Alternative Chemicals for Methyl Bromide

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Abstract

The status of the debate on managing methyl bromide emissions and on their role in depletion of stratospheric ozone is outlined. Some of the agendas and targets are discussed in the context of handling postharvest grains in both developed and developing countries in Asia. Current needs for methyl bromide fumigation are identified and applications in disinfestation of grains positioned in the global pattern of usage. Areas are explored where alternative technologies are required, and the attributes defined that should be inherent in these replacement technologies, if they are to be viable in the demanding areas of quarantine and commodity sale contracts and the increasing sensitivity to any chemical additives, especially pesticides, in foodstuffs or the environment. The technologies that would complement, supplement or replace fumigation with methyl bromide and so enable chemical control to be properly placed in appropriate pest management strategies are then outlined. Finally, the principal chemicals that are candidates for chemical-based alternative technologies are discussed in terms of their characteristics, advantages, disadvantages and the constraints that are attendant on their use. The materials include both old and new fumigants and contact pesticides, and are considered within the context of designing optimum strategies using modern management tools such as integrated pest management supported by risk assessment and precision targeting of treatments together with other decision-support systems.

Status of the methyl bromide debate, agendas and targets

The current development and future orientation of alternative chemicals for methyl bromide must be considered in their broadest context if sustainable technology that does not involve methyl bromide is to be implemented for grain storage and preservation in the tropics. Any consideration therefore must deal with the whole spectrum of activities involved in the storage, handling and protection of commodities that could become infested. The necessity for alternatives for methyl bromide stems from the reporting in 1985 of a dramatic reduction in the radiation absorbing ozone in the atmosphere in Antarctica and the demonstration that chlorine radicals from the photolysis of chlorofluorocarbons were the dominant cause of the ozone loss. Subsequent implication of bromine as more efficient in atmospheric destruction of ozone focused attention on the bromine budget of the atmosphere and the contribution made by methyl bromide from both natural and anthropogenic sources. As had happened with the dichorofluoro carbons which had been used extensively as refrigerants and aerosol propellants, programs were implemented to control the use of methyl bromide and its release into the atmosphere. Methyl bromide was formally listed as an ozone-depleting substance in 1992 by the

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Fourth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer. At the Fifth Meeting, the fifteen countries present "declared the firm determination to reduce their consumption of methyl bromide by at least 25% at the latest by the year 2000 AD and to phase out totally the consumption of methyl bromide as soon as technically possible". The Methyl Bromide Technical Options Committee of the Montreal Protocol claimed that "technically feasible alternatives exist or are at an advanced state of development for more than 90% of methyl bromide use". At the Ninth Meeting of the Parties to the Montreal Protocol, it was agreed that in developed countries usage of methyl bromide in 1999 be reduced to 75% of usage in 1991 with corresponding reductions to 50% in 2001, to 3% in 2003 with complete phase-out in 2005, but with specific exemptions for quarantine and preshipment uses and certain other critical applications. In developing countries usage was to be reduced in 2005 to 80% of the average use in 1995-1998 with complete phase-out in 2015 but again with specific exemptions as for developed countries. These specific exemptions would of course involve most uses with perishable commodities but would have less relevance to durable products. The campaign is being orchestrated by developed countries and there is continuing revision of targets. There have been dissenters in the debate, but for whatever reasons there does appear a consensus on the need to better manage use of methyl bromide. Within this constraint, it is mandatory that sustainable production of food and commerce be given a very high priority and among the rhetoric it is important to remember that some forty years ago, DDT was declared environmentally unacceptable and to be phased out but it still remains among the most extensively used pesticides in the world. Large numbers of lives have been saved from its continued use in control of vectors of disease.

There is now a vast literature on alternative technologies for methyl bromide fumigation. In today's impoverished research communities, and more so in the public domain, it is said that the search for alternatives for methyl bromide has provided the largest inflow of resources to research since Rachel Carson's "Silent Spring". A significant part of the literature targets physical approaches to management of problems that were previously addressed by methyl bromide fumigation and these approaches hopefully will have the inbuilt permanency of control that is a feature of non-chemical measures. Most studies deal with specific applications of a technology and attention has been given to economic evaluation of the options available. Few studies evaluating alternative technologies, however, have incorporated the atmospheric environmental degradation aspect in quantification of the impact of methyl bromide usage. In this context, Lubulwa *et al.* (1995), have examined the factors involved, including human health effects, and used the concepts of consumer and producer surplus to estimate the net welfare changes associated with replacement of methyl bromide in the timber export industry. Such an approach provides a new and valuable dimension in identification of the direction in which technology should progress.

Patterns of usage

Global usage of methyl bromide based on sales was 71,500 tons in 1992 of which 80% was used for soil treatment, 13% for commodity and quarantine fumigation, 2.7% for structural treatment of residential, commercial and industrial buildings, and 3.6% in industrial synthesis of chemicals. The total consumption represented a 50% increase over 1985 consumption of 48, 300 tons with soil use contributing most of the increase, and usage for other purposes remaining approximately constant.

Usage in Asia approximates one-fifth of the world total as indicated in Table 1 giving data for 1990. This excludes China and India where production and use are thought to be small. There was proportionately less use in soil treatment and as chemical intermediates in Asia with a significantly larger amount (36%) used in quarantine commodity fumigation. It is suggested that 80% of the methyl bromide involved in quarantine and structural fumigation escapes to the atmosphere.

Table 1 Methyl bromide usage in Asia in 1990 (tons)

Type of usage

	Fumigation of soil	Quarantine fumigation	Structural fumigation	Chemical intermediate	Total	% of world total
Asia	8,400	5,265	906	34	14,605	21.9
% of Asian usage	57.5	36.0	6.2	0.2	100	
World	51,306	8,411	3.,234	3,693	66,644	100
% of World usage	77.0	12.6	4.9	5.5	100	
% escaping to atmosphere	50	80	80	0	50	

Source: Lubulwa *et al.*, 1995.

Specific applications of methyl bromide fumigation are (after UNEP, 1992):

- Preplanting soil treatment against soil-borne insects, nematodes and other organisms
- Devitalization of seed
- Durable commodities (grains, legumes, various seeds, dried fruit, nuts, coffee beans, cocoa)
- Perishable commodities (fruits and vegetables)
- Animal feedstuffs
- Non-food products (timber and other forest products, cut flowers, cotton, tobacco, artefacts)
- Disinfestation of transport containers and vehicles
- Disinfestation of structures and machinery
- Quarantine applications of any of the above.

Fumigation with methyl bromide is not essential in any of the above applications, provided that equivalent efficacy can be assured and that specific regulatory requirements are appropriately amended.

Requirements of appropriate alternative technologies

Specific attributes are required in technologies for control of pests in contractual and quarantine arrangements. These can be benchmarked to methyl bromide for convenience although in reality they must stand alone. There are four critical issues to be addressed.

- Retention times involved in the treatment must be compatible with the needs of the client and usually this would be the minimum time possible. Methyl bromide typically had short exposure times—from 3 h for vacuum fumigation to 24 h for atmospheric fumigation. Although this causes a significant disruption to the normal sequence of handling activities that would be involved if disinfestation was not required, it has been acceptable in practice. Methyl bromide fumigation can be contrasted with continuous-flow processes such as irradiation or heat disinfestation where rerouting a commodity through a treatment facility is necessary but actual delays are minimal. Alternatively, longer-term treatments would be involved if phosphine or carbon dioxide were the disinfestation agents. Ideally, the time involved for treatment should be as short as possible and must be economically justifiable.
- Consistency in response of target infestations. This is essential and particularly so if proof by documentation is involved. Thus, for example, inspection for infestation may be replaced by documented proof of treatment in both quarantine and contractual arrangements. To achieve an assured outcome, there must be adequate penetration of the treated commodity to ensure that target infestations receive consistent and programable exposure to the disinfesting agent. Moreover, target organisms ideally should show little variability to the treatment, both individually and as populations, and have little propensity to development of resistance. Methyl bromide, for example, penetrates commodities satisfactorily particularly with vacuum treatments. Its insecticidal properties were first reported by Le Goupil in 1932 and the material has been used and misused intensively and extensively since then without any significant breakdown of control in the field from resistance.
- Wide spectrum of beneficial activities. Ideally the widest range of benefits possible should accrue from the alternative technology. This should involve activity against as many as possible of the range of pests present or potentially present, and consideration of both positive and negative side-effects such as on the contribution of biological control to integrated pest management and on the environment.
- Minimal residues if chemical additives are involved. Processors and consumers are very sensitive to residues of pesticides, their breakdown products, and other additive/contaminants in commodities. Markets today are moving inexorably towards a policy of residue-free commodities and it is desirable to have such a target as a goal even if in the long term. Already some countries have such a policy and, irrespective, there are considerable opportunities in niche markets.

Technologies that complement, supplement or replace methyl bromide fumigation

There are many reviews of technologies proposed as alternatives to fumigation with methyl bromide. Bell and Stormer (1997) who examined the alternatives for durable commodities, proposed the use of other fumigants, controlled and modified atmospheres, contact insecticides, inert dusts, cool storage, heat treatment, and irradiation as well as methodologies for buildings and transportation systems. There are similar detailed presentations in van

Graver (1997) and separately for chemical-based alternatives in Annis and Waterford (1996) and for physical methods in Bell (1996).

This presentation is concerned primarily with alternative chemicals for methyl bromide. They must be placed in perspective in the series of complementary, supplementary or alternative technologies that are also available, many of which are not considered elsewhere in the conference. These include methodologies that reduce the need for methyl bromide fumigation and reduce emissions of the gas into the environment where, in the short term at least, such fumigation is necessary.

Sanitation is the prime consideration as alone it may ameliorate or substantially overcome a pest problem.

1 Reducing emissions of methyl bromide from fumigation

It is estimated that 80% of the methyl bromide used in structural and commodity fumigation leaks or is vented to the ambient atmosphere during fumigation or subsequent airing. There is a potential for significant reductions to be made in these losses to the atmosphere although completely closed systems are not possible because of the slow desorption of the methyl bromide from the treated commodities. Nevertheless, there would be benefits to the overall methyl bromide budget in the short term until alternative technologies are in place.

The various emissions can be categorized as follows:

- Losses from leaky enclosures
- Discharge of gas after fumigation
- Desorption during airing and subseqent storage and handling.

Good fumigation practice dictates that losses from faulty enclosures should be minimal. Purpose-built fumigation chambers are ideal. With structures and freight containers, gastight construction is the first choice but, if provision has not been made for this, the enclosure should be sealed to an appropriate standard following methodology now widely available. Similarly, where gasproof sheets or other plastic envelopes are used, the fabric must be impermeable to the gas, all joints adequately sealed preferably by an adhesive or by welding, and the enclosure protected from damage during the fumigation.

The integrity of the seal of the enclosure should be assessed objectively by standard tests for gastightness. These are available as pressure-decay and pressure-flow tests or the more time-consuming tracer gas (CO) technique. Technologies that cater for fumigation in leaky structures are undesirable as they require excessive dose of fumigants, allow unnecessary emissions into the atmosphere and workplace, and compromise efficacy of control.

Methyl bromide can be recovered when the fumigation is complete and can be recycled for further fumigations, reclaimed for other uses or destroyed. The most common recovery techniques involve adsorption from the air/gas stream onto activated carbon or zeolite from which the methyl bromide may be removed by temperature or pressure swing adsorption/desorption processes and condensed or otherwise used or recycled. In other facilities, the fully charged sorption filters have been disposed of in landfills or incinerators although direct combustion, as with catalytic cracking, is unsatisfactory as bromine and hydrobromic acid are produced. Recovery of the methyl bromide desorbing from the commodity during airing and subsequent handling and storage is more difficult as prolonged scrubbing of the atmosphere would be involved and may be impractical in many circumstances.

2 Residual pesticides

Admixture of residual insecticides with a commodity can be regarded as an alternative control measure to fumigation in some circumstances. Such treatment was common practice until attitudes to pesticide residues hardened. Dichlorvos was the classical material because of its high vapor pressure and short residual life. Controversy over its mammalian toxicology and the realization that its apparent very short residual life was due in part to deficiencies in the extraction of residues for analysis became a limitation to its use. A broad range of other materials has been used (Arthur, 1996). These include the natural pyrethroids, many synthetic pyrethroids, other organophosphorus compounds and insect growth regulators. While the concept of disinfestation with residual pesticides must be recognized as a valid and valuable alternative to fumigation, a detailed consideration of its scope is outside the framework of this presentation. Suffice to say, however, that today, the residue situation seriously constrains use of these materials.

Surface treatments with pesticides are now generally regarded as not reducing the reinfestation rate by insect pests particularly in the tropics due to the nature of the surfaces involved and the prevailing climatic and environmental conditions. Their only use is after cleaning of stores and in association with fumigation (Gudrups, 1996).

Various plant products have been used for disinfestation treatments particularly in alternative agriculture and developing countries. They usually are prepared as powders, aqueous solutions or oil extracts and are used as contact insecticides, fumigants, repellents and antifeedants. Constraints to their use are lack of standardized formulations, analytical methodology and toxicological data for both mammals and the target pests. Lale (1995) has given a detailed overview of their use in management of stored product pests.

Insect proofing of storage and handling areas can provide the physical exclusion of the pests that has inbuilt permanency and is desirable environmentally. In this context, permanent enclosure in gasproof sheeting/envelopes has been used for long-term storage of bag stacks after fumigation with carbon dioxide or phosphine, or after treatment with a grain protectant.

3 Inert dusts

"Inert dusts" have a continuing role in pest control in grain, pulses and oilseeds and have been used in conjunction with fumigants. They may be insecticidal themselves as a result of abrasive or sorptive properties, or they may be used as carriers for insecticides to improve toxicity and residual life. The materials involved are usually amorphous silicas or diatomaceous earths. Processed silica-rich materials such as paddy husk ash are used also.

There are three basic application methods:

- Admixture with the commodity
- Surface treatment of bulk grain
- Structural treatment including bag stacks.

Admixture treatments have limited appeal in commercial practice and generally are used only for small-scale treatments where ease of application may be a consideration. When applied directly to commodities, dusts alter the physical properties of bulks including bulk density, angle of repose and handling flow rates. These changes affect handling of bulks and may reduce loading rates to levels that are unacceptable to handlers. The dust can also interfere with the operation of machinery and cause abnormal wear as well as contaminate the general environment of the storage or processing plant.

Surface treatment of bulks of grain with Dryacide®, a diatomaceous earth coated with synthetic silica, has been used as a supplement to aeration to control insect infestations which congregate in the surface layers of the bulks. Dryacide® has also been used in uncapped vertical storages being treated with SIROFLO®, a positive pressure flow-through system of phosphine fumigation. Surface treatment with Dryacide® of the uncovered top surface of grain in these silos has been shown in some circumstances to act as a gas barrier, restricting gas flow and giving a significant increase in concentrations of phosphine in these layers (Winks and Russell, 1994).

Treatment of structural fabric or bag stacks with inert dusts may involve direct application of the dust or use of water-based slurries. On a weight basis, the dusts are more effective when applied dry but the slurries are easier to apply, deposit more readily on vertical surfaces, and have a longer residual life.

4 High temperature disinfestation

Heat treatment of mill machinery is becoming increasingly popular. Machinery may be covered with heat-reflective tarpaulins and flexible ducts direct heat into the enclosures to achieve a temperature of 60-80℃. In the USA, 3% of the total methyl bromide consumed is used to treat flour mills but national food companies (Pillsbury, Nabisco, Quaker Oats, Con Agra, General Mills), however, are switching to heat "sterilization". Comparative costs per million cubic feet are quoted at US$2,000-4,000 for methyl bromide and US$747-830 for heat disinfestation using temperatures of 54-60℃ and exposures up to 18-24 hours (Anon., 1995). Other variants of heat treatment of mills have involved combinations of phosphine, heat and carbon dioxide.

Heat treatment has been widely used for disinfestation of commodities. The sensitivity of the commodity to heat is critical as the temperatures required to kill insects can induce similar changes in the commodity which may also be living material or at least of plant origin. Moreover, most commodities that can be infested by insects have low heat conduction capacities and may require extended periods of heating for adequate heat penetration if batch treatments are used. Commercially, heat disinfestation has its widest application in treatment of fruit and vegetables for quarantine purposes, for example various hot water and vapor heat treatments for fruit flies. With durable commodities such as grain, continuous-flow treatments are more appropriate. These aim at a minimum residence time of the commodity at the disinfesting temperature. Fluidized bed technology has particular application as heat transfer is most efficient and residence times are short.

5 Pheromone trapping

High capacity pheromone traps have been used for moth control. A typical application consists of a pheromone dispenser and cypermethrin to remove males from populations of *Ephestia kuehniella* with units placed at densities of 1 per 260-280 m^3.

6 Irradiation

Irradiation has had limited acceptance for pest control as an alternative or complementary measure to use of chemical pesticides. This has been despite the inherent dependability of dosing levels and pest responses, and the freedom from pesticide residues comparable with heat and cold treatments. The current campaign, however, to replace methyl bromide as a fumigant for both general pest control and quarantine applications as well as tenfold reduction in its maximum residue limit to 50 ppb has rekindled interest in irradiation as a potential alternative for short-term disinfestation. The Joint UN Food and Agriculture Organisation/International Atomic Energy Agency Division of Nuclear Techniques and the United Nations Environmental Programme are focusing attention on the role irradiation can play as a replacement for methyl bromide. A detailed summary of the current situation is provided in the report of the FAO/IAEA Consultants' Meeting on the Role of Irradiation as an Alternative to Methyl Bromide Fumigation of Food and Agricultural Commodities held in Vienna in August 1997 (Anon., 1997). Although the technology is finding an increasingly significant place in treatment of perishable commodities for quarantine and general pest control, applications in treatment of durable commodities, including grain, are few probably because of the current lack of demonstrated economic incentives and the availability of alternative technologies that are less capital-intensive and more socially acceptable.

Alternative fumigants

The expeditious course in replacing methyl bromide as a fumigant would be to identify another fumigant with the similar attributes of rapid and reliable toxic action but without the ozone-depleting implication and other residue problems. This, however, would not move technology away from use of chemicals in response to the changing attitudes of consumers towards residue-free commodities. These were once the province of niche markets but are now assuming global proportions.

Another consideration in use of fumigants concerns the escape of fumigant into the surrounding atmosphere from leaking enclosures and subsequent venting. In many circumstances, the fumigant is present in the working space atmosphere and, in recognition of this, threshold limit values have been established to indicate so-called safe levels of long-term fumigant exposure for workers. Unfortunately, with the litigious nature of society today, exposure of workers to any concentration of a fumigant is inadvisable and could have expensive consequences. With this in mind, together with the underlying health issues, a goal in development of fumigation technology should be that workers are not exposed to the fumigant at any time or at any concentration-indeed this principle is already accepted in common law. Moreover, threshold limit values that are adequate today, may require modification in the future. The situation is exacerbated by the incredible sensitivity of residue detection methodology and the inability of some authorities to recognize the difference between dependent and independent variables in attributing causal mechanisms.

1 Modified atmospheres and carbon dioxide

It follows from the above considerations that any chemical used to replace methyl bromide in a disinfestation treatment should not contain halogen atoms and should occur naturally in the environment in significant quantities or at least be harmless to life forms either in its original chemical state or as breakdown products. Modification of the composition of the ambient atmosphere would be the obvious approach. This would involve reducing the oxygen content of the atmosphere below 10% or raising the carbon dioxide content to lethal levels, ideally approximating 60%. Anoxic atmospheres are established and maintained by swamping with nitrogen produced from air by systems based on pressure swing adsorption or filtration through semi-permeable membranes, combusting the oxygen, or converting it catalytically. This is time-consuming (21-day exposures) and certainly not a direct replacement for methyl bromide fumigation.

Carbon dioxide is a toxic gas which can require extensive exposure periods (~15 days) at normal temperatures and pressure but these exposures can be reduced dramatically as the pressure is raised. High pressure fumigation with carbon dioxide was originally developed in Germany by Stahl and Rau (1985) and has now been extended to France and elsewhere. Typically, it involves pressurizing the fumigation chamber to 19 atmospheres with rise time of 90 minutes followed by 60-minute exposure and a decompression time of 30 minutes. Recovery of carbon dioxide approximates 85%. This could be a viable replacement for vacuum fumigation with methyl bromide.

In other applications, carbon dioxide is less useful as prolonged exposure periods are involved, particularly in cold countries where structural fumigations may involve exposures of several weeks. Moreover, carbon dioxide itself is involved in the atmospheric debate.

2 Phosphine

Phosphine is currently a major replacement fumigant for methyl bromide since no other similarly versatile fumigant is available. This stems from the proven effectiveness of phosphine in a wide range of applications and is despite the extended exposure periods required for its use. Of necessity, phosphine fumigation will have to be associated with a rapid treatment for some quarantine uses but it is apparent that planning for storage, handling and marketing of commodities should include provision for longer holding periods for phosphine fumigation if disinfestation is involved.

Phosphine is highly toxic to insects, man, and many other life forms. There are many reviews of its properties and use, e.g. Chaudhry (1997). It has a wide spectrum of activity against stored product pests with the caveat that at current recommended concentrations it appears to allow development of psocid infestations. The gas has a specific gravity of 1.2 and diffuses rapidly in air, reducing the need for mixing or circulation systems at least in small enclosures. Dose rates range between 0.05-1 mg/m^3 (36-718 ppm at NTP) with exposure periods ranging from a 3-5 day minimum to 10-30 days. There is considerable controversy over minimum exposure periods but unquestionably longer exposure periods ensure successful fumigations. This is a consequence of the marked differences in response of the various life stages and the necessity for exposure periods to be sufficiently long to enable the more tolerant stages to progress to more susceptible stages.

The threshold limit value for continuous daily exposure is 0.3 ppm, the lower explosion limit is 1.79% by volume in air, and air mixtures are unstable at reduced pressure. Under normal conditions, phosphine does not affect germination of seeds and may be used on living plant material including cut flowers. It is highly reactive with copper and copper alloys and cannot be used where it will come into contact with electrical and electronic equipment-including wiring and switchgear. Hence, it cannot be used in buildings, mills, and food-processing plants unless appropriate protective measures have been taken. Phosphine residues are usually of little significance. The maximum residue limit for grain is 0.1mg/kg but, in practice, residues should be at the limit of detection at the time of consumption. Generally, sorption on commodities is low, posing little problem from desorption during subsequent airing or storage of the commodities. Paddy, however, has recently been demonstrated as an exception with increased doses being used to compensate for the sorption.

In most of the earlier applications, phosphine was generated *in situ* but more recently gaseous mixtures with carbon dioxide have been used. Such formulation reduces the hazards of handling phosphine as a gas and exploits the long known feature of carbon dioxide in stimulating respiratory activity and enhancing the uptake and toxic effects of phosphine. As with other older fumigants, the early development of phosphine was for control of phylloxera in grape vines where it was generated from calcium phosphide. The subsequent development in the USA of the gas-pervious package containing aluminium phosphide that was inserted directly into the grain mass to react with moisture in the interstitial air heralded the modern course of its development as the major fumigant in the world today. A range of phosphine-generating materials is now used, formulated as pellets, tablets, and sachets in a variety of forms based primarily on aluminium phosphide but also using magnesium phosphide and zinc phosphide. Increasingly, phosphine is being generated outside fumigation enclosures, allowing better control of the fumigation and, as indicated above, supplied from off-site sources in cylinders and containing flammability-suppressing materials.

There have been many modifications of the basic phosphine fumigation process to address problems of poor distribution, leaky enclosures, and extended exposure periods. The underlying principle is to increase the effective exposure period by maintaining gas concentration. The prime consideration in achieving this should be to ensure the gastightness of enclosures through use of appropriately high standards of gas-impervious sheeting, jointing and general sealing. Unfortunately, less satisfactory measures are often employed albeit for reasons of economy or convenience. Thus, excessive decay of gas concentrations through leakage or other causes is compensated for by providing additional gas from slow release formulations, multiple dosing and continuous-flow methodology including the monitored positive pressure flow-through SIROFLO® and related systems.

Insect resistance has emerged as the major constraint to use of phosphine. It has been confirmed in Asia and Australia in a range of species including *Rhyzopertha dominica, Cryptolestes ferrugineus, Sitophilus oryzae* and *Tribolium castaneum* and recommended concentrations for low-dose flow-through systems at least need revision. Resistance appears to involve respiratory exclusion of phosphine coupled with detoxification. Resistant insects apparently survive exposure to high concentrations of phosphine over short exposure periods but are killed during extended exposure to lower concentrations of the gas. These responses again demonstrate the inherent value of long exposure periods with phosphine but negate in some measure its value as a replacement for the short-term treatment with methyl bromide.

Methyl phosphine is an analogue of phosphine under development in England as a candidate alternative fumigant. It causes much greater mortality of phosphine-resistant insects compared with their susceptible counterparts.

3 Other fumigants

Many other organic compounds have been evaluated for fumigant activity. Correspondingly there are periodic reviews of their potential as fumigants with probably the widest coverage being given earlier by Shepard (1951). Today, however, many of the compounds can be discounted because they contain halogen atoms and it does seem likely that simple volatile compounds in aliphatic series that are toxic to insects offer the best prospects.

The more important materials currently receiving attention are carbon disulfide, carbonyl sulfide, ethyl formate, hydrogen cyanide, cyanogen, ozone, sulfuryl fluoride, chloropicrin and methyl isothiocyanate.

Desmarchelier (1998) has provided a valuable resume of the potential of the three most promising materials, carbon disulfide, carbonyl sulfide and ethyl formate. He discusses the issues implicit in research leading to the commercial use of these as fumigants giving information on control of pests, effect on quality, registration, requirements for worker, environment and consumer safety including threshold limit values for 8 h exposures, flammability, methods of analysis, natural levels of occurrence, residues from fumigation and their toxicity and, finally, application methodology.

1) Carbon disulfide

Carbon disulfide was first used as a fumigant against granary weevil in 1854. It has been widely used as a soil fumigant and subsequently in control of grain pests. The vapor is 2.6 times heavier than air, diffuses slowly and will collect in low areas where it will persist for a considerable time. The initial activity against insects is as an anaesthetic from which they may partially recover but they finally succumb to its lethal action. Unfortunately, it is highly explosive in mixtures with air ranging from 1 to 50%, ignites spontaneously at 100℃, and gives off flammable vapors down to −30℃. It is rated a greater hazard than gasoline and certainly the massive explosions and destruction that have been associated with its use bring into question efforts to promote it commercially. Notwithstanding, it is still used in small-scale fumigations particularly on farms despite the risks and liability that could be incurred. Its advantages are that it can be used on seed grain and malting barley, it occurs in nature and has a workable maximum residue limit of 10mg/kg and threshold limit value of 10 ppm for long-term exposure. Formulation with other hazard-suppressing chemicals may offer an alternative approach for its use but currently the once widely used but now unacceptable 1 in 5 mixture with carbon tetrachloride has been the only such mixture developed.

2) Carbonyl sulfide

Carbonyl sulfide is currently covered by a CSIRO patent. Its properties and potential as a fumigant have been reviewed by Desmarchelier (1994) and Ren (1996). It has a boiling point of −50.2℃ and a vapor density of 2.485. It occurs at significant levels in nature, being described as an intermediate in the atmospheric sulfur cycle and the natural sulfur flux in soils and marshes presumably in bacterial sulfur cycles. Thus, emissions from fumigation could be environmentally acceptable depending on the total flux involved and it is said that such emissions could decay in practice to natural levels. Grain, for example, may contain 0.6mg/kg naturally. Carbonyl sulfide has a flammability range in air mixtures of 12-28.5% outside the normal range of use and a threshold limit value of 10 ppm. It has been suggested that the toxic action of carbonyl sulfide is through hydrolysis to hydrogen sulfide and that similar breakdown in fumigated commodities may lead to undesirable sulfurous residues. Carbonyl sulfide is currently under investigation for a wide range of applications including fumigation of grain, timber and artefacts and can be used for seed grain and malting barley. It has the advantage of not being temperature-dependent and killing insects at low temperatures down to 5℃, thus making it compatible with grain cooling and aeration. There is the added advantage with carbonyl sulfide that it reduces mould growth in wet grains.

3) Ethyl formate

Ethyl formate has been used successfully for packaging-line fumigation of dried fruit since 1927 at which time it also was patented in Europe for fumigation of cereals. It occurs naturally in a range of products including grain at up to 5mg/kg. Desmarchelier (in press) has reviewed its occurrence in the environment and its degradation.

Ethyl formate is a liquid at normal temperature and pressure (boiling point 58℃) and is soluble in water to 11.8% w/v. Its flammability limits are 2.7-13.5% by volume in air which can be offset in some measure by formulation and/or application in water. The threshold limit value for long-term exposure is 100 ppm. Its toxicity to insects was reviewed by Muthu *et al.* (1984). The treatment rate for dried fruit is 4-7ml per 11.61 (25 lb) box increasing with temperature and the maximum residue limit is set at 250 ppm expressed as free and combined formic acid. In addition to its use by direct application during packaging of dried fruit, it has been evaluated recently in commercial scale use applied to wheat as a 40g/l solution in water at the rate of 90mg/kg. Such use in grain is suggested as a replacement for disinfestation with dichlorvos and when used either as a gas or in aqueous solution as a replacement for ethylene dichloride in disinfestation of mills (Desmarchelier *et al.*, 1998).

Rational introduction of alternative technologies

Fumigation with methyl bromide is part of an integrated production-marketing system in which methodologies and strategies can be optimized using a series of management tools. Any replacement technology has to complement this system to be viable. The basic issue involved is usually pest management within a general integrated pest management framework but other less quantifiable parameters may be introduced such as regulatory or quarantine restrictions, health considerations, and non-tariff trade barriers. Irrespective, both the overall and the component systems can be quantified and modeled if sufficient data and resources are available so that all factors operating can be taken into account in predictive simulations that provide assistance to decision-makers. Longstaff (1997) has reviewed the range of decision tools available for management of pests in stored grain under the headings of knowledge acquisition and surveys, decision analyses, modelling of pest management and detection, and expert systems communicating the logical decision making to the user of the technology. A critical issue in these predictive models is locating infestations by sampling or trapping and to this end, precision targeting of the infestations by spatial analysis of the data gathered, provides a further tool for risk reduction in pest management interventions (Brenner, 1997). These approaches should be integrated with the economic evaluation and net welfare change approach discussed earlier. As more systems are developed and experience gained, objective assessments of the alternative technologies will become available enabling more rational decisions to be made on their implementation.

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