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New global challenges to the use of gaseous treatments in stored products

S. Navarro[1]

Abstract

Concerns over the adverse effects of fumigant residues in food and the environment have led regulatory agencies to take actions by imposing strict limitations on fumigant registration. Of the long list of fumigants two decades ago, very few remain today. MB has a relatively quick killing effect on insects, but because of its contribution to stratospheric ozone depletion has been phased out in developed countries since 2005, and in developing countries phase out will take place by 2015. In contrast, phosphine remains popular, even though insects have developed resistance to it. These restrictions on the use of fumigants have posed new global challenges to the food industry, and have resulted in efforts to register new fumigants, and in the development of new technologies as alternative control methods. Among the newly considered fumigants are sulfuryl fluoride, carbonyl sulphide, propylene oxide, methyl iodide, ozone, ethyl formate, and hydrogen cyanide. Sulfuryl fluoride seems to emerge as a promising candidate fumigant for disinfesting stored food commodities, food-processing facilities and as a quarantine fumigant. Other registered fumigants suffer from the limitation that they may be useful for treating a particular type of commodity or for application in a specific situation only. The potential use of volatiles of botanical origin shows promise but requires both commercial scale trials and registration procedure before they can be employed in practice. Among the new gaseous application technologies that have successfully replaced fumigants are the manipulation of modified atmospheres (MAs) alone or at high temperatures, and high pressure carbon dioxide that needs to be further explored for specific applications. A recent development is the use of MAs in a low-pressure environment. These niche applications of MAs that have resulted in very promising application treatments with market acceptability, should serve as models for global challenges for new application methods.

Key words: fumigation, methyl bromide alternatives, phosphine, gaseous treatments, modified atmospheres.

Introduction

Fumigants are widely used for pest elimination in all stored products that include cereals, oilseeds, pulses, spices, dried fruits, tree nuts and their processed foods, to prevent economic and quality losses due to insect pest attack. Fumigants may be used; a) as a hygienic measure during storage; b) to provide wholesome food for the consumer; and c) as a mandatory requirement in trade and in quarantine (Rajendran, 2001).

Increased public concern over the adverse effects of pesticide residues in food and the

[1] Department of Food Science, Agricultural Research Organization, the Volcani Center. P. O. Box 6, Bet Dagan 50250, Israel. Fax: +972-3-5582069. e-mail: snavarro@int.gov.il

environment has led to the partial substitution by alternative control methods. Therefore, non-chemical and environmentally user-friendly methods of pest control in the post harvest sector are becoming increasingly important. It is worth noting that of the 16 fumigants listed in common use some 22 years ago by Bond (1984), only very few remain today. Most of these fumigants have been withdrawn or discontinued on the grounds of environmental safety, cost, carcinogenicity and other factors. Methyl bromide (MB) has been phased out in developed countries since 2005 and will be phased out in developing countries by 2015, because of its contribution to stratospheric ozone depletion (UNEP, 2002). Although there are exemptions for quarantine and pre-shipment purposes, as well as the possibility to apply for exemptions where no alternative exists, the applicant has to demonstrate that every effort is being made to research alternative treatments. In contrast; phosphine remains popular, particularly in developing countries, because it is easier to apply than MB. However, many insects have developed resistance to phosphine over the last decade (Cao et al., 2003; Savvidou et al., 2003).

Food industries and particularly exporters are dependent on fumigation as a quick and effective tool for insect pest control in food commodities. Following on the WTO and Free Trade Policies, trade traffic of foodstuffs across the world has been considerably increased. Consequently, fumigation for disinfesting stored food commodities has been playing a significant role. Some developed countries have adopted the approach of zero tolerance of insect pests in food commodities. On the other hand, the fumigation technology that is required to obtain this zero infestation has been facing threats/constraints because of regulatory implementation and the development of resistance (Arthur and Rogers,. 2003).

The aim of the present paper is to elucidate the new global challenges to the use of gaseous treatments in stored products. These challenges derive from the increased demand of competitive markets for quality in food commodities free from pest and pesticide contaminants on the one hand, and the need to find and the cost involved in adopting alternative control measures on the other. They have resulted in efforts to register new fumigants in several countries, and in the development of new technologies as alternative control methods.

The gaseous treatments

The gaseous treatments may be categorized into three groups; a) residue-leaving fumigants that are synthetically produced volatile chemicals; b) volatile essential oils of botanical origin; and c) non-residual modified atmospheres (MAs).

a) Fumigants and their current status:

The chemical treatments discussed in this presentation are categorized under structural treatments and commodity fumigations. Among the synthetic chemical treatments, the list today is limited to MB, phosphine, sulfuryl fluoride, propylene oxide, carbonyl sulphide, ethyl formate, hydrogen cyanide, carbon disulphide, methyl iodide, ozone, and carbon dioxide.

The current most commonly used fumigants

Methyl bromide

One of the main features that make MB a commercially desirable fumigant is its speed of action. In addition, MB has a number of additional desirable features including its recognition by quarantine authorities, and its broad registration for use; it also has good penetration ability, and the commodity airs rapidly after exposure. When considering alternatives, the above properties need to be viewed against a background of MB as a highly toxic, odorless gas with substantial ozone-depleting potential and adverse effects on a number of durables, particularly loss of viability, quality changes, taint and residues.

MB plays an important role in pest control in durable and perishable commodities and particularly in quarantine treatments. The Montreal Protocol, an international treaty developed to protect the earth from the detrimental effects of ozone depletion and signed by 175 countries, is now phasing out ozone depleting compounds including MB on a worldwide basis. Accordingly, legislative changes have been made in different countries to control the use of MB, which has an average ozone depleting potential of 0.4. The ban on MB currently exempts quarantine and pre-shipment (QPS) treatments, emergency uses and certain critical uses where no alternatives have yet been developed (TEAP, 2000). However, these exemptions will be reviewed periodically in international meetings and they might not continue forever. In the absence of suitable alternatives, this loss of MB as a fumigant could seriously affect the protection of stored and exported food commodities from pest organisms. To combat this situation, one approach has been to accept the use of MB where no alternatives exist, but, after fumigation, to absorb the gas for recycling or to destroy it instead of releasing it to the atmosphere. There has been some limited implementation of recovery and recycling for MB, mainly in North America and Europe. Recovery and recycling systems are generally complex and expensive to install compared with the cost of the fumigation facility itself. These systems would also require a level of technical competence not normally found at fumigation facilities. Therefore, examples of recovery and recycle in current commercial use are few.

Phosphine

Phosphine is available in solid preparations of aluminium or magnesium phosphide and in cylinders containing carbon dioxide ECO_2 FUME® or nitrogen FRISIN®. Lately, on-site phosphine generators that can release the fumigant up to the rate of 5 kg h^{-1} are available in some countries (Argentina, Chile, China and USA). Metal phosphide formulations with slow or altered rates of phosphine release have been developed and tested in Australia (Waterford and Asher, 2000) and India (Rajendran, 2001). Improved application techniques such as the "Closed Loop System" in the USA, SIROFLO® and SIROCIRC® in Australia and PHYTO EXPLO® in Europe have been developed for application in different storage situations. Insect resistance is a serious concern that threatens the continued effective use of phosphine. Phosphine fumigation protocols have been revised in different countries to tackle the problem of insect resistance to the fumigant. Two major restrictions of phosphine are that it requires several days of exposure to achieve the same level of control as that of MB, and that it corrodes copper and its alloys and therefore electrical and electronic items need protection from exposure to the fumigant. Phosphine also reacts to certain metallic salts, which are contained in sensitive items such as photographic film and some inorganic pigments.

Newly considered fumigants

Sulfuryl fluoride

Sulfuryl fluoride has been used as a structural fumigant for dry wood termite control for the past 45 years, but it also has potential applications in disinfesting flour mills and food factories (Bell et al., 1999). Although it can be used effectively for insect pest control in dry tree nuts and food grain, data are scarce on the effect of sulfuryl fluoride on quality of the treated commodity and persistence of residues. The fumigant is more penetrative into treated commodities than MB. Insect eggs are the most tolerant stage for sulfuryl fluoride. The relative egg tolerance can be overcome by increasing the exposure period and by raising the treatment temperature (Bell et al., 1999). Sulfuryl fluoride has been registered and used as a structural fumigant in Germany, Sweden and the USA. Sulfuryl fluoride is available under the trade name "Vikane" containing 99.8 % sulfuryl fluoride and 0.2 % inert materials. Apart from the USA, China has been producing sulfuryl fluoride (trade name “Xunmiejin”) since 1983 (Guogan et al., 1999). Also, sulfuryl fluoride can be applied under reduced pressure so that the exposure period can be drastically reduced (Zettler and Arthur, 2000). The fumigant was noted as highly toxic to diapausing larvae of the codling moth, *Cydia pomonella* in stored walnuts (Zettler et al., 1999). Sulfuryl fluoride is now registered under the new trade name “ProFume®” for the protection of stored food commodities (Schneider et al., 2003). ProFume® is registered in the US to allow virtually all mills and food processing facilities to test, adapt and consider adoption as an alternative to MB. Additionally, registration coverage in EC countries for numerous milling and food processing applications is broad, and increasing (TEAP, 2006).

Propylene oxide

Propylene oxide (PPO) is a colorless and flammable liquid, and is used as a food emulsifier, surfactant, cosmetics and starch modifier. Under normal temperature and pressure PPO has a relatively low boiling point (35 °C) and a noticeable ether odor (Weast et al., 1986). It is a safe fumigant for use on food; it is registered and used in the USA as a sterilant for commodities such as dry and shelled walnuts, spices, cocoa powder and nutmeats (Griffith, 1999). A disadvantage of PPO is that it is flammable at from 3 to 37 % in air, and therefore, to avoid flammability it should be applied under low pressure or in CO_2 -enriched atmospheres. Griffith (1999), in preliminary tests on some stored product pests, indicated that PPO has insecticidal properties under vacuum conditions as a fumigant. Navarro et al. (2004) studied the relative effectiveness of PPO alone, and in combination with low pressure or CO_2.

Carbonyl sulphide

Carbonyl sulfide (COS) is naturally present at low levels in food grains, vegetables *(Brassica* spp.) and cheese. Research work on carbonyl sulfide in Australia, Germany and the USA reveal that the egg stage is highly tolerant to the fumigant. Reports from Australia indicate that the fumigant does not affect the quality of wheat, and germination is not affected. However, investigations on carbonyl sulfide carried out in China showed contradictory results. Xianchang et al. (1999) reported that carbonyl sulfide affects germination of cereals except sorghum and barley, and imparts off-odour. Milled rice after treatment of paddy rice with carbonyl sulfide at the above dosages had an undesirable odour. Change in colour was also observed in fumigated soybeans. Zettler et al. (1999) also noticed an off-odour during the first 24 h of aeration in walnuts that were fumigated with carbonyl sulfide. It is suspected that hydrogen sulfide present in the supplied product, as an impurity, is partly responsible for the off-odour problem (Desmarchelier, 1998).

Ethyl formate

Ethyl formate is known as a solvent and is used as a flavoring agent in the food industry. It is naturally present in certain fruits, wine and honey. In India, extensive laboratory tests against insect pests of food commodities and field trials on bagged cereals, spices, pulses, dry fruits and oilcakes have been carried out on the fumigant (Muthu et al., 1984). Currently ethyl formate is being used for the protection of dried fruits in Australia. It has been found suitable for in-package treatment of dried fruits. Studies in Australia indicate that, unlike phosphine, ethyl formate is rapidly toxic to storage insects including psocids (Annis and Graver, 2000).

Hydrogen cyanide

Hydrogen cyanide (HCN) is currently registered only in India, New Zealand and with severe restrictions in Germany. HCN was one of the first fumigants to be used extensively under “modern” conditions. Its use for treating trees under tents against scale insects was developed in California in 1886 (Woglum, 1949). The high dermal toxicity of the gas makes it hazardous to applicators. HCN is one of the most toxic of insect fumigants; it is very soluble in water. HCN may be employed for fumigating many dry foodstuffs, grains, and seeds. Although HCN is strongly sorbed by many materials, this action is usually reversible when they are dry, and, given time, all the fumigant vapours are desorbed. With many foodstuffs, little, if any, chemical reaction occurs, and there is no detectable permanent residue. Because of the high degree of sorption at atmospheric pressure, HCN does not penetrate well through the bulk of some commodities.

Carbon disulphide

Carbon disulfide (CS_2), an old fumigant, is used at the farm level in some parts of Australia and to a limited extent in China (TEAP, 2000). The major advantage of carbon disulfide is its small effect on seed germination. However, residues of carbon disulfide persist in treated commodities for a longer period than that of other fumigants (Haritos et al., 1999). The reduction in baking quality of wheat treated with this fumigant was shown by Calderon et al. (1970). Some of the limitations of the fumigant include high flammability, long exposure period, persistence in the treated commodity, lack of residue limits set by Codex Alimentarius and high human toxicity.

Methyl iodide

Methyl iodide has been patented as a pre-plant soil fumigant for control of a broad range of organisms including nematodes, fungi, and weeds (Grech et al., 1996) and the patent has subsequently been expanded to include structural fumigation against termites and wood rotting fungi (Ohr et al., 1998). Methyl iodide's potential as a fumigant for postharvest pest control has been known for more than 68 years (Lindgren, 1938). However, economic considerations at that time precluded its development in favor of the less-expensive MB.

Methyl iodide was found to be very effective as a space fumigant (Shaaya et al., 2003; Zettler et al., 1999), being most toxic to eggs and least toxic to adults of *Tribolium confusum* (Tebbets et al., 1986). Yokoyama et al. (1987) showed that methyl iodide could prove valuable as a quarantine treatment for *Carpocapsa pomonella* in fresh fruits and as a rapid commodity disinfestation treatment of 24h or less. The fact that the US Environmental Protection Agency has listed methyl iodide as a possible human carcinogen could preclude registration in the US, particularly in California where it is listed as a compound known to cause cancer (EPA, 1998).

Cyanogen

Cyanogen (C_2N_2) is a colorless gas with almond like odor and was patented as a new fumigant effective against insects and microorganisms (Yong and Trang, 2003). It is highly toxic to stored product insects and is fast acting. It has a good penetration through the grain mass and it desorbs quickly. It is phytotoxic and affects germination of treated seeds. But, it has potential for space and flour/rice mill fumigations and disinfestations. Yong and Trang, (2003) compared the contrasting characteristics of cyanogen, MB and phosphine as fumigants.

Ozone

Ozone, a known sterilant, can be used as an insect control agent in food commodities at levels less than 45 ppm. Ozone is readily generated from atmospheric oxygen and is safe to the environment when used for fumigation. However it is highly unstable and breaks down to molecular oxygen quickly. A major disadvantage with ozone is its corrosive property towards most of the metals (Mason et al., 1999). Active research is going on to exploit ozone as a potential quarantine treatment for controlling stored-product pests (Hollingsworth, and Armstrong, 2005).

b) Volatile essential oils of botanical origin: The application of botanical extracts as fumigants in the protection of stored products from insect attack is in its infancy (Cox, 2002). There have been many plant extracts tested for their fumigant toxicity effect on stored product insects. Pascual-Villalobos (2003) studied the insecticidal effects of a group of plant essential oils (caraway, coriander, sweet basil, and garland chrysanthemum) against the damaging legume and cereal storage pests. Essential oils containing monoterpenoides were noted to be toxic to some stored product insects and comparable to MB (Isman, 2000; Shaaya et al., 2003; Tunc et al., 2000; Weaver and Subramanyam, 2000). The tested volatile plant extracts have the characteristics of essential oils with a typical aromatic scent from the plant from which they were extracted. Therefore, because of their aromatic nature, plant extracts may be applied in empty premises or to commodities such as seeds where the scent of the volatile essential oil would not present a restriction after the treatment. Most studies on volatile plant extracts have shown their efficacy in empty fumigation chambers. Due to their strong absorption, their application in bulk stored commodities is associated with poor penetration ability into the deep layers. Large scale applications that demonstrate the penetration capacity of these volatile oils are lacking in the literature. A major delaying factor to the use of these oils is that such alternatives of plant origin require toxicological and safety data for registration for use as fumigants.

c) Non-residual gaseous treatments, modified atmospheres (MAs): The objective of MA treatments is to attain a composition of atmospheric gases rich in CO_2 and low in O_2, or a combination of these two gases at normal or altered atmospheric pressure within the treatment enclosure, for the exposure time necessary to control the storage pests and preserve the quality of the commodity. Terms used in reference to MA storage for the control of storage insect pests or for the preservation of food have appeared in the literature as CA, as sealed storage, or atmospheres used at high or low pressures to define the same method of treatment but using different means.

New application technologies that have successfully replaced fumigants

Cereal grain preservation

The initial research carried out during recent decades was concentrated first on the possible application of the MA technology to cereal grains (Adler et al., 2000; Banks and Annis, 1990; Navarro, 2006a).

Tree nuts and dried fruits preservation

The possibility of applying MAs to control insects in dried fruits and tree nuts has been reviewed by Soderstrom and Brandl (1990). The influence of low O_2 or high CO_2 atmospheres as alternatives to fumigation of dried fruits has also been investigated by Soderstrom, and Brandl (1984); and Tarr et al. (1994). Ferizli and Emekci (2000) applied CO_2 for treating dried figs in a gastight flexible storage unit loaded with 2.5 tonnes of dried figs in perforated plastic boxes. These conditions resulted in complete mortality of both insects and mites. Full scale commercial application of organic raisins is being applied in California since 1984 (Navarro, 2000).

Disinfestation of dates

As a potential alternative to MB fumigation, the influence of different CAs in causing emigration of *Carpophilus* spp. larvae from dates was compared with that of MB by Donahaye et al. (1991) and Navarro et al. (1989). A concentration of 35 % CO_2 was found to cause a similar emigration to that by MB. This method has been in use in a large packing house in Israel (Navarro, 2006b).

Application of MAs at elevated temperatures

The influence of temperature on the length of time necessary to obtain good control with MAs is as important as with conventional fumigants. Navarro and Calderon (1980) compared the effect of temperature on the exposure time required to produce the mortality of adults of three storage insects in MAs. Donahaye et al. (1994) reported on responses of larval, pupal, and adult stages of two nitidulid beetles exposed to simulated burner-gas concentrations at three temperatures of 26, 30, and 35 °C. Soderstrom et al. (1992) examined the influence of temperature over the range of 38–42 °C on the effects of hypoxia and hypercarbia on *Tribolium castaneum* adults. Their results clearly indicate that raised temperatures could be used to reduce treatment duration. Navarro et al. (2003) showed the strong influence of temperatures of 35 °, 40 °, and 45 °C on mortality of all four development stages of *Ephestia cautella* when the insects were exposed to CO_2 concentrations varying from 60 to 90 % in air. Bell and Conyers (2002) investigated the potential to kill pests using MAs at raised temperatures to increase their speed of action. These works led to the application of MAs at elevated temperatures by ECO_2 in Holland with the objective to reduce the exposure times commercially to control pests in imported tobacco products, cocoa beans, rice, cereals, grains, nuts, peanuts, pulses, seeds and spices, as well as furniture and artifacts.

Vacuum treatment and V-HF technology

In a low-pressure environment, there is a close correlation between the partial pressure of the remaining O_2 and the rate of kill. Until recently, this treatment could only be carried out in specially constructed rigid and expensive vacuum chambers. A practical solution has been proposed named the vacuum hermetic fumigation (V-HF) process that uses flexible liners (Finkelman et al., 2003). To achieve this, sufficiently low pressures (25-50 mmHg absolute pressure) can be obtained (using a commercial vacuum pump) and maintained for indefinite periods (Figure1). This technology is currently in use at commercial level for pest treatment of organic soybeans and flours in Israel.

Figure 1. A V-HF Cocoon™ holding cocoa beans in bags, under a pressure of 50 mm Hg connected to the vacuum pump in a trial site in Boston, Massachusetts (courtesy of GrainPro Inc.).

High pressure carbon dioxide treatment (HPCT)

Carbon dioxide still remains slower-acting and more expensive than phosphine or MB. CO_2 treatments can be significantly shortened to exposure times that may be measured in hours using increased pressure (10-37 bar) applied in specially designed metal chambers that withstand the high pressures. Prozell et al. (1997) exposed cocoa beans, hazel nuts and tobacco to a quick disinfestation process of exposure to carbon dioxide under pressure of 20-40 bars. Because of the high initial capital investment, these high-pressure chamber treatments are practical for high value products such as spices, nuts, medicinal herbs and other special commodities. A number of countries have adopted the use of this technology; among them are Germany and Turkey.

Modified Atmosphere Packaging (MAP)

Modified Atmosphere Packaging (MAP) is a technique used for prolonging the shelf-life period of fresh or minimally processed foods. In this preservation technique the air surrounding the food in the package is modified to a composition of low oxygen or a combination of low oxygen and high carbon dioxide. The interest in modified atmosphere packaging (MAP) has grown due consumer demand. This has led to advances in the design and manufacturing of polymeric films suitable for MAP. Under MA, products such as bakery goods, and dried foods are packaged. The effects of storage temperature and packaging atmosphere (air and N_2) on the quality of almonds were studied by Garcia-Pascual et al. (2003). Guidelines for using modified atmospheres in packaged food, with special emphasis on microbiological and nutritional aspects, have been published by the Council of Europe (Anonymous, 1999).

Museum Artifacts

The possibilities of controlling pests in artifacts using inert gases were reported by Reichmuth et al. (1991, 1993). Museums throughout the world face the challenge of finding non-toxic methods to control insect pests. Recently several publications focus on practical rather than theoretical issues in the use of oxygen-free environments, presenting a detailed, hands-on guide to the use of oxygen-free environments in the eradication of museum insect pests (Maekawa and Elert, 2002; Selwitz and Maekawa, 1998).

As interest in modified atmospheres for food preservation peaked, conservation scientists began to study how this technology could be adapted to museum needs (Selwitz and Maekawa, 1998). Although a carbon dioxide atmosphere had been favored for the preservation of foodstuffs, conservators saw more advantages in using nitrogen with low oxygen concentrations to treat museum artifacts, collectively termed “cultural property” because anoxia provides a higher degree of inertness and is easier to establish for small-scale operations. The technology of MA has received the specific terminology of “anoxia” for the treatment of museum-artifacts, libraries, and among the manufacturers and suppliers of material and equipment for the use of nitrogen.

Fresh storage of fruits and vegetables

Fresh fruits and vegetables may be shipped or stored in controlled atmospheres. This topic is covered in depth in the book of Calderon and Barkai-Golan (1990) and in a more recently published chapter by Ben-Yehoshua, et al. (2005).

Narcissus bulbs treatments

The large narcissus fly *Merodon eques* F. attacks narcissus bulbs and also bulbs of other geophytes. This species is a quarantine pest where complete mortality is required prior to export from Israel. Fumigation with MB has been used to eliminate narcissus fly infestation in flower bulbs due to its rapid killing time (4 h). However, MB is also known for its phytotoxic effect on the bulbs and its use is discouraged even for quarantine purposes in developed countries.

In experimental procedures, Donahaye et al. (1997) found that there was an extremely rapid depletion of O_2 within the sealed gastight enclosures in which the narcissus bulbs were placed for fumigation, due to the respiration of the newly harvested bulbs. This procedure also revealed the significant anoxia achieved within less than 20 hours (less than 0.1 % O_2 and about 15 % CO_2) during treatment at 28 °C to 30 °C and the possibility of using it alone as a control measure. The possibility of obtaining a bio-generated modified atmosphere utilizing the bulb respiration alone was adopted by Israeli farmers as a practical solution using specially designed flexible treatment chambers (Figure 2) (Navarro and Donahaye, 2005; Navarro, 2006a). This MA method has been successfully applied by the narcissus bulb growers in Israel and fully replaced the use of MB since 2003.

Figure 2. Narcissus bulbs in standard boxes before loading on pallets (upper left), loading the pallets containing the narcissus bulbs (left), and the general view of two sealed V-HF Cocoons™ under treatment (right) (courtesy of GrainPro Inc.).

Conclusions

No fumigant that has a broad spectrum of action like MB, and is inexpensive like phosphine, is presently available. Although there is no doubt that fumigation technology is extremely important for the protection of stored products, many demands are required from potential alternative fumigants, from the sensitivity and lack of resistance of target pests to requirements for registration of new fumigants and re-registration to maintain the use of old fumigants. However, there is increasing public concern over the adverse effects of pesticide residues in food and the environment. Existing gaseous alternatives to MB and phosphine suffer from the limitation that they may be useful for treating a particular type of commodity or for application in a specific situation only. Sulfuryl fluoride seems to emerge as a promising candidate fumigant for disinfesting stored food commodities, food-processing facilities and as a quarantine fumigant. Other fumigants are suitable to specific uses, such as propylene oxide for dry and shelled walnuts, spices, cocoa powder and nutmeats, ethyl formate can be suitable for dried fruits, carbon disulfide for seed materials, and carbonyl sulfide for grains. Plant extract essential oils and other volatiles of plant origin will need large scale demonstration of their penetration capacity, in addition to toxicological and safety data for registration for use as fumigants. The only gaseous treatment that retains the special capacity of fumigation for in-situ treatment of stored commodities, as well as offering a similar diversity of application technologies, is the MA method. MAs offer an alternative that is sustainable, safe, and environmentally benign to the use of conventional residue-producing chemical fumigants. The application of MA in several fields of application has already received recognition and successfully replaced MB and phosphine. The major fields of application of MAs are: grain and pulses stored in bulk, protection of organic products, use of anoxia for museum artifacts, and libraries, and use of MAP for the food packaging industry. Newly developed MA methods for niche applications, have resulted in very promising applications such as for the treatment of seeds, narcissus bulbs, cocoa beans, dried fruits and nuts. The global challenges in stored products are the development of new and safer gaseous treatments, and new application methods of MAs that are commercially feasible.

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