

ALTERNATIVES TO METHYL BROMIDE TREATMENTS FOR STORED-PRODUCT AND QUARANTINE INSECTS*

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■ **Abstract** Methyl bromide is used to control insects as a space fumigant in flour and feed mills and ship holds, as a product fumigant for some fruit and cereals, and for general quarantine purposes. Methyl bromide acts rapidly, controlling insects in less than 48 h in space fumigations, and it has a wide spectrum of activity, controlling not only insects but also nematodes and plant-pathogenic microbes. This chemical will be banned in 2005 in developed countries, except for exceptional quarantine purposes, because it depletes ozone in the atmosphere. Many alternatives have been tested as replacements for methyl bromide, from physical control methods such as heat, cold, and sanitation to fumigant replacements such as phosphine, sulfuryl fluoride, and carbonyl sulfide, among others. Individual situations will require their own type of pest control techniques, but the most promising include integrated pest management tactics and combinations of treatments such as phosphine, carbon dioxide, and heat.

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INTRODUCTION

Methyl bromide has been used around the world since the 1930s as a quarantine treatment for plants and to control insects in buildings and commodities (Supplemental Tables 1 and 2, see the Supplemental Material link at www.annualreviews.org); it is also widely used as a preplant soil fumigant to control nematodes, insects, pathogens, and weeds. It is the method of choice of many pesticide applicators because of its rapid action and broad spectrum of activity. In 1992 it was listed as an ozone-depleting substance under the Montreal Protocol on Substances that Deplete the Ozone Layer, and all developed countries are scheduled to eliminate the bulk of their consumption of methyl bromide by 2005 (14, 78, 119).

The loss of this important insecticide has forced pest control operators, plant managers in the food industry, and entomologists to find alternatives to methyl bromide. This diverse group of experts has developed some innovative solutions, such as high and low temperature control. These are refinements of techniques that were employed before methyl bromide was widely used. Some are completely new: precision trapping for mapping infestations over space and time, biological control, new chemical insecticides, high-pressure fumigation, and recycling methyl bromide. There are a few reviews of the methyl bromide issue and alternative pest control methods (14, 77, 78, 119), as well as general reviews of stored-product protection (63, 114, 115). Also, several web sites are devoted to this topic (23, 79, 120, 128), and many of the government or United Nations publications cited in this review are available at these sites. The goal of this review is to summarize the alternatives available to replace methyl bromide fumigation for stored-product and quarantine uses. We do not cover its uses as a soil fumigant (14, 77, 78).

Methyl bromide has a boiling point of 3.6°C and is colorless and odorless (at concentrations used for fumigation). Chloropicrin is sometimes added at 2% as a warning indicator when the chemical is used as a structural fumigant or as an active ingredient at higher concentrations of 25–67%, when used as a soil fumigant.

Le Goupil (71) was the first to report that methyl bromide is toxic to insects. In the 1930s it became widely used as the fumigant of choice for quarantine treatment for horticultural and durable commodities [fruit, vegetables, cut flowers, grain, artifacts (Supplemental Tables 3 and 4, see the Supplemental Material link at www.annualreviews.org; 24)]. In the 1940s and 1950s it came into use as space treatment to control insects in flour mills, warehouses, railcars, and ships (16, 78). It is especially important in quarantine fumigation when control in 24–48 h is desired.

Methyl bromide is a widely used fumigant because it rapidly kills insects, mites, microflora, and nematodes; it penetrates commodities including wood; it usually does not taint commodities; and it is noncorrosive and nonflammable (14, 16, 137). The mode of action is thought to be by damage to the membrane of nerve cells in insects. Methyl bromide also reacts with the sulfhydryl groups in protein (100). Insects usually die within 24 h of exposure, but at lower doses or with more resistant stages mortality may be delayed until 1 or 2 days after the fumigation.

By the 1990s, most methyl bromide (75%) was used as a soil sterilant (67), while durable commodities (13%), perishable commodities (8%), and structural disinfestation (3%) used lesser amounts (14, 78, 119). Emissions of methyl bromide from soil fumigations are estimated to be from 40–90% of the dosage applied, whereas the other uses of methyl bromide as a fumigant release 70–99% of the initial gas, which eventually reaches the ozone layer. World-wide consumption of methyl bromide grew from 16,000 metric tones (t) in 1975 to 42,000 t in 1984 and 73,000 t in 1993 (81). In 1998 most methyl bromide was used in developed countries [59,000 t, compared with 2000 t in developing countries (79)]. Consumption in the developed countries has remained stable since the early 1990s, whereas consumption in the developing countries doubled between 1991 and 1998.

In 1974 Molina & Rowland (86) raised the alarm that chlorinated fluorocarbons (CFCs), gases that were widely used as refrigerants and aerosol propellants, could be causing significant damage to stratospheric ozone. Most of the stratospheric ozone is found 19–23 km above the earth and absorbs ultraviolet-B radiation. A depleted or thinner ozone layer allows additional ultraviolet-B radiation to reach the earth, increasing the risk of skin cancer and cataracts and reducing human and animal immune response, fisheries production, and yields in some crops. Concrete evidence of the reduction in the ozone was brought to international attention in 1985 with the discovery of a “hole” in the ozone layer for part of the year over the Antarctic (81). This prompted the “Montreal Protocol on Substances that Deplete the Ozone Layer,” which was established in 1987 and today has been ratified by most countries. The goal of the Montreal Protocol is to eliminate substances that cause significant damage to the stratospheric ozone layer. The initial focus was to reduce emissions of CFCs and halons, because these products release chlorine and bromine in the stratosphere, destroying the ozone layer. In 1992, at a follow-up meeting, it was agreed that methyl bromide was a significant ozone depleter and that its use should be reduced. An excellent overview of all aspects of methyl bromide use and possible replacement, up to about 1995, is given by Bell et al. (14).

Bromine is an extremely efficient depleter of ozone, causing O₃ to lose an oxygen atom and become O₂ in repetitive actions (22). Each bromine atom from methyl bromide destroys about 60 times more ozone molecules than each chlorine atom from CFCs (14). Methyl bromide is naturally produced from biomass burning (forests, crop wastes) and from the oceans, possibly as a biological byproduct of bacteria or phytoplankton. Whereas natural sources of methyl bromide have their production buffered by natural chemical reactions, human-produced methyl bromide has tipped the scales and with the CFCs started a rapid decline in atmospheric ozone (22, 81, 90).

In 1995 developed countries froze their consumption of methyl bromide at 1991 levels and have agreed to a schedule of reductions: 50% by 2001, 70% by 2003, and 100% by 2005 (41, 78). It is proposed that developing countries will freeze their methyl bromide consumption at 1995–1998 levels in 2002, reduce their consumption by 20% in 2005, and completely phase out its use in 2015. For all countries, some quarantine and preshipment uses are exempt from these reductions, and there is a provision for critical and emergency uses (78).

PHYSICAL ALTERNATIVES

Unlike most insect pests, stored-product pests live in an environment largely determined by humans. The manipulation of the stored-product habitat can slow the increase in pest populations or be used to eliminate infestations. Ideal conditions for most stored-product insects are 25–32°C and 65–75% relative humidity (42, 59). Above and below these conditions insect growth and fitness are reduced, and in more extreme conditions insects eventually die (Table 1). There are several advantages to using physical control methods. No regulatory approval is needed, as is the case with chemical insecticides. A new insecticide can cost millions of dollars and require several years of testing before it is registered for use. Physical methods leave no residues on the product or in the treated area. They have lower risk to applicators than chemical insecticides. For example, work can continue in areas adjacent to the treated area during the treatment, which is not the case with fumigation. Although there is variation between species in sensitivity to the different physical control methods, there is no reported resistance to heat or cold.

Heat

The first record of using heat to control a stored-grain insect was the heating of grain to 69°C to control *Sitotroga cerealella* in France in 1762. There are records of heated rooms used to raise the temperature of wheat to 57°C to control *Sitophilus* spp. in Ohio in 1835 (94). Heating mills in the U.S. Midwest was a common practice from 1910 to 1930. The popularity of heat treatments declined as more flour mills used chemical fumigants such as hydrogen cyanide, chloropicrin, and

TABLE 1 Response of stored-product insect pests to temperature (adapted from 42)

Zone	Temperature range (°C)	Effects
Lethal	Above 62	Death in <1 min
	50–62	death in <1 h
	45–50	death in <1 day
	35–42	Populations die out, mobile insects seek cooler environment
Suboptimum	35	Maximum temperature for reproduction
	32–35	Slow population increase
Optimum	25–32	Maximum rate of population increase
Suboptimum	13–25	Slow population increase
Lethal	5–13	Slowly lethal
	3–5	Movement ceases
	–10 to –5	Death in weeks, or months if acclimated
	–25 to –15	Death in <1 h

eventually methyl bromide and phosphine. However, the use of heat treatments continues today. A few flour mills or breakfast food processors have used heat in part of their facilities for over 50 years (L. Clarke, personal communication). Given the concerns over insecticide residues in finished products, the use of heat treatments has become more common.

Extensive research has determined the temperature and duration of exposure required to control different stored-product insects (21, 42, 53a, 76, 113). In general, most stored-product insects are controlled under the following time-temperature combinations: 24 h at 40°C, 12 h at 45°C, 5 min at 50°C, 1 min at 55°C, 30 s at 60°C (42). There is variation among species, with *Lasioderma serricornis* and *Rhyzopertha dominica* being the most tolerant, *Sitophilus* spp. and *Tribolium castaneum* being moderately tolerant, and *Oryzaephilus* spp. and *Tribolium confusum* being least tolerant to high temperatures. Acclimation to heat can occur to a limited degree. Brief exposures to warm temperatures (35–40°C) can increase the survival of insects to subsequent high temperatures (28, 47). However, above 55°C there is little difference between acclimated and unacclimated insects (40).

Several hypotheses explain why insects die when exposed to high temperature. Phospholipid membranes become more fluid, the structure of proteins and hence enzymes are adversely affected by high temperature, pH is temperature dependent, and water stress may be a crucial factor between 35 and 43°C. However, as Denlinger & Yocum (28) pointed out, death at a high temperature is probably due to the failure of cells in a critical tissue, rather than general damage to all cells. Whole organisms are more heat sensitive than are tissues, tissues are more heat sensitive than cells, and cells more sensitive than macromolecules.

A number of factors need to be considered when preparing a facility for a heat treatment (21, 42, 56, 62). The current recommendation for heat treatment is 50–57°C air temperature for 24–36 h with a warm-up and cool-down of about 5°C/h (21, 62, 84). Although insects die in only a few minutes at 50°C (42), the air temperature in the building must be maintained for at least 24 h to insure that all refuges in the building reach 50°C. The rate of heating is set to prevent structural damage to the building. Some managers heat-treat the building only if outside temperatures are above 10°C because they are concerned that thermal gradients will cause damage to the building. Other managers in Canada regularly heat-treat during the winter when outside temperatures drop below 10°C (L. Clarke, personal communication).

Several modifications to the building are required before heat treatments (21, 56, 62, 84). Sprinkler heads should be rated for at least 85°C. Some equipment may have to be modified to withstand the heat; electronic equipment may have to be replaced with heat-tolerant components, removed from the heat, or enclosed and provided with cool air. Certain plastics warp at high temperature. The heat sources may vary depending on age of the structure and geographical location. Facilities that use heat during processing usually have central boilers that can be used to power supplemental heaters. Some facilities have traditional radiators, whereas some have combination steam/forced-air heating mounted from the ceiling. Temporary heaters, electric, steam, or propane, can be used. Many of these facilities must guard against dust explosions, so in most cases heaters must be explosion resistant. An even distribution of heat is difficult to achieve when facility floors are crowded with processing equipment and storage bins (Figure 1). Good air circulation helps minimize this problem, insuring that some areas will not be overheated, causing damage to equipment, while other areas are not heated enough, allowing insects to survive (92).

Before a heat treatment, the building should be thoroughly cleaned and waste residues removed (56, 62, 84). Cleaning before heat treatment is essential because

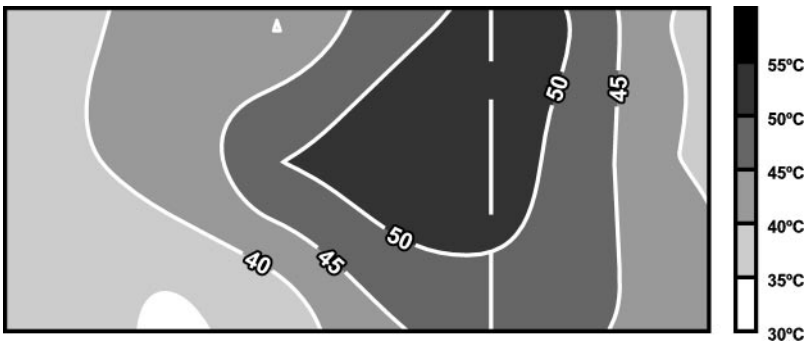


Figure 1 Temperature gradients that develop during a heat treatment of a flour mill. The target temperature is 50–57°C for 24–36 h (33).

flour and food residues are good heat insulators. Equipment should be opened and sensitive products removed, as well as aerosol cans, carbon dioxide fire extinguishers, sugar, and adhesives; roof and wall vents should be sealed and doors closed. Contact insecticides in unheated buildings should be applied adjacent to the heated building, to insure that insects escaping the heat treatment are not driven to another part of the building. The building should be inspected hourly during the treatment, to monitor temperatures, adjust heaters, and check for any problems. Also, the heat drives insects out of their refuges, and this information can be used to focus future sanitation efforts. After the heat treatment, certain lubricants may have to be replenished if there was leakage, or replaced if they are heat sensitive (56). The cost of a heat treatment in Canada and the United States is about half the cost of a treatment with methyl bromide, excluding the initial capital investment for the heaters. Facilities that use heat treatment usually do so four times a year compared to one or two fumigations with methyl bromide.

Instead of heating the entire building, some people have experimented with spot heat treatments that heat sections of the buildings or specific pieces of equipment (56, 92). The equipment is tarped, heat is ducted into the enclosure, and temperatures are maintained at 60°C for at least 1 h. Surfaces should not exceed 70°C, because this is the maximum temperature approved for PVC electrical wire insulation. The advantage of the spot treatment is that it is rapid, treats high-risk areas, and minimizes the amount of heat needed for a treatment. The main disadvantages are that it does not control all insects at once in the mill, allowing the treated equipment to become reinfested after treatment, and requires the installation of tarpaulins over the equipment to be treated.

The product itself can also be heated to kill any infestation within. There are several ways this can be achieved. In Australia fluidized beds use hot air (60–120°C) to mix and heat the grain to between 56 and 72°C in less than 1 min (42). The grain is then cooled by ambient air or by spraying the grain with water, which quickly evaporates. Long-wave radiation or microwaves can be used to heat packaged goods on the conveyer belt (42, 45).

Cold

Stored-product insects are generally unable to reproduce below 18°C, with the exception of *Sitophilus granarius*, which can reproduce at temperatures down to 15°C. Below 5°C stored-product insects are unable to move. Temperatures between 15°C and –15°C will eventually kill insects; the lower the temperature, the faster the insects will succumb to cold injury. Stored-product insects are unable to survive freezing and they freeze between –10°C and –18°C (Table 1; 42). Susceptibility to cold depends upon species, developmental stage, and acclimation. Of all the stored-product insects, *Cryptolestes ferrugineus*, *Ephestia cautella*, *Ephestia kuehniella*, *Plodia interpunctella*, and *S. granarius* are the most tolerant to low temperatures. *Cryptolestes pusillus*, *Oryzaephilus surinamensis*, *R. dominica*, *Sitophilus oryzae*, *Sitophilus zeamais*, and *Stegobium paniceum* have moderate resistance to

cold, and *Oryzaephilus mercator* and *Tribolium* spp. are the most susceptible to cold (42). Cold acclimation occurs at temperatures between 20 and 0°C and can increase the cold hardiness of insects by two- to tenfold. Although most of the common stored-product insect pests such as *Cryptolestes* spp., *R. dominica*, *Sitophilus* spp., *Tribolium* spp., and *Oryzaephilus* spp. do not diapause, over 40 species of stored-product insects have a diapausing stage. In moth species such as *P. interpunctella* and *Ephestia* spp., the diapausing stage has increased tolerance to low temperature (12).

As with heat, cooling structures used to be a common practice in cold-temperature climates, but this method of control was gradually replaced by spot treatments with a contact insecticide and a general fumigation with methyl bromide. Cold treatments took place in the winter, ideally when outside temperatures were below -17°C for 3 days; all accumulations of product were removed, the facility thoroughly cleaned, the water lines either drained or filled with antifreeze, sensitive equipment removed or insulated, the equipment opened, drive belts loosened, the windows opened, and fans used to circulate air to insure even cooling (21, 42, 144). Alternatively, instead of cooling the entire structure, only the finished product might be disinfested using low temperatures. A similar strategy can be used for commodities prone to infestation such as dried fruits and nuts. Commercial grain chillers are used in Australia, Europe, and the United States to cool seed, usually to 15°C, to prevent losses due to insect infestation and grain respiration (21, 42).

Aridity

Stored-product insects are generally more tolerant of low relative humidities than are other insects (52). The ideal relative humidity for most stored-product insects is 70% (59), with lower relative humidity reducing longevity and fecundity. However, *Tribolium* spp. and *L. serricornis*, insects that are the target species for many methyl bromide fumigations, are particularly tolerant to low humidity. The larva of *L. serricornis* is capable of actively absorbing water from the air at relative humidities as low as 43% (52). Relative humidities cannot be lowered enough to eliminate insect problems in flour mills and warehouses. However, the application of diatomaceous earth can render the insects more susceptible to desiccation (see the section below on contact insecticides).

PARASITOIDS

Despite the fact that the stored-product environment is a relatively simple habitat, over 50 parasitoids and predators attack over 75 stored-product insect pests (see 106 for a review). The advantages of using parasitoids or predators are that they leave no chemical residues, registration is simpler than for chemical insecticide, and they are effective even if there are food residues in the facility because the parasitoids and predators will seek out their hosts. Some of the disadvantages are

concerns over contamination of the finished product, availability of parasitoids and predators, and complexity of use. In the European Union parasitoids and predators can be released as long as they are indigenous. In the United States parasitoids and predators that attack stored-product insects are exempt from registration under the Environmental Protection Agency and the Food and Drug Administration and can be released in raw grain and warehouses in such a way that they do not become mixed with the final packaged food. Although there are some parasitoids and predators for *Tribolium* spp., they have not been tested in flour mills and are not commercially available at this time.

In cases where *P. interpunctella* or *Ephestia* spp. are the principal insect pests, the egg parasitoid *Trichogramma* spp. and the larval parasitoid *Habrobracon hebetor* have been used successfully instead of methyl bromide fumigations. In Germany and Austria in 1999 over 150 million *Trichogramma evanescens* were sold to control stored-grain moths in bakeries, warehouses, and flour mills (M. Schöller, personal communication). These insects are placed in the facilities 14–24 times a year at a rate that varies according to the physical layout of the facility. Sterilized *E. kuehniella* eggs are used for rearing the *Trichogramma* to insure that unparasitized eggs do not hatch and add to the infestation. To successfully control populations with parasitoids, releases must be made when pest populations are low. Monitoring with pheromone traps helps synchronize the release of the parasitoid with egg laying. The larval parasitoid *H. hebetor* is used against diapausing larvae, a stage that is not controlled by the egg parasitoid.

FUMIGANT ALTERNATIVES

Numerous chemicals are being considered as alternative fumigants to methyl bromide, but none are as fast acting as methyl bromide. Some taint the fumigated product, may be phytotoxic, leave unacceptable residues, have limited penetrating power, or may be unlikely to be registered for health or economic reasons (78, 119, 143). Fumigation under vacuum conditions can greatly speed the rate of insect control (24, 127, 149).

Candidate fumigants include phosphine, sulfuryl fluoride, carbonyl sulfide, carbon dioxide, carbon disulfide, ethyl formate, ethylene oxide, hydrogen cyanide, methyl iodide, methyl isothiocyanate, ozone, sulphur dioxide, ethyl or methyl formate, and acetaldehyde (5, 78, 119). Many of these chemicals were used as fumigants prior to the introduction of methyl bromide in the late 1930s (16, 108).

Most Likely Replacements

Phosphine is the most widely used fumigant throughout the world for insect control for most durable commodities and is increasingly used as a treatment to replace methyl bromide. It is close to an ideal fumigant except for four drawbacks: slow activity (3–15 days), the rapid increase in insect resistance to this compound

worldwide (17, 25, 83, 99, 148), flammability above concentrations of 1.8% by volume, and corrosion of copper, silver, and gold (16a, 19, 20). This fumigant is formulated as solid pellets, tablets, or sachets of aluminum phosphide or magnesium phosphide, which reacts with water vapor in the air (wheat moisture content must exceed 10% wet weight) to form phosphine gas and aluminum hydroxide or magnesium hydroxide. Other minor ingredients in the solid formulations are ammonium carbonate, ammonium bicarbonate, urea, and paraffin to regulate gas release and decrease flammability (54).

To decrease the duration needed for treatment and to increase the control over the dosage applied, several methods have been developed to release phosphine gas directly rather than have it generated with metal phosphides. One formulation is phosphine compressed as a gas in cylinders, quenched with 98% carbon dioxide to prevent combustion. This type of phosphine has been used in Australia in SiroFlor fumigations that release low doses of phosphine over long durations (142). It also rapidly controls insects in empty structures, such as a ship hold (43). On-site blending of pure phosphine with carbon dioxide, which would reduce the cost of this technique, is being tested in Australia and China. Another method to apply gaseous phosphine directly is to generate phosphine by mixing magnesium phosphide and water. This technique has been developed independently at two sites (43, 58).

Also, the combination of heat (104), carbon dioxide, and phosphine has been found to provide effective space fumigations (88). Since 1991 more than 40 fumigations have been successfully carried out using the phosphine, heat, and carbon dioxide combination method. The major problem that prevents the use of phosphine alone as a structural fumigant is that it causes corrosion at high relative humidity (16a, 19, 20) and it takes longer than methyl bromide fumigation. The combination with heat (30–36°C) and carbon dioxide (3–7%) allows complete insect control in 24–36 h with concentrations of phosphine of only 80–100 ppm. Problems of corrosion are limited at these concentrations. Without the heat and carbon dioxide, it is necessary to have a concentration of phosphine of 900 ppm to obtain the same efficiency (this concentration is strongly corrosive). To obtain good results, this method necessitates a close supervision of temperature and phosphine and carbon dioxide levels. It costs 20–50% more than a fumigation with methyl bromide.

Phosphine is widely used as an in-transit fumigant for grain exported from the United States by ship (27). Phosphine is the favored fumigant to replace methyl bromide for many uses (78, 119), but practical difficulties such as slow speed of action and copper corrosion (16a, 19, 20) must still be addressed.

Modified atmospheres with elevated carbon dioxide (>60% by volume) or lowered oxygen (<1% by volume) are effective methods to control insect populations, especially in durable commodities (136), but they act relatively slowly and require fairly air-tight storage structures (4). Periodic flow carbon dioxide fumigation is now used commercially at three grain terminal elevators to disinfest cereals of insects replacing phosphine at the port of Vancouver, Canada (B. Timlick, personal communication). In Germany and France carbon dioxide applied under pressure

provides rapid control of insects, but its use is limited to high-value crops because large quantities of gas are needed and because of the capital cost of chambers (1).

Sulfuryl fluoride is widely used for termite control in structures and lumber (16, 50), and it provides rapid control of stored-product insects (149). Eggs require much higher concentrations than larvae to be controlled. This chemical shows considerable promise and is undergoing registration procedures as replacement for methyl bromide in the United States, Great Britain, Italy, and France (78, 119, 132), but it cannot be used near food because no food residue tolerances are currently set (77, 78, 119).

Carbonyl sulfide has been studied in Australia as an insecticidal fumigant for wheat, wood, and artifacts (10, 31, 30, 125). Odors can be a problem, and there are other limitations to its widespread use. It is toxic to stored-product insects in 24 h at 25°C (149), and recent tests in Australia have demonstrated negligible residues in cereals (145). It is currently not registered in any country, but this work is being pursued in Australia. This chemical may have the potential to be widely used as a replacement to methyl bromide.

Unlikely Replacements

The market for fumigants is relatively small, and because they are toxic to humans, few companies are willing to proceed with a costly registration even though these chemicals are effective at controlling insects. Some of the older chemicals no longer have patent protection, making it unprofitable for companies to seek registration.

Sulphur dioxide has been used to control mealybugs and Lepidoptera (16, 124) and as fungal control on stored lychees and grapes (26).

Carbon disulfide is a flammable liquid fumigant and has been used on stored grain although it is highly toxic to growing plants or nursery stock. Some perishable fruits such as strawberries, peaches, and plums tolerate this fumigant (16). It has been de-registered in many countries because of possible toxic residues. It has not been used in North America since 1985 when most of the liquid fumigants were banned because ethylene dibromide was determined to be carcinogenic (117). However, it is used in Australia on flour (30) and on rice in China. Improved methods of aeration remove residues (102).

Ethyl formate is explosive, flammable, and is corrosive to metal (16). In the past it was used to control insects in dried fruit (118) and grain (9). Ethylene oxide is flammable and is usually formulated with carbon dioxide as a fire retardant (16). It gives microbial control and is used to sterilize surgical instruments and some spices. It can be used to control insects in artifacts but can produce carcinogenic compounds when used on food (133).

Hydrogen cyanide was a widely used insecticidal and rodenticidal fumigant for many years, especially in stored grain on farms (16). The high dermal toxicity of the gas makes it hazardous to applicators, and residues are often a concern. It was previously widely used on durables such as grain (5) and on fresh fruit (16). It is occasionally used for artifacts but can chemically react with pigments, is soluble

in water, and is slowly desorbed (122). Methyl iodide has potential for treating perishable commodities because it is not phytotoxic at application rates (129). It controls diapausing larvae of codling moth *Cydia pomonella* in 3 h at 25°C (149). Methyl isothiocyanate has been experimentally used on grain (35) and effectively kills insects, including *S. granarius*. It has also been tested as a wood fumigant to control insects with significant results (46).

Ozone kills stored-grain insects such as *S. oryzae*, *O. surinamensis*, *Tribolium* spp., and *Ephesia elutella* (36, 37, 147) and various fruit flies. Constant levels of about 50 ppm ozone for 3 days must be maintained throughout bulk grain, so it must be continually supplied (65). It also can reduce fungal infection on the seed surface by 50–63% (57, 65).

CONTACT INSECTICIDES

Several classes of contact insecticides have a role to play in the replacement of methyl bromide. The organophosphorus compounds have been widely used as grain protectants when applied to grain prior to infestation (110). Widespread, continuous use of some of these chemicals, such as malathion, pirimiphos-methyl, chlorpyrifos-methyl, fenitrothion, and dichlorvos, has led to extensive insect resistance throughout the world (114). This class of insecticide is favored for use on stored grains because of relatively low mammalian toxicity and suitable rates of degradation that are directly related to temperature and product moisture content (137).

As a result of the United States Environmental Protection Agency Food Quality Protection Act of 1996 (H-R. 1627 Public Law 104–170), many organophosphorus and carbamate insecticides are no longer considered safe to be on the market, based on toxicological reevaluation that is to be completed by 2002 (38). All of the four chemicals listed above are currently under review.

Synthetic pyrethroids, although more expensive than organophosphorus insecticides, often have a fairly low mammalian toxicity and in some cases can be more toxic to insects at cool temperatures than at warmer temperatures (55, 131), offering greater flexibility than other insecticides. The pyrethroids are much more toxic than organophosphorus chemicals to members of the Bostrichidae such as *R. dominica*, the lesser grain borer, and *Prostephanus truncatus*, the larger grain borer (15, 110), and their residues in grain degrade slowly (110). Botanicals such as pyrethrum (synergized with piperonyl butoxide) and azadirachtin from the neem tree can be effective on stored grains, but because they cannot be patented, there is little commercial interest in them (110).

Insect growth regulators, such as methoprene and hydroprene, that are juvenile hormone analogues disrupting the molting process of insects are registered as crack and crevice sprays and are used mainly in tobacco warehouses to control the cigarette beetle, *L. serricornis* (137). Methoprene is also effective against *O. surinamensis*, *R. dominica*, *Trogoderma granarium*, *P. interpunctella*, and

E. cautella, but *S. oryzae* requires higher concentrations (110). Fenoxycarb and diflubenzurons have also been tested on grain or structural surfaces and are effective in controlling insects by offering direct toxic action as well as acting as growth regulators (105, 134). Bifluorides are used in Europe to preserve wood by means of a 10 min submersion. They are not used in North America (5).

Diatomaceous earth is composed of the minute, fossilized silicon dioxide remains of diatoms. Deposits are found around the world, each having its own physical characteristics and toxicity to stored-product insects (44, 68, 116). It can be used in combination with other treatments to control pests in structures (33) by speeding desiccation of the insects. It can also be applied directly to grain to control insects (11) at levels as low as 100 ppm for *C. ferrugineus*. Higher dosages up to 900 ppm do not affect the baking and milling quality of cereals (69), but test weight is significantly reduced at concentrations above 100 ppm.

METHYL BROMIDE RECAPTURE AND REUSE

One method to limit contamination of the atmosphere with methyl bromide is to use it in air-tight containers, recapture it following fumigation, and then re-use it when needed or destroy it (13, 43). There are several methods of recapturing or destroying methyl bromide after use. These include the use of activated carbon or zeolite (hydrated silicate of calcium and aluminum), condensation (methyl bromide's boiling point is 3.6°C), absorption onto liquids, mixing with ozone, or direct combustion and catalytic destruction (13). These methods are being developed mainly for quarantine fumigations, as this use of methyl bromide is not currently slated to be phased out.

Activated carbon can absorb chemicals up to 30% by weight. It is used in a few fumigation chambers, but huge amounts would be required for large ship hold or mill fumigation. Typically, a 70-kg filter is used for a chamber of about 30 m³. Methyl bromide recovery is about 40–50%, and the activated carbon, once fully charged, is buried or later heated to release and re-use the methyl bromide (77, 78). More recent studies have removed 95% of the methyl bromide vented from fumigation chambers (72), and a commercial unit is being used for quarantine operations at the Dallas/Fort Worth airport.

Adsorption to zeolite is used commercially to trap chlorinated fluorocarbons and also works well for methyl bromide (89). A recapture unit using zeolite was built for use with a 2100 m³ fumigation chamber in the Port of San Diego (126). The recapture rate was 95%, and the methyl bromide could be released by heating for future use (77, 78). Zeolite pore sizes can be determined during manufacture, limiting the compounds adsorbed, although high moisture can deactivate the zeolite, but the system was abandoned due to technical problems. A refined process has been developed and has been tested on empty ship holds and fumigation chambers (43). This recapture unit is now being coupled with a device that can destroy methyl bromide on site.

Condensation of methyl bromide has not been considered feasible because of the low concentrations in air used during fumigation [16 to 24 g/m³ for flour mills (16)] and its low boiling point. However, refrigeration using liquid nitrogen to condense methyl bromide has been used in a facility in Los Angeles (77, 78) and can recover 98% of the fumigant if used in conjunction with activated carbon.

Absorption of methyl bromide onto liquids using alkali and organic amines has been tested on fumigated freight containers (103). Another experimental method used sodium carbonate and ethylene diamine, which produced nonvolatile products that could be disposed of safely (87). The production of large volumes of contaminated liquid on a commercial scale makes this method unattractive. Direct combustion and catalytic destruction of methyl bromide is possible, but it is expensive; the apparatus is not easily transportable and the byproducts themselves (Br₂ and HBr) are hazardous (6, 13).

Ozone can be used to break down methyl bromide (54, 77). A theoretical efficiency of 90% methyl bromide removal from an air stream exiting a fumigation chamber is possible. Activated charcoal filters would remove the remaining 10% methyl bromide.

ALTERNATIVES FOR PERISHABLE PRODUCTS

Perishable items include fruit, vegetables, ornamental plants, flower bulbs, cut flowers, and fresh root crops. Typically, such products must be marketed quickly before a loss in quality occurs, so rapid fumigation is a necessity, except where in-transit treatments can be carried out. Quarantine and preshipment fumigations are often required for the receipt or export of these commodities (94a). World production of dried fruit for 1997–1998 (Supplemental Table 3, see the Supplemental Material link at www.annualreviews.org) indicates the amount of products available for treatment. Major insect pests of dried fruit and nuts are given in Supplemental Table 2. Methyl bromide may be retained for some time as the only acceptable quarantine treatment as it takes several years to approve new treatments on a bilateral basis (119). There are several approved alternatives to methyl bromide for many quarantine pests: new fumigants, insecticidal dips, physical processes (cold, heat, irradiation, oil or wax coatings, high pressure water) or a combination of treatments (78, 119). In the past, fumigation of perishables used 8.6% of annual methyl bromide production (77).

Possible chemical alternatives to methyl bromide for use on perishables include acetaldehyde (2), ethyl formate, hydrogen cyanide (16), methyl formate, and sulphur dioxide as a fungicide (26). Other chemicals can include methyl sulfonal fluoride and propylene oxide (51).

Structural/space treatments of homes, flour mills, ships, and containers can use combination treatments of carbon dioxide, heat, diatomaceous earth, and phosphine, sulfuryl fluoride for termites [no food tolerances are set (77)], iodomethane, and carbonyl sulfide.

QUARANTINE

Methyl bromide is widely used to control pest insects, mites, rodents, and fungi (16), and it is effective against most species of pests at doses of 24–48 g/m³ for 2 h at 5–30°C (24). As this speed of action cannot be matched by other fumigants, it is widely used for rapid quarantine disinfestation (Supplemental Table 4, see the Supplemental Material link at www.annualreviews.org).

Many alternatives to methyl bromide for quarantine purposes are physical methods. For example, heat can be used to disinfest mills, lumber, or artifacts (66). Radiation in the form of electron beams, X-rays, or gamma rays can be effective in killing insects. Phosphine mixed with carbon dioxide or nitrogen in compressed gas cylinders gives rapid fumigant release and a faster fumigation (43). Quarantine and preshipment fumigations can be done in-transit with phosphine, especially on grain in specially designed ships that are gas-tight and have recirculating systems (107, 130).

Fumigation

A recent study on phosphine demonstrated that 1–3 g/m³ for 24 h at 15°C killed the spider mite, *Tetranychus urticae*, but not the moth, *Carposina niponensis* (111). Carbonyl sulfide or methyl iodide are not phytotoxic to fresh lemons (93), so they may be useful tools in the future.

Chemical Dips

Low levels of the insect growth regulator tebufenozide (5 ppm) are lethal to *Epiphyas pistivittana* larvae at 40°C with an atmosphere of 2% O₂ and 5% carbon dioxide (139), so it may be effective in treating apple exports. Dipping apples in dilute ethanol can be effective in controlling *T. urticae*, both diapausing and nondiapausing forms (29).

Controlled Atmospheres

Atmospheres with elevated levels of carbon dioxide are generally slow fumigants (136). Larvae of *T. granarium*, one of the most vigilantly watched quarantine insects in the world, require 17 days for control at 30°C, with 60% carbon dioxide (112). In many species, one immature life stage shows a higher tolerance to carbon dioxide than adults (3).

Quarantine treatments that control the spider mite, *Tetranychus pacificus*, the moth, *Platynota sultana*, and the thrips, *Frankliniella occidentalis*, on grapes take 12 days at 0°C, with 45% carbon dioxide and 1.5% O₂ (85).

Extreme Temperatures

There are over 200 cases where low temperature is an approved treatment for quarantine pests (78). For example, a protocol to control fruit flies as specified by

the USDA (Animal Health and Plant Health Inspection Service–Plant Protection and Quarantine treatment protocol for fruit flies) is to hold the fruit at 1.1°C for 18 days (123). Mealybug on apples imported to the United States can be controlled by storage at 0°C for 42 days (60).

Heat is widely used in storage facilities in Hawaii to control quarantine insects (8). Some authors such as Mangan & Shellie (75) have proposed a standardized testing procedure and analysis for heat treatment of various pests and crops. Immersion of products in hot water has been used for guavas (46.1°C, 35 min), limes (49°C, 20 min), and apricots (46–50°C, 11 min) (49, 64).

High-Pressure Water

A process for high-pressure water treatment of apples and kiwi fruit has been patented. High pressure water removes the mealybug, *Pseudococcus viburni*, and moth, *E. pistivittana*, effectively (138). This process cannot be used on soft or fragile commodities because of physical damage to the commodity.

Irradiation

Gamma rays, X-rays, accelerated electrons, or microwaves have all been used experimentally to control quarantine insects. The FAO/ International Atomic Energy Agency promotes the use of radiation, recommending minimum doses of <4000 Gy for nematodes, <300 Gy for most insects, 100 Gy for Diptera, and 150–320 Gy for mites. At these levels most fruits and vegetables are not damaged (119). Gamma irradiation can be used to control the leafroller, *Ctenopseustis obliquana*, on dried fruit: 70.1 Gy applied to immatures results in sterile adults; 150 Gy applied to immatures prevents adult emergence; 215 Gy prevents larvae from pupating (73). Muskmelons are intolerant to methyl bromide or heat treatments, but gamma ray doses up to 1000 Gy had no effect on the melons, offering a method of quarantine treatment to kill insects (70).

Cherries, apricots, and peaches can be treated with 300 Gy with little quality loss, but 600 Gy causes a loss of firmness, internal breakdown, and color changes, thus limiting doses that can be used for quarantine purposes (34).

Blueberries treated with 92 Gy of gamma rays were not damaged, and this dose was also a suitable quarantine treatment for plum curculio, *Conotrachelus nenuphar* (53). Accelerated electrons at 400 Gy sterilized seven species of pest insects on cut flowers, but some flowers, such as chrysanthemums, were damaged, and the insects were still able to transmit viruses (32). Accelerated electrons at 750 Gy do not damage blueberries, and they sterilize the apple maggot *Rhagoletis pomonella*, blueberry maggot *Rhagoletis mendax*, and *C. nenuphar* (82). Microwaves can be used to disinfest sweet cherries of *C. pomonella* at 915 MHz, but great care must be taken not to overheat the fruit (61). A portable pallet irradiator has been developed to treat up to 4160 kg of produce per hour, and is currently being tested in the United States (119).

Wax Coatings

Wax coatings on fruits and vegetables can be an effective method of killing all stages of mites by suffocation (48). The wax also helps to preserve the fruit and vegetable.

Combination Quarantine Treatments

Many combinations of treatments have been tested, with varying degrees of success, depending on the product and the pest (119). Some combinations include cold and low oxygen, heat and high carbon dioxide, sequential fumigants, heat and irradiation, heat followed by cold storage, low temperature and fumigation, or low temperature storage of grapes with slow release sulphur dioxide pads (0.2 to 1.0 ppm) to control *P. sultana* (146).

INTEGRATED PEST MANAGEMENT

Integrated pest management (IPM) has been defined as a decision-making process that evaluates pest populations and then uses a variety of tools to suppress populations effectively, economically, and in an environmentally sound manner (109). IPM was first used in orchards and vegetable farms in response to calendar-based pesticide application schedules (109). IPM can reduce pesticide applications substantially and has reduced the cost of pest control. However, the implementation of IPM is difficult in systems in which the economic thresholds are low, such as the case of a food processor producing a product for retail sales.

Sampling

Monitoring of the types of insects, their numbers, and location is an important part of any IPM program (15a, 52a). Stored-product insects can be difficult to sample because populations often have a clumped distribution, access to sampling sites can be difficult, and because of cryptic behavior of the insects. In food processing plants and warehouses there are several types of sampling. Visual inspection is the most common method. Besides looking for insects, insect tracks should also be noted. Some inspectors carry an open pheromone lure to increase the chance of detecting an infestation. There are several commercial insect traps available to sample insect populations, some are baited with pheromones (95, 98). Sampling the commodities upon receipt into the plant is a valuable tool to prevent establishment of new pest populations. Samples can be taken from the commodities, shaken to separate the insects from the commodity, or placed on a Berlese funnel to detect some internal seed feeders. Inspection of the finished product with ELISA-based myosin or chitin tests, or KOH digestion to determine insect fragment counts will be a final check on the flour (101).

One problem with sampling is the interpretation of the results. Traps and visual inspections only give a relative number, not the absolute population. Several

factors affect trap catch numbers: temperature, trap placement, and changes in the physical environment (food processed, construction, lighting), in addition to the numbers of insects in the sampled area. Wileyto et al. (140) developed a technique using self-marking stations and sticky traps to estimate the absolute population of *P. interpunctella*.

Normal trap densities give a rough approximation of where the infestation is located within a facility. A technique called precision trapping (7a, 18) has been developed to pinpoint the location of infestations. This method uses many more traps per unit area than traditional trapping protocols. The data are then plotted over the map of the facility and isobars of insect density are calculated using spatial statistics (Figure 2). This method pinpoints pieces of equipment and indicates entry or produce that are the source of infestation. Often, the infestation is localized and can be dealt with by sanitation or treatment of a small area, rather than the entire facility. A similar method uses triangulation instead of mapping software to pinpoint infestations (95, 96).

Pheromones Used as a Control Method

Three different methods have used pheromones to control stored-product insects: mating disruption, males cannot find females; mass trapping, males are removed by trapping; or attracticide, males are lured to a dispenser that contains a lethal dose of a contact insecticide (95, 98). All these methods use sexual pheromones of either the pyralid moths or *L. serricornis*. These methods have not been attempted with the aggregation pheromones of *Tribolium* spp., perhaps because aggregation pheromones are less attractive than sexual pheromones. Because one male can mate with several females, these methods must be effective at preventing mating or capturing males.

In Italy and Hawaii mass trapping has significantly reduced populations of *P. interpunctella* and *L. serricornis* (95, 96) using sticky traps or using high-capacity funnel traps to reduce *E. kuehniella* populations (121). Trap densities of one trap/300 m³ are effective. As with many of the field experiments, it is not possible to have an untreated mill and true replication, but it is clear these methods caused significant declines in the pest populations (95). In all these studies there was improved sanitation to reduce populations. Mating disruption has only been tried experimentally, not in commercial settings (95).

In the trials in Italy (121) methyl bromide fumigations were cut in half. However, as mass trapping alone could not eliminate the need for fumigations, attracticide was investigated by Trematerra (121). Attracticide is achieved by placing 2 mg of pheromone on one side of a laminar dispenser and 10 mg of cypermethrin, a pyrethroid contact insecticide, on the other side. Moths in the untreated mill reached peaks of 400 males trapped over two weeks, whereas in the mill using attracticide there were never more than 20 males caught over two weeks.

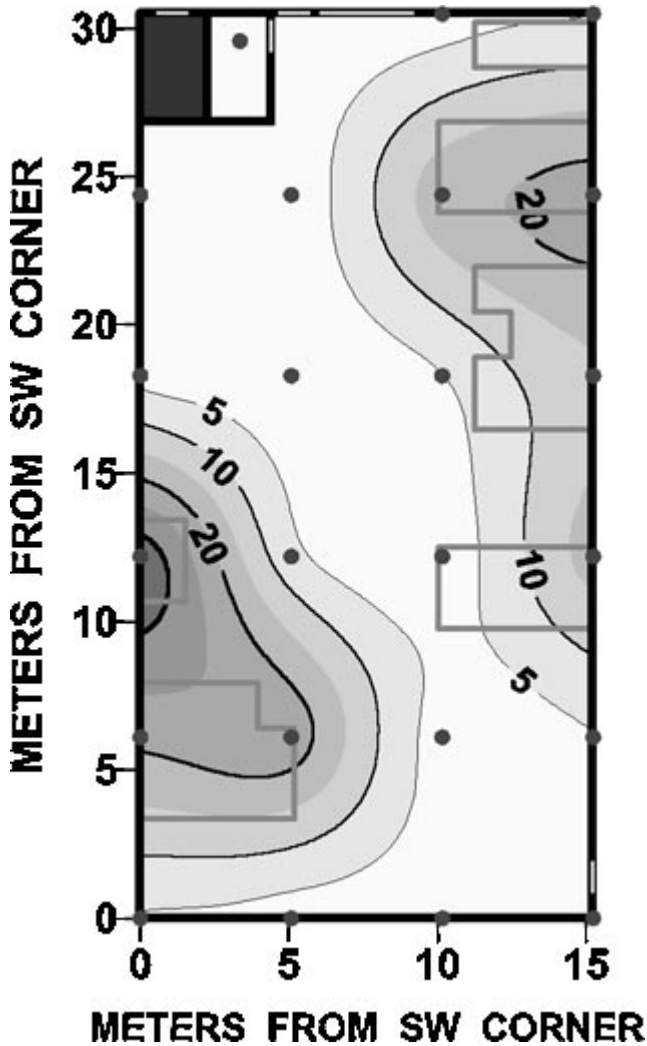


Figure 2 The spatial distribution of *Lasioderma serricorne* in a botanical warehouse during storage of saw palmetto. Trap locations are indicated by dots and locations of stacked bags by the rectangular outlines (7a).

Sanitation

Good plant design and a rigorous sanitation program can significantly reduce the ability of insects to establish and flourish in a food processing facility or warehouse. The most important design feature in a food processing facility from an insect control point of view is the number of harborage for insects or voids that

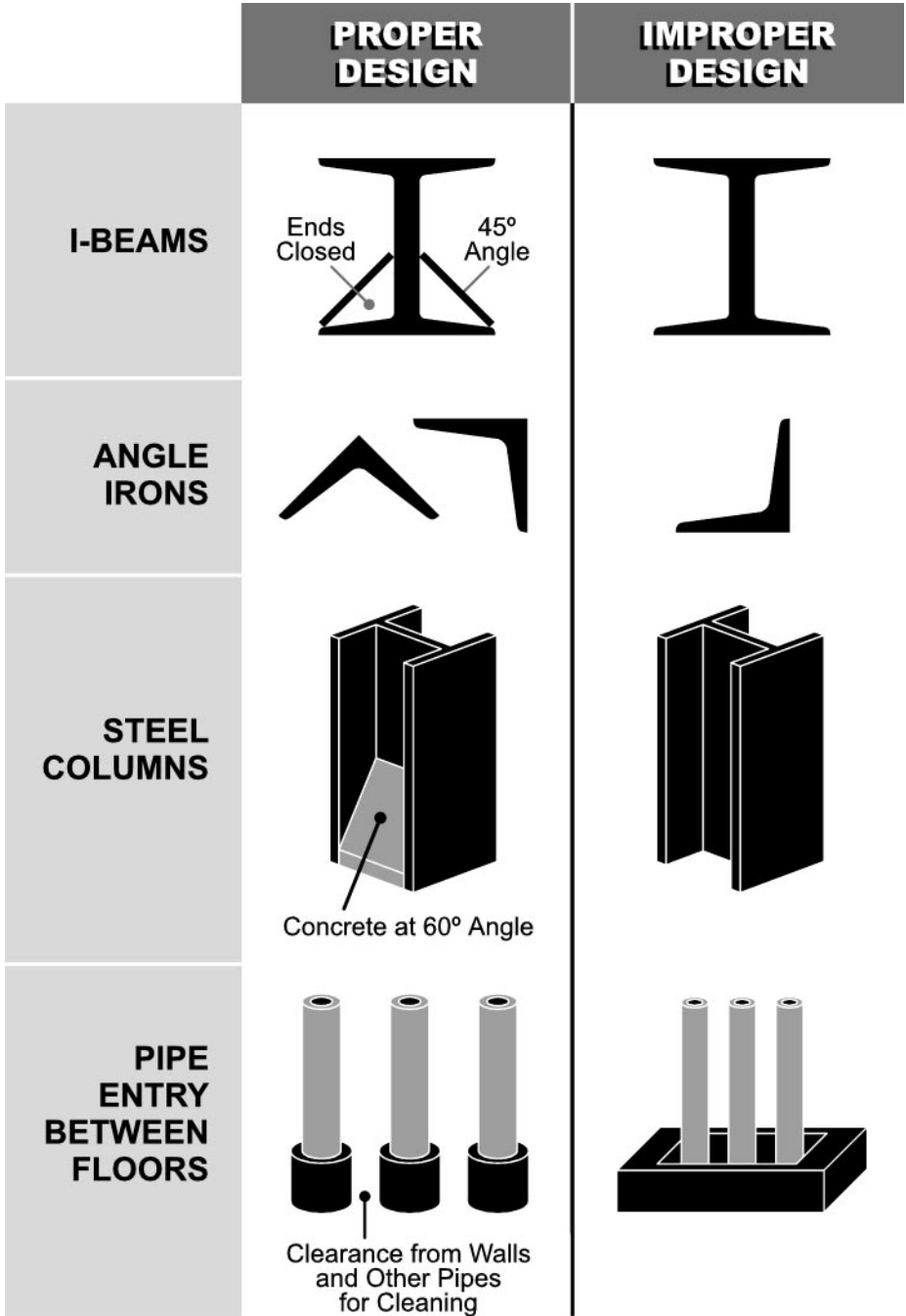


Figure 3 Methods to avoid dust collection in food processing facilities (modified from 62).

collect dust (62, 84). Structural and functional elements of the building—angle iron, I-beams, ceilings, pipes, and processing equipment—can be designed without voids or to enable thorough cleaning (Figure 3). Concrete floors are preferred over wooden floors because there are fewer cracks, making them easier to clean. Many of the older facilities have wooden floors that can be sealed and refinished to eliminate cracks. Windows should be screened to prevent insects entering the plant. Outside lights should be placed so that they do not attract night-flying insects to loading docks or open doors.

Using a powerful central vacuum system is the best cleaning method, as it does not spread dust and insects as does a compressed air blow-down (62). Vacuuming pulls dust from voids that sweeping cannot retrieve. Broken packages or stock that is not rotated can be major causes of insect infestations. A system of insect traps will aid in locating these localized infestations (7a, 52a).

During processing, insects can be eliminated from the product or killed. Most flour mills have impact machines, or pin mills, that subject grain or flour to severe impact. Seeds or flour are dropped onto a rotating disk with studs. Insects are killed or injured when they collide with the studs or the walls of the discharge hopper (97). These machines were originally used to further reduce particle size; hence, products such as semolina (durum wheat flour) that are at the final particle size may be damaged if run through an impact machine. The flow of flour, the usual product run through impact machines, may have to be reduced to insure adequate control of insects. Double rotor impact machines can operate effectively at two to four times the throughput of single rotor impact machines. Sifting flour over a screen with a 0.420 mm mesh will remove most larvae and adults, but a screen with a 0.149 mm mesh is needed to remove insect eggs (62).

CONCLUSIONS

Methyl bromide has been an important fumigant for commodities, structures, and quarantine use because of its rapid action and broad spectrum of activity. Certain industries and regulators have come to rely on methyl bromide and do not believe they can operate without it. However, as in the case of ethylene dibromide and other liquid fumigants that were banned in the mid 1980s, alternatives will be found. The Swedish and Danish governments banned methyl bromide in 1998. Danish mills, with capacities up to 150,000 tons/year, have relied on IPM and increased sanitation to deal with infestations (91). There has been a renaissance and improvement of old techniques, such as heat, cold, and sanitation, and development of new ones, such as mass trapping, attracticide, and combination fumigations. Some of these techniques have been refined by workers in the industry (56, 88, 96). There is no single replacement for all the uses of methyl bromide. Each insect problem will require its own solution, mainly revolving around integrated pest management. The most promising alternative fumigants are currently phosphine and sulfuryl fluoride. The most promising nonchemical alternatives are extreme temperatures

and sanitation. Although alternatives to methyl bromide are often more expensive and labor intensive, they are practical and do not deplete the ozone layer.

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