressure in special chambers (Isikber et al. 2004). If the structure to be fumigated can be placed under vacuum, still more PPO will be driven into the gas form. Elevating temperatures above ambient conditions is not typically used as a way to drive more PPO into a gas form. PPO is highly flammable. Ignition sources must be removed from the space or structure being fumigated.

As a fumigant, PPO has shown potential to control storage pests (Isikber et al. 2004) with one recent test indicating PPO is toxic to two species of postharvest insects at relatively low doses (Creasy and Hartsell 1998). PPO is generally most effective against the egg stage of a species, which is contrary to the action of most other fumigants (Ferguson and Pirie 1948, Navarro et al. 2004, Ryan and Bishop 2003). Research is under way to engineer more applications for PPO to fill the void created by the regulations that restrict MeBr use.

Ethyl formate

Ethyl formate (EF), also known as ethyl methanoate, is a fruity smelling ester molecule (Table 1) that occurs naturally in several foods. It is used as a food additive and can be insecticidal at high concentrations. EF is designated a GRAS (generally recognized as safe) compound by the FDA with a current Occupational Safety and Health Administration permissible exposure limit of 100 ppm (300 milligrams per cubic meter (mg/m^3) as an 8-hour time-weighted average concentration. Like PPO, EF is flammable (rated 3 by the National Fire Protection Association) and exists predominantly as a liquid at room temperatures and pressures, so similar strategies are used to facilitate its dispersion into the fumigated commodity and structure.

Ethyl formate has been shown to be an effective fumigant for control of various arthropods, including thrips, aphids, Pacific spider mites, and omnivorous leafrollers (Simpson et al. 2004, 2007). Scenarios where ethyl formate has been demonstrated to be effective are those where the targeted pests predominantly reside on the surface of the commodity. Due to EF's flammability, a commercial formulation named Vapormate has been proposed. It contains 16.7% EF by weight dissolved in CO_2 and is applied from a pressurized cylinder (Ryan and Bishop 2003, Finkelman et al. 2010). To date no commercial product has been registered in the United States or elsewhere. Ethyl formate penetrates poorly — relative to MeBr, PH_3, and SF — to target internal feeding insects. This limitation is exacerbated with commodities that contain water because EF decomposes in water at a rate that is directly related to temperature. Formulation in CO_2 may aid in penetration. Of course, the "benefit" of this decomposition is that the residues formed from fumigation with EF are not typically of regulatory concern. Research efforts are under way across the globe to incorporate EF as much as possible into scenarios where it is effective, particularly quarantine and pre-shipment scenarios where control of surface pests is required on fresh produce. As with PPO, fumigant applicators are encouraged to contact distribution source and respective manufacturers for the most up-to-date applications, allowances, and restrictions.

Commodity Fumigations

Cereal grains, oil seeds, legumes, and other plant products

Phosphine is by far the most commonly used fumigant applied to bulk commodities for disinfestations in the United States and throughout the world. Aluminum phosphide (AlP, see page 6, previous section) is the common formulation applied to bulk cereal grains and many other stored products. A typical application label for AlP pellets and tablets lists 31 raw agricultural commodities, ranging from popcorn to wheat; 24 processed food products such as candy, flour, nuts, and "other processed foods"; and several nonfood products such as feathers, tobacco, and seeds. Tablets of AlP are larger than pellets and generate 1.0 gram of hydrogen phosphide gas when fully reacted, which is five times that generated from each of the smaller pellets.

The application rates of AlP to commodities such as wheat or corn are given in broad doses and exposure time periods to allow for variation in the temperature and the gas tightness of the structure being fumigated. Fumigation below 40˚F is not allowed, because the temperature would be too cold to provide adequate reaction of the phosphide salt to yield the hydrogen phosphide gas. Temperatures up to 53˚F require 8 to 10 days of exposure, while those above 68˚F can be completed in 2 to 3 days. The maximum number of pellets allowed to be added to a bulk commodity is 900 per 1,000 bushels; while up to 180 tablets can be added to the same size bulk. When treating spaces that are empty or that house product, the maximum number of pellets is 725 per 1,000 cubic feet or 145 tablets in the same volume. The labels permit application of a range of pellet or tablet numbers for various structure or commodity situations, such as vertical concrete silos, sealed round steel bins, rail cars, warehouses with finished products, barges, and such. If there is any chance that the structure being fumigated is not well sealed, it is recommended that application of AlP be done near the highest dosage rate.

Homogenous distribution of phosphine gas, or any fumigant gas, in a structure or bulk of stored commodity is important for an effective fumigation. Placement of pellets of AlP in a bulk of cereal grains or oil seeds must be well planned after the applied dose (number of pellets or tablets) is calculated to allow for the best distribution of gas. An automated gas recirculation system is a preferred feature (Figure 7). It allows gas from a phosphide source to be drawn from the top of a grain mass or structure and returned to the bottom of the mass and distributed so it can be evenly upward through a grain mass as it rises. Recirculation requires that the majority of phosphide pellets or tablets be deposited at the top and bottom of the mass, and the active system can move the gas to the other spaces of the grain mass. For structures lacking active recirculation, the pellets or tablets need to be distributed at various depths in the mass, with the majority being in the lower half of the grain. Such a distribution is best accomplished when the grain is loaded into the structure, and pellets are added while loading. The intricacies of proper phosphide application, recirculation, and gas distribution are beyond the scope of this chapter but are covered further by Reed (2006) and Walter (2006).

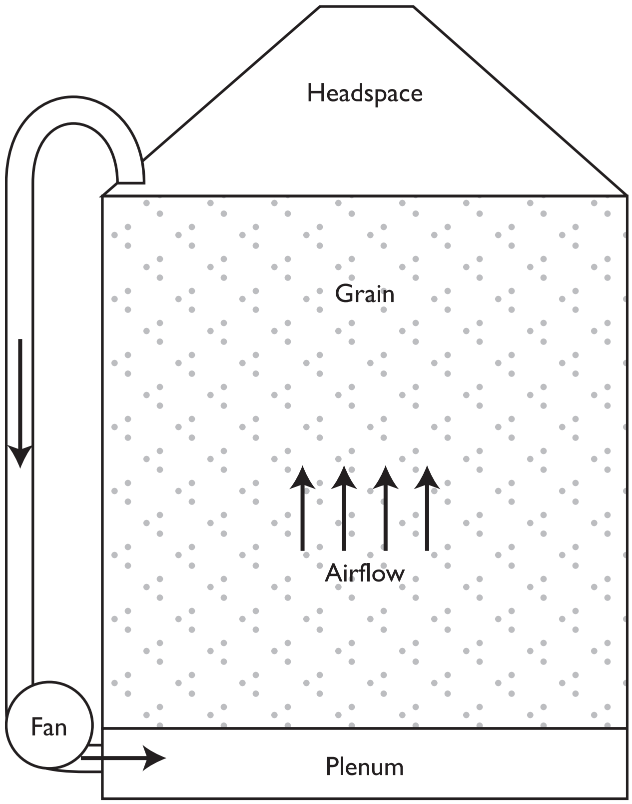

Figure 7. *Recirculation fumigation, or "closed-loop fumigation" system, depicted in a storage bin. Phosphine gas generated from aluminum phosphide inside the bin of grain is accumulated near the inside of the roof at the top, collected from the top headspace, and drawn down through a tube by a suction fan to the base of the bin where the gas is pushed back in to the bin at the bottom, where it can evenly flow into the bulk of the grain mass (Oklahoma Cooperative Extension Service, publication BAE-1111).*

Magnesium phosphide (MgP) also generates PH_3 gas after reaction with humidity in the air, but the rate of generating gas is much faster than that of AlP. Thus MgP is often the fumigant of choice when treatment time is critical for commercial activity and the fumigation must be expedited. Otherwise, AlP is adequate and typically recommended when there are no time constraints on the space or commodity being treated and hold time for the gas can be maximized.

Methyl bromide, sulfuryl fluoride, and carbon dioxide represent other fumigants that are legally available for treating grain, oilseeds, and other bulk agricultural products. Methyl bromide is the most toxic of the fumigants available, and it remains currently labeled in the United States for treating all the commodities and structures considered here, but its availability is limited, and future use threatened with the current phase-out and ultimate ban under the Clean Air Act. With reduced availability, the cost of MeBr has also increased. These factors provide practical reasons why a fumigator may chose something other than MeBr. Nevertheless, there may be a need to use MeBr, such as a required short treatment time, so the applicator should be skilled with the use of this material. The high toxicity of MeBr is good for killing insects and other pests but also threatens killing the germ of grain and other seeds if concentration or exposure time is too high. Dead germ results in poor storage quality, so application of MeBr must be done carefully. Sulfuryl fluoride is registered in the United States for fumigation of grain and grain products. As with MeBr, SF is applied from gas cylinders and may be viewed as easier than applying pellets or phosphine tablets. Special training and experience are required. Sulfuryl fluoride does not affect germ quality and has a unique chemical structure and mode of action that is different from those of other fumigants, including phosphine. SF represents a viable alternative to phosphine for situations in which pest populations are suspected or known to be resistant to phosphine (e.g., see Chapter 13).

Dried fruits, nuts, and similar durable commodities

An estimated 9 to 20% of durable commodities are destroyed or contaminated by pests after harvest (Pimentel 1991). This requires food handlers and processors to implement pest management programs tailored to commodity-specific scenarios. In particular, insect and microbiological pests can seriously affect production, commercial market access, food safety, and subsequent profits. The dried fruit and nut sector is concerned with disinfesting raw products of field pests within hours or days after harvest and controlling storage pests in processed "stored product" amenable to (re)infestation and microbial colonization. The existing infrastructure and logistical constraints of commercial production and consumer demand dictate that fumigation be used for this protection. The standard fumigant for years, MeBr, is no longer obtainable due to the Montreal Protocol and the U.S. Clean Air Act.

At present, phosphine and sulfuryl fluoride (SF) are registered fumigants being considered as alternatives to MeBr for postharvest treatment of insect pests in dried fruits and nuts. Postharvest use of SF on dried fruit and nuts, which has nearly the same infrastructural requirements as MeBr, has increased consistently since its registration in 2004. The majority of the dried fruit and tree nut market have transitioned from MeBr to SF since 2009. Phosphine in its various commercial forms (pellets, generators, cylinders), has been used in a postharvest capacity to treat dried fruit and nuts for decades, and new application technologies have been developed to reduce fire hazard and decrease the exposure time required for insecticidal efficacy. Alternative fumigants such as ammonia, ozone, methyl iodide, ethane dinitrile, ethyl formate, and carbonyl sulfide have been researched and proven effective in certain situations; however, work continues on these to develop more efficacy data, industry acceptance, and registrations for their use on foodstuffs, including dried fruits and nuts. Because of the relatively serious postharvest pest pressure that accompanies commercial dried fruit and nut production, U.S. industries have been at the forefront of researching viable alternatives to MeBr. The majority of dried fruit and nut industries have successfully incorporated MeBr alternatives, including phosphine and SF, into routine treatment regimes for pest control. Certain other U.S. dried fruit and nut industries still request critical use exemption allowances for MeBr due to industry-specific technical and economic limitations of phosphine and SF, which are briefly described below.

Disinfestation of fruit and nut pests originating in the field

With respect to field disinfestations, which are primarily conducted in chambers or controlled-atmosphere rooms, several dried fruit and nut industries are granted critical use exemptions for methyl bromide because of a need to treat rapidly (within hours), particularly during peak harvest periods that coincide with the highest-value product and market demand (e.g., California walnuts and dates intended for holiday markets in December). Since 2009, there has been nearly a complete conversion from MeBr to SF for treatment of in-shell and shelled walnuts, using vacuum or normal atmosphere fumigations. Numerous studies report that for post-embryonic life stages of postharvest insect pests, SF is generally more toxic than MeBr for a given species (Kenaga 1957, Thoms and Scheffrahn 1994). Insect eggs are relatively more tolerant to SF than to MeBr, often requiring many times the dosage required to control adults of the same species (Walse et al. 2009).

The recently developed Horn-Diluphos System (HDS) safely and rapidly delivers 100% phosphine (Vaporphos), achieving levels approximately 10,000 ppm within hours, even under commercial cold-storage conditions (Horn et al. 2005). With the HDS, the use of phosphine as a MeBr alternative for field disinfestations is expected to increase across the world, particularly for dried fruit and nuts that need to be marketed shortly after harvest (California walnuts and dates) or are preferentially treated at temperatures below 50°F to avoid phytotoxicity and quality damage. Research is under way in the United States and abroad to engineer phosphine fumigations to be efficacious in the shortest time possible through the integration of physical (e.g., vacuum) and chemical approaches, such as the use of mixtures containing other physiologically active gases (oxygen and nitrous oxide, for example).

Stored product disinfestations

With respect to stored product treatment of dried fruits and nuts, alternative strategies to overcome the need to use high ovicidal dosages for SF would be to conduct two, time-separated fumigations: one to kill all postembryonic life stages and most eggs, and a second fumigation about 2 weeks later, after surviving eggs have hatched, to kill larvae that survived the first fumigation while in the egg stage. Attention must be stringent so multiple fumigations with SF or modification of exposure intervals on the same commodity do not exceed the cumulative maximum "CT" dosage (1,500 oz-hour/1,000 cubic feet) allowed by the label.

Phosphine is routinely used to disinfest many types of dried fruit and nuts as well as other durable commodities stored in a variety of containment devices, including silos, chambers, ship hulls, bins, or under tarpaulins. When applied at recommended doses (500 to 2,000 ppm), complete mortality of all insect life stages is species-specific and typically requires exposures of 2 to 7 days, as compared to 2 to 3 hours needed for MeBr. From both a technical and economic perspective, phosphine use is not without limitations due to logistically challenging time and volume requirements, as well as corrosion issues that are prohibitive to many U.S. industries. Applicators must be mindful that the development of phosphine-resistance in target insect populations can occur when environmental factors, concentration, temperature, and hold-time goals are not properly achieved.

Agronomic and horticultural seeds

Seed treatment is much like that for cereal grains and edible beans in that the same products are labeled, and the doses, temperatures, and hold times are the same. The economic value of seeds for agronomic and horticultural crops are many times higher than the value of food-commodity crops, so seed managers must be more vigilant to damage caused by insect infestation and the potential damage from excessive fumigation that can result in seed sterility. Methyl bromide is by far the most toxic of the gases considered in this chapter, and as a general biocide it poses the highest risk for seed viability if used in that context. As mentioned, mortality of seeds can occur if MeBr is applied at a high concentration for a long period, and thus can represent a serious loss for commercial agronomic and horticultural seeds compared to commodity grains. Seeds are fairly tolerant of high doses and long exposure to phosphine, but care should also be taken in these situations to avoid seed sterility. Sulfuryl fluoride (SF) is gaining wide acceptance for seed treatments due to flexibility in using short duration fumigation exposures to meet shipping schedules, seed tolerance to SF concentrations applied, and lack of adverse effects on expensive computerized equipment used to process seeds. Carbon dioxide is relatively safe for seeds, but is less effective for controlling arthropod pests compared to MeBr and phosphine, as CO_2 treatments need to be conducted by someone with expertise using this compound as a fumigant.

Dried animal products

Products considered here include dried milk, cheeses, dried meats, dried fish, animal skins, wool, leather, feathers, bone meal, silk, and any other product derived from vertebrate or invertebrate animal bodies or their products. The pest species of insects and mites important for animal products are also discussed in Chapter 5 and include the cheese mite, redlegged ham beetle, warehouse beetle, and related species in the beetle family Dermstidae, and the common species of clothes moth from the moth family Tineidae. The currently registered fumigants MeBr, phosphine and SF can all be used on these pests but will vary in effectiveness depending on the specific pest. The product being treated may be affected negatively by the fumigant. Current registrations relative to product should be checked before treatment. For example, permitted critical use exemptions of MeBr for fumigation of southern dry-cured ham product to control cheese mite and ham beetle remained constant in 2011 and 2012 (Table 2). Since the critical use exemptions of MeBr for treatment of ham and cheese will eventually end, fumigation with phosphine is being evaluated as an alternative. Limited, positive research exists on quality effects of fumigants on commercial stored animal products (e.g., Sekhon et al. 2010), so the applicator must work from experience and with precautions to quality effects as well as attention to treatment efficacy.

Processed foods and value-added products

Numerous processing facilities of human and pet foods, and warehouses holding value-added food products relied on MeBr as the “fumigant of choice” at varying frequency for decades before the current phase-out and ban of this product under the international Montreal Protocol and U.S. Clean Air Act. In the 1990s it was estimated that more than 220 commercial wheat flour mills in the United States and Canada produced flour for bread-making, and that these facilities conducted between one and three MeBr fumigations each year. The use of MeBr has fallen dramatically since the official ban in 2005 and the current year-to-year use by the pest control industry following the critical use exemption regulations.

Phosphine is considered by many as an impractical substitute for MeBr in most flour mills and food processing plants because of the risk of corrosion and damage to electronic devices, combined with the quick turnaround time needed for most mills that operate nearly around the clock to meet business requirements. Many mills and food processors have substituted nonfumigation practices to manage insect pests, or they use a combination of fumigant alternatives with occasional MeBr fumigation as allowed or available in a given year under the critical use exemptions. Others have converted to using SF as an effective, noncorrosive substitute for methyl bromide, while still others have converted to using heat treatments at a regular frequency for large-scale general pest control activities (see Chapter 15).

Large finished-product warehouses and regional food distribution centers can typically use IPM and nonfumigant pest control methods since they have many employees and many nonfood products for which fumigation would not be necessary. The pest control and processed food industries in North America continue to operate with dramatically lower levels of MeBr than those used before 1993. At this writing there is "some" MeBr still being used, SF has been widely adopted, heat treatments are being adopted and highly refined, and improved methods of IPM and fumigant alternatives allow the flour milling and food industries to meet customer needs and quality standards.

Factors Affecting Fumigation Efficacy

Concentration, Time, Temperature, and Other Factors

Understanding the relationship of fumigant concentration, exposure time, and temperature during fumigation is critical for determining the proper dosage for control of the pest of interest. For SF and MeBr, the dosage of the fumigant is calculated by the "CT concept" as follows:

Dosage (D) = Concentration (C) × Time (T)
or
D = C × T (CT)

The units for C = ounce (oz) of fumigant/1,000 cubic ft (ft^3), which are equivalent to grams (g) of fumigant/cubic meter (m^3).

The unit for T = hours (hrs), which equals exposure time defined as the number of hours the target pest is exposed to the fumigant.

Therefore, CT is the product of Concentration (C) and exposure Time (T) expressed as oz-hrs/1000 ft^3 or g-hrs/m^3.

D = C × T = oz-hr/1000 ft^3
or
g-hrs/m^3 = oz-hr dosage

If you increase the exposure time, less gas will be required to achieve the dosage level (CT) for control. Contrarily, if you decrease the time of exposure more gas will be required to get to the appropriate dosage (CT) for control.

Phosphine differs from the previous model because the relationship of dosage and toxicity to insects is not linear. Phosphine is most effective over longer exposure times of 1 day or longer. In general, longer exposures to phosphine even at low concentrations result in better efficacy than shorter exposures at higher concentrations.

Knowing the target pest is critical because different pest species as well as life stages require different fumigant dosages for effective control, and this varies by fumigant. For SF the postembryonic stages are most susceptible, while the egg stage is most tolerant. For phosphine the egg stage is also primarily the most tolerant stage, but depending on species, temperature, and exposure duration, pupae have also been shown to be the most tolerant stage. For MeBr the most tolerant stage are pupae, but in a study looking at susceptibility of red flour beetles, the only life stage that had survivors was large larvae (Hartzer et al. 2010).

Temperature is also a critical factor to consider for a successful fumigation. Arthropods are cold-blooded, so temperature affects their metabolism. In cool temperatures, i.e., 68°F (20°C) and below, insects move and respire at a lower rate, so fumigant uptake is less. As temperatures drop, more fumigant is required. Eventually, it is too cold to fumigate to get the control desired, or the fumigation becomes economically unfeasible. The labeling for ProFume states it should not be applied for insect control if the temperature is below 40°F (5°C). In fumigated spaces with higher temperatures — for example, 78 to 86°F (25 to 30°C) — insects have increased metabolism, which will improve fumigant intake. Less fumigant is required when the temperature is higher, and often, higher temperature fumigations are more efficient. Planning fumigations during the warmer seasons and during the warmer times of day can positively affect the temperature and overall effectiveness. In addition, fumigators can use permanent built-in heating systems or temporary leased heaters to increase the temperature in the area to be fumigated. The exception to the temperature factor is when target pests are rodents. They are warm-blooded animals and do not require increased fumigant as the temperature decreases.

Other factors that can affect fumigant dosage include atmospheric pressure, insect diapause, and formulation of phosphine. Vacuum fumigations conducted at lower atmospheric pressure in specially designed chambers can improve penetration of the fumigants SF or MeBr into commodities and provide control at lower dosages. Vacuum fumigations generally are not conducted with metallic phosphides, but as stated in the previous section on dried fruit and tree nuts, testing is under way. Some insects, including stored product moth larvae and beetle larvae, can undergo a dormant state known as diapause. This dormant state is generally less susceptible to fumigants. Formulation has been shown to affect dosage rate of phosphine, as less cylinderized phosphine is required to achieve control in comparison to AlP pellets.

Gas tightness, persistence, confinement, and sorption

To reiterate what is discussed throughout this chapter as key to a successful fumigation: maintain adequate gas concentration for a sufficient hold time by ensuring good seals for gas tightness, proper starting concentration, and maintenance of the desired concentration throughout the exposure. The term "sorption," used frequently when discussing fumigation of a raw agricultural commodity, gives the impression that the commodity acts like a sponge, absorbing the fumigant into the commodity, then desorbing back into the air space. In fact, researchers have rarely been able to recover presumably absorbed gas from a fumigated commodity. Thus "sorption" must be thought of as any loss of gas other than from leakage, probably due to chemical breakdown or reactivity with surfaces, that ultimately results in a lower concentration and less persistence of active gas in the treated space. Monitoring gas levels with appropriate detection equipment is key to knowing the delivered concentration of a fumigant.

Tolerance and/or resistance within and among pests

Variation exists within and between pest species as to their level of susceptibility to a given fumigant pesticide. In general, because fumigants act in the gas stage, one generalization is that life stages or species with low levels of respiration, such as the egg stage or the pupal (pre-adult) stage, are more difficult to kill under fumigation conditions that would easily kill more highly respiring larval and adult stages that are active and breathing in fumigant gas. Among species, variation in tolerance exists that is not easily explained by respiration. It may be related to an inherent ability due to natural detoxification or other physiological differences. Among grain insects, it is well know that the lesser grain borer, *Ryzopertha dominica*, is more difficult to kill with fumigants and other insecticides compared to other common grain insect species. Genetically based, heritable resistance to fumigants, especially phosphine, has evolved in certain populations of grain insect species (see Chapter 13), which poses challenges for effective phosphine use in the future. Genetic resistance to other gases — such as MeBr, SF, or CO_2 — has not been reported. Fumigators must be aware that variation exists in tolerance and susceptibility to fumigants for various reasons. Such phenomena provide additional justification for applying fumigants properly for the most effective result only when applications are clearly needed.

Safe Use of Fumigants

Human injury during fumigation can occur from overexposure to the fumigant or mechanical injury during fumigation. The wide spectrum effectiveness of fumigants makes them potentially lethal to humans. Fumigant application usually involves physically demanding work, such as climbing ladders and lifting heavy equipment in potentially dangerous environments, including grain bins, at heights, and near industrial equipment. For these reasons, it is critical for fumigators to follow federal, state, and local safety regulations when fumigating.

The fumigator should carefully read and understand the fumigant labeling — which may include an applicator manual — and always have a copy of this labeling readily available at the fumigation site. All fumigant labeling provides product-specific information about safety equipment and procedures required to prevent overexposure, first aid, note to physicians on treatment, and an emergency number. For any type of overexposure, fumigant labeling recommends immediate medical attention. This is essential because the onset of acute adverse symptoms can be delayed for a day or more, even in life-threatening exposures. There is no antidote to overexposure to fumigants; physicians can only treat the symptoms.

Overexposure to a fumigant by inhalation is of greatest concern for fatal exposure. Acute and lethal exposures to fumigants cause pulmonary edema (fluid in the lungs) in humans, resulting in death by respiratory failure or cardiovascular collapse. General symptoms of overexposure to fumigants can include:

- Nausea
- Slowed body movement, slurred speech
- Abdominal pain
- Numbness of hands and feet
- Difficulty breathing

Inhalation exposure is prevented by wearing a self contained breathing apparatus or supplied-air respirator when fumigant concentrations exceed the permissible exposure limits established on product labeling. The permissible exposure limits vary by fumigant and are 5 ppm for MeBr, 1 ppm for SF, and 0.3 ppm for phosphine. A full-face cartridge respirator is not permissible respiratory protection to prevent inhalation exposure to MeBr or SF, but can be worn with phosphine when concentrations are at or below 15 ppm.

The Occupational Safety and Health Administration (OSHA) has specific and detailed regulations on use and maintenance of respiratory protective equipment. These regulations require employees to be trained in the proper use and maintenance of the equipment per manufacturer's directions, be fit-tested for the respiratory equipment, and have an evaluation by a health care professional to determine fitness to wear respiratory protection. OSHA regulations are available for viewing and printing at no charge at *www.osha.gov*.

Airborne concentrations of phosphine and SF should be monitored after introduction where workers are present, using appropriate detection devices. The purpose of monitoring is to determine when and where workers need to wear respiratory protection, and to seal leaks from the fumigated space.

Fumigant overexposure to skin or eyes is another concern for fumigators. Any dermal exposure to fumigants in the liquid or solid phase during application should be avoided. MeBr can produce chemical burns. SF and phosphine/inert gas mixtures produce frostbite-type burns due to rapid evaporation of these materials from skin or eyes. Spent dust from metallic phosphides can be very irritating to the eyes.

Dermal exposure to fumigants packaged in cylinders is prevented by wearing long-sleeved shirts and pants during fumigant introduction. Rubber gloves and rubber boots should not be worn when applying these fumigants. Cloth or leather gloves should be worn when handling metallic phosphides and their spent dusts. With the exception of metallic phosphides, fumigant labels require eye protection, such as goggles or full-face shield, to be worn during fumigant introduction. When introducing fumigants using an introduction hose connected to a pressurized cylinder, eye protection also can prevent potential mechanical injury if the hose accidentally bursts or disconnects.

Fumigant labeling requires two persons trained in fumigant use to be present when there is the greatest potential for worker exposure — during fumigant introduction, reentry into the fumigated structure before aeration, the initiation of aeration, and after reentry when testing for clearance.

All fumigants are classified as hazardous materials by the Department of Transportation (DOT) and as a result have extensive regulations regarding their transportation. These regulations include vehicle placarding, driver licensing, vehicle safety kits, inspections and maintenance logs, and fumigant documentation. Hazardous materials must be secured within the vehicle so they do not move during transport. Fumigants should always be transported in a separate air space from vehicle occupants. Cylinders must be transported and stored in an upright position with the valve cover and safety bonnet attached. Fumigators should check with the state's DOT enforcement agency to confirm current transportation requirements for fumigants. An exception to DOT regulations may be obtained from the supplier (e.g., Degesch America Inc.) for transporting small quantities of their metallic phosphide formulations.

Fumigants should be stored in a locked, vented enclosure that is posted as pesticide storage. It is advisable to not store fumigants in an occupied building, unless the storage area has a separate ventilation system that provides constant aeration during building occupation in case fumigant leaks from storage containers.

Fumigation workers should receive verified training on general safety procedures and proper handling of all equipment they will use at a fumigation site.

This training could include CPR and first aid, along with OSHA requirements on proper use of ladders, working at heights, or around power lines and industrial equipment, and lifting heavy equipment. At each fumigation site, fumigation workers should be updated on additional precautions and safety equipment (such as bump hats) that they may need to work safely at that location and what to do in case of an emergency. Any specialized equipment, such as boom lifts, used to prepare the building for fumigation should only be operated by personnel trained to use the equipment.

Confined space entry restrictions have numerous requirements that must be met before workers can enter concrete or steel grain bins to do work to prepare for fumigation, such as cleaning or sealing of bin intervent systems. The extent and cost of these confined entry requirements may preclude some companies from allowing workers into bins, thus sealing before fumigation can only be done externally and may not be optimum.

EPA requires all fumigation areas be posted with warning signs. The information on the warning sign (skull and crossbones, English/Spanish signal words, date of fumigation, fumigant name, and name, address, and telephone number of the applicator) is standardized by EPA. Other requirements for warning signs can vary by product use pattern. Warning signs are placed on each side of a structure, including both sides of railcars by ladders and on all entrances of a fumigated structure, including doors of fumigation chambers and railcar hatches. Warning signs are placed before fumigant introduction and are removed only after testing with approved clearance detection devices has demonstrated that fumigant is aerated per label requirements.

Doors to fumigated structures must be locked during fumigation. In addition, labeling for ProFume requires barricading or secondary locking to prevent unauthorized persons from entering the fumigated space. At food storage and processing sites, site employees may participate in preparing the facility for fumigation. At these facilities, which can be large and complex, it is imperative for the fumigator to ensure all personnel have exited the area to be fumigated before reentry deterrents are applied, and the fumigant is introduced.

Low level, nonoccupational exposure to fumigants can occur from other sources, such as bystander exposure to fumigant dissipating onto neighboring properties during fumigation and aeration, or off-label exposure of commodities. Potential bystander exposure to fumigants is minimized by preventing excessive leakage from structures during fumigation and controlling the fumigant's release during aeration. Fumigant contamination of commodities is prevented by ensuring that the fumigant is labeled for the commodity and the applied dosage does not exceed the label rate or tolerances for the commodity. Spent dust from metallic phosphides must not contact processed food or commodities (with exception of brewers rice, malt, or corn grits used in the manufacture of beer).

The availability of fumigants in the future is dependent upon fumigators practicing stewardship in handling these products today. Increased concern about public safety since the September 11, 2001, terrorist attacks on the United States emphasized the importance of security when managing fumigants. Fumigant inventory should be carefully tracked. Containers should be secured to prevent unauthorized access when stored or transported. Background security checks should be conducted on new employees.

Detection equipment serves different objectives during the fumigation process. Gas leak detectors, such as continuous monitoring halogen leak detectors for MeBr and SF (TIF detectors, Miami, Fla.), are used to determine where fumigant may be leaking from confined spaces. Leak detectors indicate the presence of fumigant at concentrations above the permissible exposure limits set by EPA, and other gases can interfere with readings, depending on the leak detector. Leak detectors are important tools to identify areas requiring additional sealing to improve confinement.

Detection equipment capable of accurately measuring low concentrations of fumigants is mandatory to confirm fumigant clearance before reoccupation of a treated structure or handling/processing of a treated commodity. Fumigant detectors provide either point-in-time measurements or continuous readings, depending on the type of gas detection sensor used. Commonly used single reading detectors for measuring low concentrations of MeBr and phosphine are color diffusion detector tubes, available from numerous manufacturers (Matheson Gas Products, Rutherford, N.J.; Draeger Safety, Pittsburgh, Pa.; Sensidyne, Clearwater, Fla.; RAE Systems, San Jose, Calif.). These tubes utilize a pump to draw a specified volume of air through a tube containing a chemical reagent. The reagent changes color in the presence of the fumigant. The length of the stain or intensity of the color is proportional to the fumigant concentration. Some ambient gases, high temperatures, or humidity can affect the readings. These colorimetric tubes are simple to use, do not require calibration, are single-use only, and have a limited shelf life.

A variation of the color diffusion detector tubes is available for phosphine (Draeger Safety, Pittsburgh, Pa.). The system uses chips containing capillaries filled with reagent for a colorimetric reaction. An optical analyzer reads the reaction, and the concentration is digitally displayed. This technology is more accurate than the color detector tubes because the amount of air samples and analysis of color reaction is automated.

A badge that directly measures exposure to phosphine (e.g., Draeger Safety Inc., Pittsburgh, Pa.; Scott Instruments, Exton, Pa.) can be worn by workers to verify any exposure to phosphine. The badges operate by direct diffusion exposure. The intensity of the color on the badge is directly proportional to the gas concentration and exposure time. The user compares the badge color to a dose estimator wheel to determine total exposure.

Continuous reading electrochemical sensors are available to detect low concentrations of phosphine and are useful for monitoring worker exposure. Electrochemical sensors function like a chemical battery, generating current proportional to the amount of gas passing through the catalytic electrode. They respond slowly after saturation with high concentrations of fumigant. These electronic detectors are portable, battery-operated, and typically have a digital display of gas concentration (Examples: Pac Series, Draeger Safety, Pittsburgh, Pa.; PortaSens, ATI, College Oaks, Pa.; ToxiRE, RAE Systems, San Jose, Calif.). Gases, such as carbon monoxide, can interfere with the detection of phosphine by certain sensors, so these electrochemical sensors maybe used to monitor aeration before final clearance testing with color diffusion tubes.

The photoionization devices measure the electrical charge of UV-ionized gas samples and are available to detect MeBr and phosphine (example: MiniRAE, RAE Systems, San Jose, Calif.). High fumigant concentrations need to be diluted before reading using a dilution probe. Other gases can interfere when measuring MeBr, and phosphine can cause coatings to form on the photoionization device lamp. Coatings need to be removed by cleaning.

It is important to confirm that the detection equipment used to verify fumigant clearance is approved for use on the fumigant label. Currently, only two clearance detectors are approved and manufactured for use with SF; the Interscan (Interscan Corp, Chatsworth, Calif.) and the SF-ExplorIR (Spectros Instruments, Miss.). The Interscan analyzes the gas sample in a furnace, releasing SO_2 that is measured by a sensor. SO_2 and other gasses, such as H_2S, HCN_2, and Cl_2, can interfere with the Interscan sensor. These gasses do not affect fumigant measurement by infrared wavelength absorption, the method of detection used by the SF-ExplorIR.

Equipment for detecting fumigants is rapidly evolving. Fumigators should contact fumigant manufacturers for information on the latest technology approved for use with a specific fumigant.

The Fumigation Management Plan

The EPA initiated the requirement of a fumigation management plan to be written, on file, and followed during phosphine fumigations along with the agency's re-registration eligibility decision for phosphine products issued in the late 1990s. At this time, a fumigation management plan is required for fumigation with ProFume and likely will be required for MeBr following completion of its registration review at EPA. A fumigation management plan is an organized, written description of the required steps involved to help ensure a safe, legal, and effective fumigation. The plan helps those involved with fumigation comply with pesticide product label requirements. Federal and state regulators, along with distributors and product manufacturers, provide templates that assist a fumigator in writing a fumigation management plan for the specific job. The process of writing the plan familiarizes the fumigator with the specific pesticide label for the product being applied and ensures that the fumigator is knowledgeable about the specific facility, commodity, and characteristics of the fumigation. The fumigation management plan is to be placed on file with the fumigation company for future reference. Relevant sections of fumigant labeling should be reviewed by appropriate company officials (supervisor, foreman, and safety officer) in charge of the site. Labeling may require local fire companies and/or other emergency agencies in the area to be notified before the fumigation. Fumigation management plans are revised each time the same facility is treated, so the plan allows for a collective learning experience about each specific fumigation and should enhance safety, efficiency, and effectiveness.

The Future of Fumigation

Stored product protection using fumigant insecticides is subject to changes in label registrations, specific procedures, fumigant application methods, and information about controlling pest populations, among other variables across various levels of government. At this writing the effective and common chemical fumigants available for treating stored products and associated structures in the United States include phosphine, SF, and MeBr. Methyl bromide continues to be phased out under the Montreal Protocol, and more specifically for the United States, the Clean Air Act. MeBr is still allowed in many situations up to an annual cap guided by critical use exemptions, but its use for general stored product protection is expected to end within the decade, leaving the stored product industry with phosphine and SF. With only two effective synthetic fumigant active ingredients available, alternatives should be considered, and fumigants should be used only when needed as tools in carefully monitored IPM programs.

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