Fumigation — an endangered technology?

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Abstract

Fumigation is becoming an endangered technology. Continued efforts will be required to prevent it becoming extinct. There are many pressures on use of particular chemicals, ranging from development of resistance from the target pests to increasing demands for registration and reregistration to maintain use. Bond (1984) was able to list a wide range of materials as fumigants for stored products, yet ten years later there are only two left in widespread use — phosphine and methyl bromide. Even these remaining materials are under pressure. Methyl bromide has been listed as an ozone-depleting material and will be subject to controls from 1 January 1995 in developed countries. Environmental restrictions on release of phosphine make its use difficult or economically impossible in some parts of the world. There have been some recent developments in our knowledge of phosphine which may assist in keeping this fumigant available. These include studies on its atmospheric fate and detection of its natural occurrence in humans.

The technique of fumigation is sufficiently important to stored product protection for much effort and expense to be justified in supporting existing fumigants and their registration. Also, reregistration and modernisation of those few other fumigants that remain available, though little used, is needed to maintain the choice of materials for fumigation. There may yet be new fumigants to be discovered or recognised.

Introduction

Fumigation, as a technology, is widely used for disinfestation of durable foodstuffs. There is no doubt, from the point of view of stored product protection, that the technology is versatile and valuable. Usually, fumigation gives a quick, low cost and effective solution to problems of insect attack or pest presence in commodities such as stored grain, oilseeds, pulses, coffee and cocoa beans, and dry products derived therefrom.

However, there is a diverse range of pressures, which have led to increasing restriction of the practice of fumigation in many parts of the world. These include problems with environmental contamination, health concerns both for the public and workforce, particularly with respect to potential or suspected carcinogenicity of some fumigants, effects on treated products, including production of residues, and general market/consumer aversion to use of chemicals. Many of the forces leading to increased restriction or regulation of fumigation are not purely technical in nature, but they are potent and real nonetheless.

The science and practice of fumigation is now left with two principal fumigants, phosphine and methyl bromide. In two decades the choice of fumigants has apparently been reduced from a wide range of candidates. We must now ask whether this trend will continue and whether now fumigation can be considered an endangered technology. One where only a few extra restrictions and some unexpected discoveries or changes in attitude could lead to extinction of fumigation as presently carried out in some or all regions of the world.

In this paper, I highlight the current importance of fumigation for protection of stored products worldwide. This is followed by consideration of the shrinking list of available fumigants, with a summary of why they have been discontinued, then a discussion of the threats to our remaining accepted materials. Some recent developments are also noted which suggest that all is not lost and there may be hope for continued use of fumigation. Perhaps even new materials may be added to the list.

World Use of Fumigants on Durables

Globally, only two fumigants for durable commodities remain in widespread use. These are phosphine and methyl bromide.

Many countries use fumigation with either, or both, of these materials as their principal method of disinfestation of cereal grain stocks for domestic use, or import and export. Exact figures for the global use of these fumigants are not available, but it is possible to approximate the tonnage of grain and similar commodities treated from estimates of methyl bromide and aluminium phosphide, the precursor of phosphine, for agricultural and post harvest use.

Table 1 gives an estimate for recent usage of methyl bromide and phosphine on durable commodities (foodstuffs). These figures must be taken as broad approximations only. Nevertheless, they indicate the magnitude of use and current reliance, globally, on fumigation of durables. They are remarkably consistent with those given by Muller (1992).

Dichlorvos is also still available for treatment of raw commodities, but its use is more restricted. Dichlorvos can be regarded as a fumigant and its vapour is extremely toxic to insect pests of stored grain. However, it is usually applied as an aerosol or as a grain protectant and is not considered in detail here.

Many countries have become reliant on fumigation as their primary means of controlling or eliminating infestation in cereal grain and similar foodstuffs. Two examples will suffice to illustrate this: Japan, which requires fumigation with methyl bromide to treat imported grains found to be infested, to meet phytosanitary requirements, and Australia, which uses phosphine increasingly as a residue-free system to protect grain in store against infestation. Table 2 and Figure 1 show tonnages and proportions treated in Japan and Australia respectively.

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Table 1. Estimates of annual global fumigant usage on durable foodstuffs (1992 data)

Fumigant	Estimated usage (t)	% grain treated
Phosphine	1900[a]	47[b]
Methyl bromide	6700[c]	15[d]

[a] Based on worldwide metal phosphide production of 4060 tonnes per year (Muller 1992) and assuming this to be equivalent to 2380 phosphine per year, with 20% discount for uses other than fumigation of durables, particularly rodent control. Use of cylinder-supplied phosphine ignored.
[b] Based on a world grain harvest of 1350Mt and assuming a treatment rate of 2 g/t phosphine with 50% of grain treated retreated once.
[c] Based on a total commodity usage of 8400 t (Watson et al. 1992) and assuming half of this was for non-foodstuffs, notably timber and perishables, and that CIS, PRC and India used 2500 t in total on durable foodstuffs not included in data of Watson et al. (1992), and that usage on durable foodstuffs, apart from grains, could be neglected.
[d] Based on a world grain harvest of 1350 Mt and a treatment rate of 25 g/t and no retreatments, and usage on durable foodstuffs other than grains ignored.

Table 2. Methyl bromide treatments of grains imported into Japan (1992)

Grain	Tonnage (Mt)	Treated (%)
Wheat	6.1	15
Barley	1.5	13
Maize	16.5	67
All grains	23.6	51

Data source: Japan Plant Quarantine Data Base (1992)

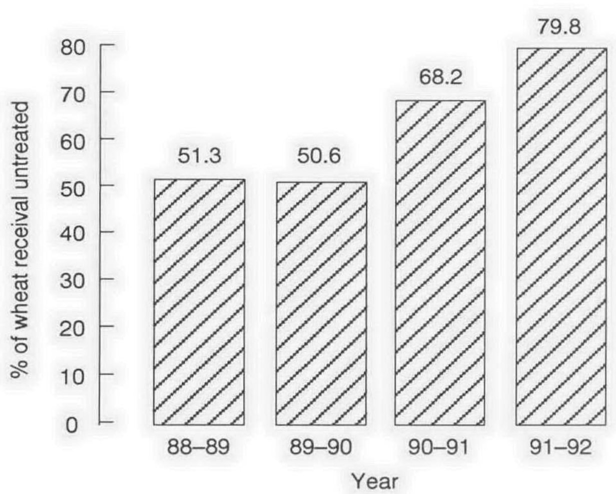

Fig. 1. Percentage of wheat received untreated into the central handling system in Australia. Most of this is subsequently fumigated with phosphine. Data source: Australian Wheat Board.

Overall, protection of durable foodstuffs in much of the world is carried out with the aid of fumigation. The level of fumigant use is such that the technique must be recognised as a major tool. Therefore, loss, or even severe restriction of its use, would have very serious repercussions. It is thus important to consider whether the two remaining materials in widespread use, and the others still available in some countries, are under threat and to assess the likelihood that their use will be curtailed, or even banned.

Status of Fumigants (Past and Present)

Many materials have, in the past, been applied as commodity fumigants for control of insect pests. In 1984 Bond was able to list more than a dozen materials, many of which were in widespread use for this purpose. Since then the use of many of these has been discontinued, at least in some regions of the world.

The reasons why particular materials are no longer available vary widely, but several have been lost through lack of interest internationally, resulting from want of support for continued national or international registration. Despite lack of international registration or banning of use on commodities in some countries, the same materials are still accepted in others (e.g. carbon tetrachloride in parts of francophone Africa, ethylene dibromide in India) where local considerations may outweigh the risks identified in other countries.

It is instructive to consider the threats to the fumigants listed by Bond (1984) so as to be warned of what might happen and, where possible, to take action to preserve the technique of fumigation. I am not suggesting here that those involved in stored product protection, either as researchers or practitioners, should seek to defend a fumigant in the face of good evidence against it, but only that data should be provided to ensure that materials are not lost unnecessarily.

'Bond's list', with slight modification, is given in Table 3, together with the major threats to continued use of these fumigants. It will be noted, in many cases, that these threats have become reality in that they have resulted in banning or deregistration of particular materials at least in some countries. Paradoxically, one of the main reasons why some materials have fallen into disuse has been the success and effectiveness of phosphine and methyl bromide. Both these materials, in specific circumstances, have properties which are close to ideal for a fumigant. These include low cost, high penetrant ability, ease of airing, lack of effect on end use qualities of most commodities, and acceptability of residues resulting from their use. If phosphine and methyl bromide had never been available, it is likely that materials with recognised major problems in current use, e.g. carbon disulphide and hydrogen cyanide, would still be available, albeit without the wide application of phosphine and methyl bromide. Amongst other drawbacks, carbon disulphide is notoriously flammable, while hydrogen cyanide has poor penetrant ability, significant storability problems and a severely adverse public image.

Table 3. 'Bond's list'. Fumigants listed in Bond (1984), with current status and threats, real or alleged, to continued use.

Fumigant	Threat[a]	Status[b]
Acrylonitrile	Suspect carcinogen, residues	
Carbon disulphide	Lack of interest	*
Carbon tetrachloride	Ozone depletor, residues	
Chloropicrin	Almost forgotten	*
Dichlorvos	Residues, alleged carcinogen	*
Ethylene dibromide	Environmental contamination, fertility effects, alleged carcinogen	
Ethylene dichloride	Not very effective, alleged carcinogen	
Ethylene oxide	Suspect carcinogen, residues	
Ethyl formate	Almost forgotten	*
Hydrogen cyanide	Lapsed Codex Alimentarius registration	*
Methallyl chloride	No food registration	
Methyl bromide	Ozone depletor, alleged carcinogen	*
Methyl formate	Almost forgotten	*
Phosphine	(see text)	*
Sulphuryl fluoride	No food registration	
Trichloroethylene	Not very effective, residues	

[a] 'Suspect carcinogen' refers to A2 status in ACGIH (1993). 'Alleged carcinogen' refers to statement 'Substance identified by other sources as a suspected or confirmed human carcinogen' in ACGIH (1993) or more recent studies.
[b] Materials marked '*' are either still in common use or may no longer be registered but do not at present appear to have data on their effects technically sufficient to deny registration.

Threats to Methyl Bromide and Phosphine

Methyl bromide

There are a number of threats to the continued use of methyl bromide as a commodity fumigant. These include:

- status as an ozone-depleting substance;
- increasing regulation of chemicals generally;
- alleged carcinogenicity;
- concern over residues in commodities;
- toxicity to humans.

Undoubtedly, the main current threat arises from its listing as a recognised ozone-depleting substance at the Copenhagen meeting (1992) of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer ('Montreal Protocol'). Article 2H of the Protocol states:

> Each Party shall ensure that for the twelve-month period commencing on 1 January 1995, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Annex E does not exceed, annually, its calculated level of consumption in 1991. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed, annually, its calculated level of production in 1991. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1991. The calculated levels of consumption and production under this Article shall not include the amounts used by the Party for quarantine and pre-shipment applications.

While use for 'quarantine and pre-shipment' fumigation is currently exempted from restriction, there is no guarantee that such exemptions will continue, particularly in the light of strengthening concern over the state of the ozone layer and hardening evidence with regard to the role of bromine in ozone depletion. At least some commodity fumigations are likely to fall within the categories of quarantine or pre-shipment treatments. The restrictions on methyl bromide are due to be reconsidered in late 1995 by the Parties to the Montreal Protocol, and it is not certain that this exemption will continue.

Another major and continuing concern is over the possible carcinogenicity of methyl bromide. Methyl bromide is categorised by the American Council of Governmental Industrial Hygienists (ACGIH) as a 'substance identified by other sources as a suspected or confirmed human carcinogen'. Titles and contents of scientific publications quite frequently refer to the substance as mutagenic or carcinogenic (e.g. Danse et al. 1984; Djalali-Behzad et al. 1981; Singh et al. 1982).

The other threats to methyl bromide are generally concerned with public reaction to use of chemicals. Methyl bromide is highly toxic to humans, a fact reflected in the low current maximum permissible levels for workspace environments (e.g. ACGIH 1993). Any accident with methyl bromide could result in pressure to lower these levels still further. Even the current levels are such that extensive airing periods, and safety zones, may be required, adding to the inconvenience and cost of treatments. There is also often a direct linkage between permissible workspace levels and those tolerated in the environment around treatments. Lowering of these already very low levels could make monitoring of those levels technically very difficult as well as imposing further costs on the system. The overall cost and difficulty, both logistic and technical, resulting from regulations relating to workspace and environmental permissible levels, have already resulted in trends away from methyl bromide use. Thus, the adoption of nitrogen-based CA treatments at the grain export terminal in Newcastle, Australia (Cassells et al., these proceedings), was driven in part by the cost and inconvenience of carrying out fumigation with methyl bromide, while restrictions on fumigation with methyl bromide in Germany have become sufficiently onerous for alternatives, including use of organophosphorous pesticides, to become a preferable pest control option in many circumstances.

While it is clear that there are some severe threats to the long term use of methyl bromide on durable commodities, there have also been some developments which may help prolong its use, although possibly at considerable cost. These involve development of sealing systems for a variety of storage types (Ripp et al. 1984), including bag stacks (Annis 1990), to contain the gas, and progress towards practical scrubbing systems for removal of methyl bromide from air streams (Anon. 1994). Both address the problem of potential adverse impact of methyl bromide on the environment and workspaces.

Overall, the long term prognosis for the continued use of methyl bromide as a fumigant on stored products generally appears poor, and it would be prudent to consider alternatives as a matter of urgency.

Phosphine

While there is quite widespread concern over the future of methyl bromide, this is not so with phosphine. However, even phosphine cannot be regarded as immune from attack. We must consider both the threats to phosphine as well as any developments that may help to permit its continued use.

Threats include:

- toxicity and effects on humans;
- environmental and workspace restrictions;
- resistance by pests;
- accidents.

The recent publication of data which apparently showed genotoxic effects of phosphine on humans, in this case fumigators, at low levels of exposure (Garry et al. 1989; Alranya et al. 1988) has highlighted the vulnerability of phosphine to unexpected new data. Considerable damage has been done to the reputation of phosphine and it can be expected that the papers which refer to the alleged genotoxic effects will continue to be widely cited, even though the actual effects appear unproven.

Phosphine is known to be very toxic to mammals and, in consequence, permissible workspace atmospheric concentrations are set at very low levels, in most countries at 0.3 ppm v/v (e.g. ACGIH 1993), but some even lower at 0.1 ppm (e.g. Germany). The required monitoring of these concentrations already imposes substantial costs on the conduct of a fumigation. Any extension to phosphine of the general historical trend towards continued lowering of maximum permissible levels will substantially increase these costs. A further consequence of low permissible levels of phosphine in the workplace is a still lower maximum permissible level in the environment around fumigation. Different regions have different formulae to determine the latter value, but, where it is set, it is typically at least 10x less than the workspace value. The need to meet such requirements has already made phosphine fumigations in some parts of the world (e.g. North Carolina, Germany) extremely difficult to carry out.

The development of resistance to phosphine by pests, particularly in the Indian subcontinent, has made effective phosphine fumigation much more difficult to achieve. The problems of resistance to phosphine are discussed elsewhere in this Conference (Winks and Hyne, these proceedings). The level of resistance which has developed so far has been insufficient to prevent the effective use of phosphine but does require considerable improvements in application technology for successful treatments, including both better containment of the gas and prolonged exposure times. The development of high levels of resistance to phosphine, and particularly development of the ability to withstand increased exposure periods, would certainly jeopardise the use of phosphine as currently carried out in at least most tropical countries. The apparent ease with which resistance to phosphine develops suggests that such a resistance pattern is not impossible. This contrasts with the situation with methyl bromide, where only slight increases in tolerance have been observed to date (Champ 1986).

A further, and possibly more serious, threat is that of the effect that an accident in use would have on phosphine. Fumigation, including that with phosphine, is a potentially hazardous process requiring careful, skilled application to ensure a safe, effective outcome. Any accident arising from poor practice, including fires arising from incorrect application, or storage and handling of formulations, is likely to result in calls for further regulation and restriction of use of phosphine.

There have been several developments in our knowledge of phosphine which are likely to lend positive support to the continued use of phosphine as a fumigant. These involve its atmospheric fate, natural occurrence and improved application technology.

With the continued use of methyl bromide under threat from its influence on the ozone layer, there has been an immediate need to define more closely the fate of phosphine emitted from fumigations. While it can be expected that phosphine would eventually be oxidised to innocuous phosphorus oxyacids, the rate that this occurs is important as it determines the quantity of the gas that can enter the upper atmosphere. Recent studies (Frank and Rippen 1987; Dévai et al. 1988) have shown phosphine at ground level is attacked by hydroxyl radicals and that the atmospheric lifetime is very short.

The identification of phosphine at low levels as a normal constituent of human faeces, and thus of the lower gut, shows that humans are likely to be constantly exposed to low levels of phosphine. This data may help to decide safe levels of exposure, but it should also be noted that Gassmann and Glindemann (1993) suggest, disturbingly, and without experimental support, that phosphine in the gut may be a cause of colon cancer.

Finally, continued use of phosphine has been strongly supported by recent technical developments in containment and application technology. Recent advances in sealing of grain storages and bag stacks (van S. Graver and Annis 1994) have allowed much reduced dosages of phosphine and substantially reduced the rate of uncontrolled leakage. In situations where sealing is not feasible or economic, the SIROFLO® technique (Winks 1993) offers an alternative which creates much lower concentrations in stores than 'traditional' application methods, with consequent decrease in risk of exposure to high concentrations in the vicinity of a treatment. SIROFLO® concentrations typically are 50 ppm or less in the storage, while normal concentrations in stores treated by addition of aluminium phosphide tablets frequently exceed 500 ppm at some stage. SIROFLO® exposures also typically use less phosphine in total than conventional treatments in poorly sealed systems.

Alternative Fumigants

'Old' fumigants

Bond's list (Table 3) contains several materials which have fallen into disuse because of inconvenient properties and lack of commercial support rather than because they have toxicological or other features which are sufficient to actively prevent their use. These are carbon disulphide, chloropicrin, hydrogen cyanide and ethyl and methyl formate. The existence of these materials, and their historical use as fumigants, gives some hope that a replacement could be found for methyl bromide or phosphine, should the use of either be restricted or banned. Both carbon disulphide and hydrogen cyanide have lost their former status under the Codex Alimentarius as approved materials with agreed international tolerances. In the case of carbon disulphide this was a 'guideline' tolerance, but with HCN the position lost was a well established Maximum Residue Limit. Reinstatement of these materials will require provision of a full toxicological data package and extensive field trials. Since both are commonly available chemicals without patent protection, it appears unlikely that commercial companies, normally the providers of supporting data for registration, will do this. Competitors can easily benefit from such registration without financial penalty. It is a very real question as to what organisations could, or should provide the required information, given that this would probably require investment of tens of millions of dollars.

Public organisations may be the appropriate bodies to seek to obtain or support registration of 'old' fumigants, to maintain their use for public benefit. This could be the impetus for effective international collaboration.

New fumigants

It has been a well known assumption that no new fumigants will be developed for stored product protection. There have been recent developments that have challenged this belief. It remains true that no new fumigants have been registered for some decades. However, there is active work on use of ozone (Yoshida 1975), carbonyl sulphide (Desmarchelier, these Proceedings) and methyl isothiocyanate (Ducom, these proceedings) and there is no reason to believe that further candidates will not be identified. It may also be that well known fumigants in other fields, such as methallyl chloride or sulphuryl fluoride, may yet find application in disinfestation of stored foodstuffs.

As with reregistration of old fumigants, the cost and effort required to gather the necessary data are major disincentives to registration of new materials as fumigants for use on foodstuffs.

Conclusion

In summary, fumigation *is* an endangered technology. There is no doubt that it is a most valuable tool for the protection of stored products. Some would argue that it is *the* most valuable, and critical to the continued protection of food stocks globally. Nevertheless there are many pressures from a wide variety of sources which are actively threatening particular materials. Neither of the two most widely used and accepted fumigants, phosphine and methyl bromide, are secure in the long term. Methyl bromide use will be banned by 2001, at least in the USA (EPA 1993), unless current legislation is challenged and changed. Phosphine use appears to be assured at present, though the historical trend of continued loss of fumigants for stored product protection should warn us that we cannot assume it will be always so. We should not be complacent.

It falls to those involved with the science of stored product protection to defend the practice of fumigation. We need to provide the data necessary to ensure that the continued use of fumigation is well based, and to counter and anticipate criticism. When faced with evidence of problems we need to appreciate them and, if possible, find ways to overcome them.

Without continuing and consolidated effort internationally, fumigation will not only be endangered, it will become extinct.

References

ACGIH. 1993. 1993–1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. The American Conference of Governmental Industrial Hygienists, Cincinnatti, USA, 124 p.

Alvanya, M.C.R., Rush, G.A., Steward, P. and Blair, A. 1988. Proportionate mortality study of workers in the grain industry. Journal of the National Cancer Institute, 78, 247.

Annis, P.C. 1990. Sealed storage of bag stacks: status of the technology. In: Champ, B.R., Highley, E. and Banks, H.J., ed., Fumigation and controlled atmosphere storage of grain: proceedings of an international conference, Singapore, 14–18 February 1989. ACIAR Proceedings No. 25, 203–210.

Anon. 1994. Report of the Methyl Bromide Technical Options Committee. In: Report of the Technology and Economics Assessment Panel, Chapter 6, Nairobi, United Nations Environment Programme, 29 p.

Bond, E.J. 1984. Manual for fumigation for insect control. Rome, FAO Plant Production and Protection Paper No 54, 432 p.

Champ, B.R. 1986. Occurrence of resistance to pesticides in grain storage pests. In: Champ, B.R. and Highley, E., ed., Pesticides and humid tropical grain storage systems: proceedings of an international seminar, Manila, Philippines, 27–30 May 1985. ACIAR Proceedings No. 14, 229–255.

Danse, L.H.J.C., van Velsen, F.L. and van der Heijden, C.A. 1984. methyl bromide: carcinogenic effects in the rat prestomach. Toxicity and Applied Pharmacology, 72, 262–271.

Dévai, I., Felföldy, L., Wittner, I. and Plósz, S. 1988. Detection of phosphine: new aspects of the phosphorous cycle in the hydrosphere. Nature, 333, 343–345.

Djalali-Behzad, G., Hussain, S., Osterman-Golkar, S. and Segerbäck, D. 1981. Estimation of genetic risks of alkylating agents VI. Exposure of mice and bacteria to methyl bromide. Mutation Research, 84, 1–9.

EPA (Environmental Protection Agency) 1993. Regulatory action under the Clean Air Act on methyl bromide. United States Environmental Protection Agency, Office of Air and Radiation Stratospheric Protection Division, Washington DC, USA, Update, Winter 1993, 1p.

Frank, R. von and Rippen, G. 1987. Verhalten von Phospine in der Atmosphäre. [Fate of phosphine in the atmosphere]. Lebensmitteltechnik, Juli/August 1987, 409–411.

Garry, V.F., Griffith, J., Danzl, T.J., Nelson, R.L., Whorton, E.B., Krueger, L.A. and Cervenka, J. 1989. Human genotoxicity: pesticide applicators and phosphine. Science, 246, 251–255.

Gassmann, G. and Glindemann,D. 1993. Phosphane (PH3) in the biosphere. Angewandte Chemie, International Edition England, 32, 761–763.

Muller, D.K. 1992. Malathion update. Fumigants and Pheromones, 29, 7.

Muller, D.K. 1993. An alternative to methyl bromide in store products. Fumigants and Pheromones, 31, 5.

Ripp, B. E., Banks, H.J., Bond, E.J., Calverley, D.J., Jay, E.G. and Navarro, S., ed. 1984. Controlled atmospheres and fumigation in grain storages. Proceedings of an international symposium on practical aspects of controlled atmosphere and fumigation in grain storages, Perth, Australia, 11–22 April 1983, xiv + 798.

Singh, H.B., Salas, L.J. and Stiles, R.E. 1982. Distribution of selected gaseous organic mutagens and suspect carcinogens in ambient air. Environmental Science Technology, 16, 872–880.

van S. Graver, J. and Annis, P. 1994. Suggested recommendations for the fumigation of grain in the ASEAN Region. Part 3. Phosphine fumigation of bag-stacks sealed in plastic enclosures: an operations manual. Kuala Lumpur, Malaysia, ASEAN Food Handling Bureau/Canberra, Australia, ACIAR, 79 p.

Watson, R.T., Albritton, D.L., Andersen, S.O. and Lee-Bapty, S. 1992. Methyl bromide its atmospheric science, technology, and economics. Nairobi, United Nations Environment Programme, 41 p.

Winks, R.G. 1993. The development of SIROFLO in Australia. In: Navarro, S. and Donahaye, E., ed., Proceedings of the international conference on controlled atmosphere and fumigation in grain storages, Winnipeg, Canada, June 1992, 399–410.

Yoshida, T. 1975. Lethal effect of ozone gas on the adults of *Sitophilus oryzae* (Coleoptera: Curculionidae) and *Oryzaephilus surinamensis* (Coleoptera: Cucujidae). Science Report of the Faculty of Agriculture, Okayama University, 45, 10–15.