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Alternatives to phosphine fumigation of stored grains: The Indian perspective

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Abstract

Out of a total about 10% post-harvest loss of grains, a significant 6% are damaged during their storage. Fumigation of the stored grains is considered indispensable to check this avoidable loss. Methyl bromide (MB), a cheap, broad spectrum fumigant, has to be phased out honouring 'Montreal Protocol'. Phosphine widely used worldwide, is the only fumigant currently used in India, because of its low cost, availability and residue-free treatment. But one serious limitation of use of phosphine is development of resistance in the major stored grain insect-pests. There are several other fumigants like sulfuryl fluoride, propylene oxide, carbonyl sulphide, ethyl formate, hydrogen cyanide and methyl iodide which have been found promising but cost remains a serious factor, especially for a country like that of India. Beside fumigants, use of Modified Atmospheres (MAs) seems to be the best bet for pesticide free organic storage. However, the technology of MAs can be well adapted where cheap sources of nitrogen or carbon dioxide are available and the storage structure is well sealed. Biogas, produced from the cow dung at farm level in many households of Punjab (India) has shown promising results to control the insect-pests in stored grains and pulses without affecting their germination and quality. Ozone, a strong oxidant, has also been successfully tried for control of stored grain insect pests, but its corrosive property towards most of the metals, is a concern. Though many volatile plant oils have proved quite effective to check the stored grain insect-pests but lack of systematic toxicological data has limited their use as practical agents for the safe storage of food grains. In the present scenario, it seems worthwhile to continue to use phosphine as fumigant for the control of stored grain insect-pests with its improved formulations exercising all the precautionary measures, till a new one equally competent is made available. Further, experimentation with other new fumigants should be continued to explore their potential. There is need to undertake further field level trials with biogas in the stored grains.

Key words: Stored grains, insect pests, fumigants, phosphine

The swelling population of India needs to be fed by producing more and protecting more. Protection of food grains is the primary duty of any nation. Unfortunately, the post-harvest losses in India remain static at 10% since decades (Dhuri 2006). That means more production of food grains also lead to its more wastage. Out of this, huge grain loss takes place during its storage which is estimated to be around 6%; the major factor being improper storage resulting from damage by insects, moulds and rats. Higher moisture contents accentuated these losses. The golden principle of 'storing the grain dry' needs to be followed.

Fumigation is considered as quick and effective tool for control of stored grain insect-pests. The concept of 'Zero tolerance of insect-pests in food commodities' has made fumigants further indispensable. However, given to the regulatory concerns and development of resistance, use of conventional fumigants such as phosphine has become very challenging. Therefore, strenuous efforts are being made to find its alternatives. Environmental safety, efficacy and cost shall determine the value of a fumigant. Fumigation registration takes into account any adverse effect of its residues in food and the environment. Since the last 3 decades, several fumigants have been withdrawn or discontinued on the bases of above parameters.

Fumigants can be used: a) as a hygienic measure during storage; b) to provide wholesome food for consumer; and c) as a mandatory requirement in trade and in quarantine (Rajendran 2001). Many fumigants have been withdrawn on the grounds of environmental safety, cost, carcinogenicity and several other factors (Navarro 2006). After phasing out of methyl bromide in view of Montreal Protocol, the only synthetic fumigant, phosphine is being used for protection of stored grains in India. However, apart from methyl bromide and phosphine, the world has seen development of several new fumigants such as sulfuryl fluoride, carbonyl sulphide, propylene oxide, methyl iodide, ozone, ethyl formate and hydrogen cyanide. This article deals with the scope and limitations of both old and new fumigants, with special reference to the Indian scenario.

Phosphine

At present, phosphine (PH_3) is the only fumigant exclusively used in enclosed situation for killing stored gain insect-pests in India. The phase-out of methyl bromide has drastically increased its use not only in quantity, but in variety of stored products other than the food grains such as spices, cocoa beans, dried fruit, nuts and even fresh fruits (Horn *et al.* 2005). Phosphine is available both in solid and gaseous formulations i.e. tablets of aluminium or magnesium phosphide and in cylinders containing carbon dioxide ECO2FUME® or nitrogen FRISIN®. The tablets upon coming in contact with water from the grain moisture releases phosphine gas. Phosphine acts on two enzymes, oxydase cytochrome and catalase (Ducom 2006) which regulate the conditioning of oxygen to enter the mitochondrion. Blocking their action makes it impossible for oxygen to penetrate into the cell leading to formation of super oxides which are the true biocidal agents. The deactivation of the enzymes occurs at low phosphine concentrations, but it proceeds according to the acquisition of resistance. For example, in Australia, the minimum concentration to block the enzymes went, for all species, ranges from 25 ppm in 1990 to more than 100 ppm in 2004. In other countries, 200 ppm has been chosen, like in France, the UK or Australia (Ducom 2005).

Cylinder-based formulations allow a quick gas release and concentrations build up very quickly (Ducom 2006). With a solid formulation, it is necessary to introduce all at once a quantity which takes into account sorption and leaks. With cylinder based formulations, the dosage can be adjusted from time to time to be above the minimum concentration and the total quantity delivered is then lowered. Phosphine can also be produced very quickly and independently of weather conditions with generators using special solid phosphide formulation which can be put into water without exploding. Phosphine is produced almost as quickly as with cylinder-based formulations, without the need to transport the cylinders.

Development of resistance in target insect pests remains an all time serious issue relating to use of phosphine as fumigant. It has developed resistance in a number of pest species (Schlipalius *et al.* 2006; Aurelio *et al.* 2007; Lilford *et al.* 2009; Ahmed *et al.* 2013). Apart from this, the other limitations of use of phosphine are requirement of several days of exposure to achieve the desired level of control. Further, phosphine is known to erode copper and its alloys and hence electrical and electronic items need protection from its exposure. Phosphine is also reactive to some metallic salts which are contained in sensitive items like photographic film and some inorganic pigments. Many deaths have been reported in India where its tablets have been used as suicidal weapon (Garg *et al.* 2009).

Methyl bromide

Methyl bromide (MB) played significant role as a cheap, broad spectrum, effective fumigant with remarkable penetration ability and quick action. But it is known to have detrimental effect on the stratospheric ozone layer. Considering this, it has already been phased out in all the developed countries of the world since the year 2005 and by the end of the year 2015, its use has been banned in the developing countries as well, including India as per the Montreal Protocol, an international treaty signed by 175 countries in 1987. However, quarantine and pre-shipment (QPS) treatments and critical uses where no alternative has yet been available, the ban has been exempted (TEAP 2000). The methyl bromide exemptions, shall, however remain a subject of review in the light of further advancement of research in this area. The scientists are trying to develop the technologies that allow the recovery of methyl bromide to recycle or destroy instead of release it to the atmosphere. Such technologies seem to have some scope to be implemented in North America and Europe though these are complex, expensive and need technical assistance (Novarro 2006). Hence, there may be only limited use of this technology.

Sulfuryl fluoride

Sulfuryl fluoride (SF) is being used as structural fumigant for dry wood termite control since over half a century. It is an inorganic, non-flammable, odourless and colourless gas used to fumigate buildings, transport vehicles, wood, flour mills, food factories, dried fruits, tree nuts and cereal grains (Cox 1997; Bell *et al.* 1999; Navarro 2006). It is produced in USA under the trade names of Vikane (998.8% SF + 0.2% inert materials) and Profume (Novarro 2006) and in China under the trade name Xunmiejin (Guogan *et al*. 1999). Sulfuryl fluoride seems to have the potential of replacing methyl bromide in terms of similar exposure time of 24 hours at normal conditions (Emekci 2010). Moreover, it has some advantages over methyl bromide such as faster diffusion rates in the treated commodities (Novarro 2006). But, the fact that it has the potential of acting as a greenhouse gas, may restrain its use as a fumigant, in future. The fumigant has also been observed as highly toxic to diapausing larvae of codling moth, *Cydia pomonella* in stored walnuts (Zettler *et al.* 1999).

Insect eggs are the most tolerant stage to the fumigation action of sulfuryl fluoride which is also a limiting factor. To overcome the failure in the control of egg stages of pests, use of sulfuryl fluoride in combination with other fumigants such as hydrogen cyanide (HCN), CO_2, phosphine or heat has been proposed. In Germany, a combination of 2 g m^{-3} of HCN and about 30 g m^{-3} of sulfuryl fluoride provide successful control of the pests within 40 hours. By combining sulfuryl fluoride with heat could provide complete control of egg stages of main pests of stored products. Further, sulfuryl fluoride can also be applied under reduced pressure so that the exposure period can be drastically reduced (Zettler and Arthur 2000).

Propylene oxide

Propylene oxide (PPO) is a colourless, flammable liquid commonly used in the chemical industry as an intermediate industrial product besides its use as a food emulsifier, surfactant, cosmetic and starch modifier. Under normal temperature and pressure, it has relatively low boiling point (35 °C) and a noticeable ether odour (Weast *et al.* 1986). It is a safe fumigant for use on food and has been registered and used in USA since 1984 as a sterilant for commodities such as dry and shelled walnut, spices, cocoa powder and nutmeats (Griffith 1999). Since PPO is flammable from 3 to 37% in air, it has to be used under low pressures or in CO_2-enriched atmospheres to avoid flammability (Isikber *et al*. 2006). Therefore, PPO with low pressure can replace methyl bromide at commercial level in quarantine and pre-shipment (QPS) conditions where low pressure treatments are technically and economically available and feasible. In contrast to methyl bromide, PPO is not an ozone depletor and degrades into nontoxic, biodegradable, propylene glycol in the soil and in human stomach (Emekci 2010).

Carbonyl sulphide

Carbonyl sulphide (COS), a major sulphur compound naturally present in the atmosphere at 0.5 (± 0.05) ppb, is colourless gas present in foodstuffs such as cheese and prepared vegetables of the cabbage family (Wright 2000). Its traces are naturally found in grains and seeds in the range of 0.05-0.1 mg/kg (Wright 2000; Novarro 2006). As per laboratory findings, COS is effective on a wide range of stored-product pests in all stages, including mites, at concentrations from 10 to 40 g/m^3, at exposure time 1 to 5 days at temperature ≥ 5 °C (Desmarchelier 1994). COS as a fumigant for fumigation of durable commodities and structures was trademarked in Australia as COSMIC-™ since 1992. BOC Limited has an agreement with CSIRO for its manufacture and worldwide distribution (Ducom 2006). Studies in Australia, Germany and the USA revealed that egg stage was highly tolerant to the fumigant; the effective exposure period, however, was half that of phosphine at temperatures above 5 °C (Rajendran 2001). There was no adverse effect on the quality of bread, noodles or sponge cake (wheat), the malting and brewing characteristics of barley, nor a significant effect on germination or plumule length (Desmarchelier *et al*. 1998; Wright 2003). However, there are contradictory reports in the literature on negative effects of COS on germination of cereals except sorghum and barley, off odours in walnuts, in milled rice, and colour change in soybeans (Navarro 2006).

Ethyl formate

Ethyl formate (EF), a volatile solvent, highly flammable, boils at 55 °C and vaporizes rapidly at normal temperature (Emekci 2010) that occurs naturally in a variety of products including beef, cheese, rice, grapes and wine. It is generally recognized as a safe compound (Desmarchelier 1994). It is used as flavouring agent in the food industry (Rajendran 2001; Novarro 2006). It is known to break down into naturally occurring products i.e. formic acid and ethanol. The mode of action seems to be the inhibition of Cytochrome C Oxidase by the formic acid resulting of the hydrolysis of EF (Haritos and Dojchinov 2003).

In India, extensive laboratory tests against insect-pests of food commodities and field trials on cereals, spices, pulses, dry fruits and oilcakes have been carried out on the fumigant. Effective commodity dosage ranged from 300 to 400 g m^{-3} with 72 hour exposure period (Rajendran 2001). EF is registered in Australia for disinfestation of dried fruits and is particularly used for dried sultanas where it is added as a liquid to packages of fruit before they are sealed (Annis and Graver 2000).

To overcome flammability of EF, BOC Limited has developed and registered Vapromate® (for use in Australia since 2005), a cylinderised formulation of 16.7% (w/w) ethyl formate in liquid carbon dioxide (Ducom 2006). It is a new cereal grain, stored product and fresh produce fumigant for application by pressurised cylinders. CO_2 acts in two ways: the mixture in this proportion is non-flammable and it has a synergetic effect; its action is rapid, in a range of 4 to 24 hours. Further, it is a safe fumigant since TLV is 100 ppm for EF and 5000 for CO_2. In case of phosphine-resistant field strain of *Ryzopertha domonica* (F);

laboratory strains of *Tribolium castaneum* (Herbst) and *S. oryzae*, a single dose of 450 g m^{-3} of Vapromate was found to be sufficient to obtain high level of mortality (> 99%) of all stages of *T. castaneum* and *R. dominica* (Haritos *et al*. 2006). Forced flow application of ethyl formate and CO_2 vapours through the grains by means of a pump at a flow rate of 6 l per minute, not only provides more even distribution of the fumigant but also causes very high level of mortality of *S. oryzae* and *T. castaneum* mixed stage cultures (Haritos *et al*. 2006). EF when used with methyl isothiocyanate (MITC), a soil fumigant, could significantly reduce the dosage of EF to below the flammable level. A mixture of EF and MITC (95% EF + 5% MITC) has been patented under the name of GLO2 (Ren *et al.* 2008). GLO2 has been found effective against all stages of the major stored grain insect pests. It is fast acting (less than 24 hours) and requires a short withholding period, about 8 days, but much less with aeration.

Hydrogen cyanide

Hydrogen cyanide (HCN) is a colourless liquid with smell of bitter almonds, flammable and lighter than air. Currently, it is registered only in India, New Zealand and with severe restrictions in Germany (Navarro 2006). Earlier HCN has been used to fumigate mills in various countries (France, Germany, Switzerland) (Rambeau *et al*. 2001). HCN can be used for fumigation of many dry foodstuffs, grains and seeds.

Due to high degree of sorption at atmospheric pressure, it does not have the quick effective penetration that methyl bromide has (Emekci 2010). It is easily dissolved in water and thus will bind with moisture and can be difficult to ventilate. Although HCN is strongly sorbed by many materials, this action is usually reversible when they dry, and, given time, all the fumigant vapours are desorbed (Navarro 2006). Further, the high dermal toxicity of the gas makes it hazardous to applicators.

Carbon disulphide

Carbon disulphide (CS_2) is an old fumigant used at the farm level in some parts of Australia and to a limited extent in China (TEAP 2000). Though, the fumigant has only small effect on germination, but residues of carbon disulphide 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 (Navarro 2006).

Methyl iodide

Methyl iodide (MI) was patented as pre-plant soil fumigant for the control of broad range of organisms including nematodes, fungi and weeds (Grech *et al*. 1996). The patent was subsequently expanded to include structural fumigation against termites and wood rotting fungi (Ohr *et al*. 1998). Potential of MI as a fumigant for post-harvest pest control has been known since about 77 years (Lindgren 1938). But its development could not be pursued in favour of less-expensive methyl bromide. MI is most toxic to eggs and least toxic to adults of *Sitophilus granarius*, *Sitophilus zeamais* Motschulsky, *Tribolium confusum*, and *Plodia interpuntella* (Goto *et al*. 2004). Though, MI is considered as a carcinogenic compound, the US Environmental Protection Agency (EPA) has registered it as a soil fumigant since 2007 (EPA 2009).

Ethane dinitrile/Cyanogen

Ethane dinitrile (EDN), also known as cyanogen (C_2N_2) is a broad spectrum fumigant since it can be used against soil insect pests, weed seeds, nematodes and fungi. It is a colourless gas with an almond like odour and is environmentally safe. The threshold limit value (TLV) of 10 ppm (v/v) compares favourably with that of both methyl bromide (5 ppm) and phosphine (0.3 ppm). It is highly toxic (much more toxic than methyl bromide) to stored product insects and is fast acting (except *Sitophilus* sp.) (Docom 2006) with good penetration capability through the grain mass and it desorbs quickly. Germination of seeds is affected due to phytotoxic properties of EDN.

EDN has great potential for space and flour/rice mills fumigations (Navarro 2006). CSIRO holds patent for use of EDN as a fumigant in the major worldwide markets (Emekci 2010). BOC Limited has signed an exclusive global license agreement with CSIRO for EDN as a soil, timber fumigant and grain sterilant. It is marketed under the trade name Sterigas 1000 Fumigant in Australia (Ryan *et al*. 2006).

Biogas

Biogas, containing about 35% carbon dioxide and rest mainly the methane, primarily produced from cow dung to be used as cooking gas, can also be used to control the stored grain insect pests at farm level. In India, detailed experimentation has been done on this aspect. The killing action is because of the carbon dioxide in the biogas. Though carbon dioxide has been found very effective against the stored grain insect-pests, but its cost and transportation to the site of actual use did not make it viable alternative. One major advantage with biogas is that it is to be used just from the site of production within the farm.

Simply we need some pipes and arrangement to divert it through the air tight grain storage structures as and when needed. This makes it very cheap and convenient to use.

Considerable work has been done in India and China to prove the applicability of biogas as stored grain insect control agent. Pioneering research work on biogas was done in Punjab state of India by Singh and co workers in early 1990's where they reported that it can be used in airtight metal or PVC bins to check infestation by major stored grain insect pests for about 3 months with just one exposure of 6 days (Singh *et al.* 1994). Continued research (Sharma *et al*. 2006) also revealed control of the pulse beetle, *Callosobruchus maculatus* (Fab.) resulting in 100% mortality of both egg and adult stages of the beetle. On-farm trials by passing biogas from the plant through the stored wheat up to 10 quintals, showed success of the technology in ensuring insect-free wheat (Chhuneja *et al*. 1998). The biogas did not affect germination or quality of the wheat.

The optimum biogas flow rate required to remove the oxygen from an empty container and partially grain filled container was found to be 40 ml per minute sustained up to a time leading to an equivalent of three times the volume of the grain container. Using these fumigation conditions 100% adult mortality was observed in *Tribolium castaneum* and *Rhizopertha dominica* within 24 hours and *S. oryzae* within 48 hours (Chanakya *et al.* 2015).

Ozone

Ozone (O_3), a powerful oxidant and a known sterilant, had great potential to be used as insect control agent and inhibitor of mould spore development in the stored grain at levels less than 45 ppm (Rajendran 2001; Navarro 2006; Pimentel *et al*. 2009; Tiwari *et al.* 2010; McDonough *et al*. 2011). Ozone can be readily generated from atmospheric oxygen on the treatment sites and is safe to the environment. However, being highly unstable, it quickly breaks down to the molecular oxygen. But, a major disadvantage with ozone is its corrosive property towards most of the metals (Mason *et al*. 1999). This has, therefore, necessitated a special ozone air delivery and return system for an effective ozonation treatment of the storage facility (Campabadal *et al*. 2007). Ozonation experiments yielded 100% mortality for *Sitophilus zeamais* and *Tribolium castaneum*, placed at 0.6 m below the popcorn grain surface (Campabadal *et al*. 2007). Research on ozone treatments to kill stored product insects, including the maize weevil *Sitophilus zeamais*, the rice weevil *Sitophilus oryzae*, the red flour beetle *Tribolium castaneum*, the confused flour beetle *Tribolium confusum*, the lesser grain borer *Rhyzopertha dominica*, the Indian meal moth *Plodia interpunctella* and the Mediterranean flour moth *Ephestia kuehniella* (Kells *et al.* 2001; Leesch 2003; Athanassiou *et al.* 2008; Isikber and Oztekin 2009; Geovana *et al.* 2015) is being undertaken in different parts of the globe.

Modified Atmospheres

Use of Modified Atmospheres (MAs), rich in carbon dioxide and low in oxygen, dates back to ancient times when Egyptians practiced hermetic storage of grains (White and Leesch 1996). Presently, importance of MAs has been enhanced given to the demand for pesticide-free organic food. Terms used in reference to MA storage for control of storage insect pests or for preservation of food have also appeared in the literature as CA (Controlled atmosphere), as sealed storage, or atmospheres used at high or low pressures to define the same method of treatment but using different means (Navarro 2006). Technology of MAs can be well adapted where cheap sources of nitrogen or carbon dioxide are available and the storage structure is well sealed (Rajendran 2001). Till now, MAs composed of either CO_2, N_2 or inert gases have classically been used in different parts of the world for the fumigation of a variety of commodities including grains, pulses, tree nuts, dried fruits, coffee and cocoa beans, spices, medicinal herbs, geophytic bulbs and historic artifacts (Adler *et al*. 2000; Cheng *et al.* 2013).

Low-oxygen atmosphere generated on-site from air through pressure-swing absorption and subsequent filtration through a carbon molecular sieve or through membrane systems or from locally available liquid nitrogen sources has been exploited for disinfesting and storage of food grains in Germany and Australia. Carbon dioxide-rich atmosphere has been found suitable for the protection of dried fruits in Israel and Turkey and for treating grain elevators in Canada (Donahaye *et al* 19984 Ferizli and Emekci 2000; Emekci *et al*. 2007).

Carbon dioxide treatment requires a longer exposure period of 10 days or more; this drawback can, however, be overcome in combination with positive pressure or elevated temperatures which increases performance of MAs. Significant reduction in exposure time to a few hours can be obtained with the use of high carbon dioxide under high pressures ranging between 10-37 bars (Emekci 2010). Eggs, especially in early stages of development were known to be less sensitive to high pressure carbon dioxide treatments than other stages (Adler *et al* 2000; Navarro 2006). Increase in temperature also helps MAs to decrease the lethal exposure time significantly (Donahaye *et al*.

1994).

Hashem *et al*. (2014) studied the susceptibility of the different life stages of the Indian meal moth *Plodia interpuntella* and almond moth *Ephestia cautella* to MAs containing 40, 60 and 80% CO_2 in air at 27 °C. They showed that five days were adequate to kill all eggs and pupae of the two moths under all these MAs. Exposure time needed to be extended to 6 and 7 days at 80% CO_2 to obtain complete mortality of larva of *Ephestia cautella* and *Plodia interpuntella*, respectively. Hashem *et al.* (2014) studies showed that no adults were produced from 4th instar larva of *Sitotroga cereallela* treated with MAs after a 264 h (11 day) exposure for 25% CO_2, 240 h (10 day) for 40% CO_2 and only 168 h (7 day) for 60% CO_2 .

Volatile plant oils as fumigants

Though plant products are known to be mixed with stored grains to ward off insect pests since centuries ago but application of plant oils as fumigants in the protection of stored products is in its infancy (Cox 2002). There is enough literature on the fumigant action of different volatile essential oils of botanical origin to control stored grain insect pests (Shaaya *et al*. 1997; Tunc *et al.* 2000; Weaver and Subramanyam 2000; Rajendran and Muralidharan 2005; Isikber *et al.* 2008; Korunic *et al.* 2008; Rajendran and Sriranjini 2008). Unfortunately, standard test methods applicable for fumigants have not always been followed in the assays (Rajendran 2001). Perhaps, mortality of insects exposed to plant products has been assessed too early. The time taken to express mortality response by the insect treated with fumigants is known to vary between compounds and between the doses of a particular chemical. Besides, data on the toxicity of plant sources against mixed -age cultures containing all developmental stages of stored product insects are lacking (Rajendran 2001).

Most of the research with plant oils as fumigant was carried out in empty fumigation chambers and thus may not reflect the actual fumigation situations where penetration of the plant extracts into deep layers fails, due to strong absorption by the commodity (Emekci 2010). Moreover, aromatic scents of the essential oils permit them only to be applied in empty premises or to the commodities such as seeds where the scent of the volatile essential oil would not present a restriction after the treatment. Another important constraint for the use of botanical extracts is that such alternatives of plant origin also need toxicological and safety data for registration for use as fumigant (Navarro 2006).

Conclusions

Methyl bromide (MB), a cheap, broad spectrum fumigant with remarkable penetration ability and quick action that has been phased out honouring 'Montreal Protocol' is yet to find an equally competent alternative. This is both a challenge and urgent necessity. Phosphine is widely used worldwide, and is the only fumigant currently used in India, because of its low cost, availability and residue-free treatment. But limitation of use of phosphine is development of resistance in the major stored grain insect pests, the world over. There are several other alternative fumigants which are location/situation specific, but cost remains a serious factor, especially for country like India. One such alternative is sulfuryl fluoride which has been found quite promising to fumigate buildings, transport vehicles, wood, flour mills, food factories, dried fruits, tree nuts and cereal grains is marketed in USA (Vikane; Profume) and China (Xunmiejin). But, the fact that it has the potential of acting as a greenhouse gas, may restrain its use as a fumigant, in future.

Propylene oxide, though a safe fumigant for use on food and has been registered and used in USA since 1984 as a sterilant for commodities such as dry and shelled walnut, spices, cocoa powder and nutmeats, is flammable and has to be used under low pressures or in CO_2-enriched atmospheres to avoid flammability. Carbonyl sulphide, as a fumigant for durable commodities and structures was trademarked in Australia as COSMIC-™ since 1992. However, there are contradictory reports in the literature relating to negative effects of carbonyl sulphide on germination of cereals except sorghum and barley, off odours in walnuts, in milled rice, and colour change in soybeans.

Ethyl formate, quite effective for dried fruits and several other stored products, is registered in Australia since 2005 (Vapromate®). To overcome its flammability a cylinderised formulation of 16.7% (w/w) ethyl formate) in liquid carbon dioxide has been developed. Hydrogen cyanide (HCN) is registered in India, New Zealand and Germany (Navarro 2006), can be used for fumigation of dry foodstuffs, grains and seeds. But, due to high degree of sorption at atmospheric pressure, it does not have the quick effective penetration as that of methyl bromide. But high dermal toxicity of the gas makes it hazardous to applicators. Methyl iodide, though recommended by US EPA as soil fumigant since 2007; but there is a question mark on its acceptability because of having carcinogenic effect. `

Though efficacy of various plant oils as fumigant, is amply on record, but lack of systematic toxicological data utilizing standard techniques does not reflect any worthwhile future for application of the same as successful agents to control stored grain insect-pests. Use of Modified Atmospheres (MAs) seems to be the best bet for pesticide-free organic storage but the technology of MAs can be well adapted where cheap sources of nitrogen or carbon dioxide are available and the storage structure is well sealed. This does not appears to be very practical for developing or under-developed countries, particularly at the farm/ farmers' level. There is a better option for countries like India if source of bio-gas is available at the farm level in the form of biogas plant wherein the gas is produced from the cow dung. Ozone (O_3), a powerful oxidant and a known sterilant, also has a great potential to be used as insect control agent and inhibitor of mould spore development. However, being highly unstable, it quickly breaks down to the molecular oxygen. Further, a major disadvantage with ozone is its corrosive property towards most of the metals. This has, therefore, necessitated a special ozone air delivery and return system for an effective ozonation treatment of the storage facility.

Given to the kind of storage facilities in India, at present phosphine in tablet form is the only fumigation technique adopted for disinfestations of godowns and even at the farm level farmers are using it to save their stored grains from the damage by insect-pests. One way to increase the efficacy of phosphine could be to use it in cylinder-based formulations with or without carbon dioxide or generators producing phosphine by pouring a granular form of aluminium or magnesium phosphide in water. Though it may not be very appropriate to use CO_2 given to the filling and transportation of CO_2 cylinders but the farm houses where bio-gas plants are installed, use of biogas will both be economical and convenient. Though some work has been done in this direction, more efforts are needed to show its practicability as a cheap and convenient way of saving the stored grains from the attack of stored grain insect-pests at the farm level storage. This could be a good substitutes in all those farm houses where bio-gas plants are installed.

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