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METHYL BROMIDE ALTERNATIVES

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ABSTRACT

Methyl bromide (MeBr) is the fumigant of choice for almost all commercial and quarantine fumigations for disinfestation. Since 1992, it is regulated as a significant ozone depleting substance and it is phased out since 2005 with several exemptions like quarantine and preshipment, critical uses and article 5 countries. The main characteristics of MeBr are excellent effectiveness on insects, mites and nematodes, whatever the temperature if it is above 5°C. The exposure time is between 2 to 24 h, and the dosage changes with the temperature. As direct alternatives, only two fumigants remain, phosphine for all stored products and sulfuryl fluoride (SF) for some stored products and structural fumigations. For commercial fumigations, there are two ways to find alternatives: keep the same technique with a curative disinfestation or change completely the way of the treatment. The same (in-kind) techniques are fumigants, included phosphine gas, controlled atmospheres including high pressure CO_2, and also contact insecticides, heat and cold, irradiation and some other techniques. The other way is to completely change the production, for example by introducing a better IPM. For quarantine fumigations, it is much more complicated because all the standards used for disinfestation come from lot of studies carried out in many countries, often long ago, giving international rules, based on the probit 9 (99.9968% efficacy). The change to another curative disinfestation like heat, cold or other fumigants needs new studies to prove the quarantine efficacy which means money and time. Systems approaches capitalise on cumulative pest mortality from multiple control components to achieve quarantine security in an exported commodity. In conclusion, many techniques exist for commercial and quarantine MeBr fumigations but they require changes in habits and many times have economic implications. Nevertheless, the ban of MeBr is a fantastic opportunity to find new ways from old or new techniques.

INTRODUCTION

Methyl bromide (MB) is a very old fumigant, discovered in 1932. It was used for almost all the fields where disinfestation was a necessity, for commodities, wood and wooden products and quarantine on an infinite number of products. It has very particular properties, since it can kill all types of insects, mites, nematodes, etc. at any stage, very quickly, in 24h maximum, whatever the temperature; only the dosage varies with the temperature.

Unfortunately, in 1992, it was identified as an ozone depleting substance and it has been banned for use on stored commodities since January 2005, except for some uses under the CUN[1] rules and Quarantine and Preshipment. Alternatives to MB are to be found for all uses of MB. But, it is impossible to find a universal alternative like MB. That is why, for each family of product, or even for each species for quarantine purposes, an alternative has to be found or searched for. In fact, many compounds or techniques were available, but they were not in use because they were too specific, too expensive or led one to change the disinfestation method. Since MB permitted any disinfestation quickly, efficiently and cheaply, the incentive to do research was blocked. The decision of the parties at the Montreal protocol allowed one to have a new look at what existed other than MB and gave the signal for a lot of research which has often led to progress in quality on products, residues, human safety, etc. Every four years, the MBTOC[2] has requested there be an assessment report update on all the alternatives to methyl bromide and each year, it has the duty to evaluate the CUNs in light of the available alternatives and other criteria like registration, economics, etc…These assessments (1994, 1998, 2002, 2006 and 2010) are the basis for this paper and they can be found on the website at this address: http://ozone.unep.org/teap/Reports/MBTOC/index.shtml.

HOW METHYL BROMIDE WAS DISCOVERED AND FIRST USED?

MB was discovered by Mr Le Goupil, who was searching for an alternative to carbon disulfide (CS2) and hydrogen cyanide (HCN) to decrease fire risks. These fumigants were used under partial vacuum (Mallet system) for quick treatments in harbours. He carried out experiments with MB among some other compounds. He found that MB was an insecticide by itself, in a vacuum with an exposure time of 1.5h and different dosages. Even if the insects seemed to be alive just after the exposure time for the lowest dosage used, 25g/m^3, they die very quickly after some hours. He presented its efficacy at the "Academie d'Agriculture" in 1932. Two years later, the harbours of Bordeaux, Le Havre and Marseille, were fumigating quite a lot of their imported products with MB. At that time, MB was not considered very toxic for humans, except in massive doses.

MB is a very good fumigant for many reasons: it is fast-acting; in 1.5 h to 2 hours or 4 hours in a vacuum, in 24 h at normal atmospheric pressure, the temperature does not change the exposure time, only the dosage is adapted to this temperature, a bigger dosage at low temperatures and conversely at high temperatures. It is very cheap. Its efficacy is very well known, since it has been used for almost 80 years and the CTP gives a very good criterion for efficacy.

Nevertheless, it also has some adverse effects. It leaves some bromide residue with acceptable MRL, but residue is present and sometimes exceeds the MRL. It has some negative effects on fruits, vegetables and seeds, which are manageable if precautions are taken. Its human toxicity is at a high level, acute and chronic, and it can be carcinogenetic.

[1] CUNs : Critical Uses Nominations, but these require a country to demonstrate, year after year, the need for MB for some production.

[2] The Methyl Bromide Technical Options Committee (MBTOC) is the technical body for MB of the Technical and Economical Assessment Panel (TEAP) which advises the Parties to the Montreal Protocol.

Last, but not least, it was identified as an ozone-depleting substance and should be banned for all uses in the future.

These negative aspects have led companies to use some "alternatives", in fact, phosphine instead of MB, but just when the time and temperature were not a constraint and mainly for dried fruits and nuts, herbs and beverages.

For post harvest, MB was used as an insecticide and acaricide for all commodities, structures and, for quarantine, for wooden pallets, logs and many fruits and vegetables. The need for alternatives is huge, because one alternative can work on one product, or for one situation, but not for other ones.

HOW IS AN ALTERNATIVE TO METHYL BROMIDE DEFINED?

What is a real alternative to MB? It is difficult to answer this question since we can see the problem from different viewpoints.

The first viewpoint is linked to exposure time and temperature. Strictly speaking, an alternative to MB is a treatment, which kills pests in one shot and in a very short time whatever the temperature. Only heat and CO2 under pressure can compete with it, also methyl iodide in the future if it is registered and irradiation if available. Less strictly speaking, it is a treatment, which kills pests in one shot, but exposure time will depend on the temperature and it may be long. Typically, these alternatives are phosphine and CA.

There is another way, i.e., to completely change the production process. For example, for shipment, to avoid the necessity to have to carry out a quick treatment just before shipment, all the conditions of pest control should be changed. That has to be designed in the long term and may cost a lot.

The second view is a problem of efficacy, mainly for quarantine: Some pests are only killed by MB, or at least until now. Alternatives have to be found through research and the difficulty comes from the fact that lot of niches have to be studied.

The parties to the Montreal Protocol have defined what is an "official" alternative. *MBTOC assumes that an alternative (Refer Decision IX/6 1(a)(ii)) demonstrated in one region of the world would be technically applicable in another unless there were obvious constraints to the contrary e.g., a very different climate or pest complex. Additionally, it is recognised that regulatory requirements or other specific constraints may make an alternative available in one country but unavailable in another specific country or region. When evaluating CUNs, MBTOC accounts for the specific circumstances of each Party*.

This definition is not really only about technique, but it is necessary to have such a definition to evaluate the CUNs.

MBTOC has identified some remaining uses without technically effective alternatives: disinfestation of high-moisture fresh dates, cheese and cured pork products infested in storage in the USA, immovable museum artefacts (especially when attacked by fungi in some circumstances). Obviously, the MBTOC concept takes into account much larger considerations than just the technical points presented above. In these cases, alternatives exist but are not possible to use for the specific circumstances.

In fact, almost all uses of MB have an actual or theoretical alternative. There are just a few examples where there is still no alternative. Below are two examples.

Ditylenchus dipsaci Filipjev is a quarantine pest living in part inside alfalfa seeds, and only MB may kill it. Some countries do not use disinfestation, but that means that any lot recognized as infested is withdrawn. It costs a lot. That is the fact now in France where MB, like in all the EU, is banned for all uses and the loss for the seed companies is very high.

Cocoa beans are stored long before shipment in very big warehouses on the harbour in tropical conditions, like in Abidjan, Cote d'Ivoire. There is no way to control 100% of the infestations in these conditions. Usually, phosphine fumigation is carried out some days before shipment. If the ship comes sooner than scheduled, and if, just before loading, the stock is recognised as infested, the only means to export cocoa beans is to use MB fumigation.

ALTERNATIVES FOR COMMODITIES

There are many viable alternatives to methyl bromide fumigation for commodities, including: Integrated Pest Management (IPM), fumigants (phosphine, sulfuryl fluoride), contact insecticides, temperature manipulation (heating and cooling), controlled atmospheres (low oxygen and fumigation with carbon dioxide), and some other means less effective ones, which cannot be called alternatives like *Bacillus thuringiensis*, insect growth regulators, viruses, biological controls, etc.

IPM is a broad, rational, ecological approach to solutions of pest problems by combining, either concurrently or sequentially, biological, physical and chemical tools to ensure pest control while ensuring the protection of the environment, a maintaining of profitability and fulfilment of consumer demand for decreased or no pesticide use. An IPM program has to provide effective for pest prevention, based on an accurate pest monitoring system and provide training for industry staff for the tools employed to maintain an acceptable level of control. In the context of phasing out methyl bromide, IPM should be defined as a means of minimising chemical use, but also incorporating full site or curative treatments, involving fumigation or other processes as part of the program. IPM should be considered a required pre-requisite for any means to control insects. It is not an alternative to MB by itself.

Phosphine is the only fumigant, as methyl bromide was, which is widely registered for disinfestation of durable commodities. It is, in fact, the only available alternative extensively in use, for most commodities: cereals and legumes, dried fruit and nuts, beverage, herbs and spices, etc. It is a cheap fumigant, leaving no residue after desorption. It has replaced MB long before its regulation by the parties of the Montreal Protocol each time when temperature and time were not a constraint.

Its action against pests tends to be much slower than methyl bromide, with long exposures required, particularly under low temperatures. This is due to the mechanisms of phosphine action, which requires active oxygen metabolism and mitochondrial activity to allow, through respiration, the toxicity of phosphine. These mechanisms were well described by Kuang et al. (2008). That is why phosphine is usually not recommended at temperatures below 10ºC, or even 15ºC in some countries for stored product insects. Depending upon the temperature, fumigations with phosphine require from three to fifteen days for full effectiveness, this is in contrast to the 24-hour period used for methyl bromide over a wide range of temperatures.

Solid formulations produce *in situ,* by reaction of atmospheric moisture, the phosphine gas. They can be made of aluminium phosphide, or less commonly, magnesium phosphide in several presentations such as tablets, bags and pellets, which are widely available and have been in use for over 50 years. Phosphine generated from metallic phosphides is produced slowly and that is another negative aspect of these formulations as an alternative to MB.

Two types of phosphine gas production have been developed to overcome its slow release. The first type are the cylinder-based formulations containing phosphine mixed with carbon dioxide at 2% (Eco_2Fume®), nitrogen at 1.7% (Frisin®) or pure phosphine (Vaporphos®) developed in recent years. The pure phosphine in cylinders has to be mixed with nitrogen to reduce the phosphine concentration (Horn Diluphos System®).

The second type are the generators working with formulations of metal phosphides and water to produce phosphine at a very high rate (phosphine generators from Degesch, Liang Mao Technology Development Co and UPL). With these devices, it is necessary to introduce the phosphine into a recirculation system, which is designed to give a perfect, even concentration of phosphine. Because the fumigant is rapidly available, it has been possible to shorten to some extent the exposure time whilst still maintaining fully effective disinfestation. In addition, phosphine is produced whatever the temperature and the humidity.

With these new quick production processes can we say that phosphine may replace MB? Not exactly, because temperature remains a constraint, which controls the exposure time. Even at 30°C, the biology requires 3 days to kill all stages. In conclusion, phosphine is an alternative to MB only if time and temperature are not a constraint.

Sulfuryl fluoride is an excellent example of the potential risks, which can happen when an alternative seems at first sight very good, but some hidden aspects suddenly appear.

Sulfuryl fluoride was developed in the late 1950's in the USA as a structural fumigant, mainly for termite control. Sulfuryl fluoride is highly toxic to post-embryonic stages of insects, but the eggs of many moths and beetles are difficult to control, especially at lower temperatures (Ciesla and Ducom, 2010). Early research indicated that the lower activity on eggs is primarily due to slow penetration through the chorion and eggshell.

The U.S. Environmental Protection Agency (EPA) first registered the agricultural use of sulfuryl fluoride in 2004 as an insecticide. Two main usages were registered, structural fumigation and commodity fumigations for cereal grain, beans, dried fruit, tree nuts, cocoa beans, etc. Temporary tolerances were established in 2001 for residues of fluoride resulting from the post-harvest treatment with SF. The tolerances are measured and expressed as ppm of fluoride. In EU, very few tolerances were established to allow a SF fumigation. The tolerance for nuts (25 ppm) is too low to allow treatment of chestnuts in normal fumigation practice. For cereals and cereal products, 2 ppm is usually not enough to allow a fumigation, even too low for inadvertent contact during a structural fumigation.

Very recently, on May 1 2012, the EPA opened a second comment period on the proposed order to revoke residue tolerances for sulfuryl fluoride (SF) on food and cancel associated uses. The Agency found that when residues on food products are combined with fluoridated drinking water and toothpaste, aggregate exposure levels are too high. The tolerances could be soon withdrawn and the use of SF reviewed.

A typical application rate is 40 to 60 g m^{-3} for a fixed duration of 24 hours with CTP's not over 1500 gh/m^3, essentially for reasons of residue.

Controlled or modified atmospheres is based on carbon dioxide and nitrogen. Low oxygen atmospheres, typically created by adding nitrogen to a fumigation enclosure, require that there be a maximum of 1% oxygen for effective action. Carbon dioxide atmospheres are typically applied at about 60% CO2 in the air. At this level, there is about 8% oxygen present, normally enough to support most stored product pests indefinitely. CO2 is thus regarded as having a toxic effect on insect pests and not acting just as an inert gas that reduces the oxygen level to below that supporting life. Most species are completely controlled by exposures of 1 - 3 weeks at 25 – 30°C.

In conclusion, CAs are useful alternatives if time is not a problem, but require a high level of investment cost. But, like for phosphine, CAs are a real alternative to MB only if time and temperature are not a constraint

The latest method combines carbon dioxide with high pressure of 20 to 40 bars and controls all stages and species of insects within less than three hours. It requires a gas-tight chamber, which can withstand pressure of this kind and may require a high capital investment. This method is really an effective alternative to MB, since it acts in several hours, whatever the temperature.

Heat treatment, if possible, is a real alternative to MB. Most stored-product insects are killed within hours after exposure to temperatures of 50°C or more (Fields, 1992), and, at lower temperatures, mortality can be related to the time that the insects are exposed. High temperature treatments are used for disinfestations of dried fruits and nuts and grains. Recently, heat treatment has been adapted to the treatment of dates in Israel by Navarro *et al* (2004). The treatment of 2 hours at 50°C resulted in 92% disinfestation of key pests; at 50 – 55°C, 100% mortality was observed. Navarro and co-workers noted that in their samples, the pests emigrated from the dates during the treatment.

Cold, at around 5°C, is typically used to prevent damage, multiplication and reinvasion of pests. Is not an alternative. However, freezing, with temperatures at around -20°C, is a real alternative to MB, but the treatment time is long, typically, one week, to allow the product to be frozen in the centre of a big bag, for example.

These treatments may be useful in specific instances, such as small museum objects or small quantities of cereals where a mild non-chemical disinfestation is required. Under these circumstances, they can present an alternative to methyl bromide use.

Dupuis et al (2006) examined the use of cold to kill all life stages of the bean weevil (*Acanthoscelides obtectus* (Say)) in beans immediately after harvest. The beans are used for both seeds and human food. They found that a temperature of -22°C has to be reached in the centre of the bean mass to ensure disinfestation.

Contact insecticides are used only on cereal grains. They work through residual deposits on the grain. These compounds are alternatives to phosphine more than for MB.

ALTERNATIVES FOR STRUCTURES

Structural fumigation is a pest management technique that provides broad-spectrum control and the ability of the fumigant gas to kill the pests that are not on the surface and cannot be readily contacted by other types of pesticide applications. The ability to penetrate through packaging materials, walls, and other areas to hidden infestations is particularly valuable in structural fumigation. That is why MB was used and an alternative to MB has to be a gas or heat.

Since the 1900's, pest control in mills and other structures were based on occasionally full site treatments. Contact insecticides were not yet discovered and to decrease insect pest populations, the only solution was a full site treatment. Fumigation was the most widely used technique, but in some countries such as the USA, heat was also used. The only fumigant used was hydrogen cyanide (HCN). MB came much later as an alternative to HCN. There were some reasons to change: it was easier to apply than to manage the impregnated cardboard HCN formulations, there was much better penetration in all parts of the machinery and equipment even if it was full of accumulations of flour and milling residues. For example, in France, mills were fumigated with HCN until the 70's, in Switzerland until the beginning of 2000 and still in use in many eastern European countries. Nevertheless, its use should be reconsidered positively because of its efficacy against the major flour mill insects, *Tribolium* spp. A CTP of ~5 g h m^{-3} gives a LD90, at all stages, at 20°C instead 1000 g h m^{-3} or more for SF (Rambeau et al, 2000). Gas introduction should be revised.

Now in, pest control is essentially based on IPM. IPM should be considered a required pre-requisite for any means to control insects by an accurate pest monitoring system, associated with contact insecticides and full-site treatment. The presence of food and other materials in these facilities dictates the type of treatment, which may be utilised. Some fumigants, for instance, have no food tolerances set or may adversely react with non-food materials in the structure.

Sulfuryl fluoride is non-corrosive, an important characteristic for a fumigant, especially in settings where sensitive equipment and electronic devices are present. Sulfuryl fluoride is highly toxic to post-embryonic stages of insects, but the eggs of many moths and beetles, especially eggs of *Tribolium castaneum* (Herbst), are difficult to control, especially at lower temperatures. Efficacy of treatment for eggs was significantly enhanced by increasing the temperature from 25 to 30°C and a complete control of eggs of most species was obtained by a concentration time product of 1000 g h m^{-3} at 25°C and about 700-800 g h m^{-3} at 30°C.

A concern is the MRL for fluoride residues arising from SF treatments on cereal grains, flour and other derivatives. In some countries, like in EU, MRLs are uniform for all grain and grain products at 2 ppm fluoride. As a result, the flour present in the milling machinery has to be withdrawn by turning the mill one hour. That is an extra cost. In addition, if flour bins are built inside a building, SF may penetrate through the concrete or some leaks and the F^- residues will be very quickly higher than the 2 ppm limit. Klementz et al (2008) found, in these situations, residues between 3 to 10 ppm. But it is just impossible for the miller to empty these locations. This situation could also happen in the US if the MRL for cereals and cereal products were significantly decreased or removed.

At last, it should be mentioned that SF has been identified as a greenhouse gas. It is a strong absorber of IR radiation and has a long atmospheric lifetime (on the order of 30-40 years). It has a very high Global Warming Potential, GWP of ~4000, CO2=1. But it is not a current problem since its abundance in the atmosphere is very low, 1.5 ppt ($1.5x10^{-6}$ ppm) in comparison with 390 ppm for CO2 (Andersen, 2009).

Heat treatment of structures is an age-old technology for managing insects associated with food factories and especially flour mills. In general, heat treatment involves raising the ambient temperature of a food-processing facility to 50-60°C and holding these temperatures for 24 h to kill all life stages of stored-product insects. Some companies extend this time to at least 36 h. Flour is a good insulator, and before heat treatments, flour mill staff do extensive cleaning to remove flour that can serve as refuge for insects to escape the heat. It is a useful action to avoid future infestation.

Mortality in insects at high temperatures depends on both the temperature and time of exposure. Insects are killed by desiccation and protein denaturation.

Heating the building may be carried out by different techniques. With forced air gas or steam heaters, the building is placed under positive pressure during the heat treatment. The heaters are placed outside the building. It allows heat to reach gaps in the building and equipment much better than static heaters. Heating may be conducted with many static electric heaters placed inside the building on different floors and different places. For both techniques, several fans should be placed on different floors to redistribute heat and to uniformly heat the building. During heat treatments, fans should be moved to eliminate cool spots-areas where the temperature is less than 50°C.

In addition to food-processing facilities, heat treatment can also be used in empty storage structures (bins, silos), warehouses, feed mills, and bakeries. It is an environmentally benign method for managing insects.

In conclusion, heat treatment is very effective as full-site disinfestation, except in crevices or in the basements which are difficult to heat to the required temperature.

Contact insecticides are part of IPM, used when monitoring shows an increase in pest population, and between the full-site treatments. They are used in two ways. The first, by spraying the surfaces with long-lasting insecticides such as pirimiphos methyl, chlorpirifos methyl, deltamethrin, etc. The second way, by fogging in the volumes with quick-acting insecticides, like pyrethroids or dichlorvos. Dichlorvos was banned in EU in 2008, and since then, we do not have effective foggings, because it is the only contact insecticide with a high vapour pressure, able to kill insects anywhere. There is no alternative to dichlorvos.

ALTERNATIVES FOR QUARANTINE

Quarantine pests are listed pests. These pests are potentially of economic importance to the area endangered thereby and not yet present there (Quarantine pest, e.g. list A1 for EPPO, European and Mediterranean Plant Protection Organization), or present, but not widely distributed and being officially controlled (Regulated non-quarantine pest, list A2 for EPPO).

A quarantine pest is not a common pest. In many countries, there is a confusion between unacceptable pests, which are qualified as quarantine pests whereas they are only common pests, even if they are of commercial importance. For example, for cereals or rice, pests are common, but they are often called quarantine pests. The difference is important for disinfestation: the target efficacy for control of a quarantine pest should be better than 99.997% mortality (probit 9). For "commercial" pests, most of the time, a 99% kill of all stages is recognised as sufficient.

Methyl bromide is the treatment of choice for many reasons, particularly because it is effective against all life stages of a wide range of pest organisms, fast-acting and recognised by almost all countries as a quarantine treatment. All other alternatives are more or less specific to a particular species. It is a field in continuous progress. MB used to be the unique compound used for treatment. Already, many alternatives have been discovered, but it is very difficult now to be able to search for all needs. Alternatives include many chemical, physical or even logistic systems.

The development of postharvest quarantine treatments can be both expensive and time-consuming. It is necessary to determine the most tolerant stage of the pest to the treatment by laboratory studies, then on a full scale, with a mortality of > 99.997%.

Wood Packing Materials

Heat according to ISPM 15 is currently the only recognized treatment, apart from methyl bromide. Potential alternatives have been submitted to the IPPC and are under evaluation. These include SF, SF + methyl isothiocyanate (MITC) mixture, hydrogen cyanide, phosphine, methyl iodide and ethanedinitrile (EDN). Their efficacy against the main species of insects: of *Agrilus planipennis* (Emerald Ash Borer), *Anoplophora glabripennis* (Asian longhorned beetle) and *Bursaphelenchus xylophilus* (Pinewood nematode, PWN) is evaluated by the IPPC with the target of probit 9. Until now, any of these compounds was accepted.

MITC is a very effective compound used for soil disinfection and is also available mixed withethyl formate. The mixture is registered only in Japan for wood-boring insects. HCN is a very effective gas, but sorption is important and decreases the actual concentration.

Methyl iodide is very close to MB except that it does not deplete the ozone layer, since it is rapidly photo-decomposed by UV-light and remains for only a few days in the atmosphere. It seems to possess a lethality similar to MB. Some research has begun on its efficacy on certain wood-boring insects.

EDN has the widest spectrum of efficacy among the new fumigants. It is a gas at room temperature, with an almond-like odour. It is more toxic than MB; it can be used for treating soil, insect pests, weeds and diseases**.** It cannot work in dry conditions. The molecule belongs to Linde under the name of Sterigas™ . It is very promising for wood treatment.

Wood and Logs

Logs, timber and wooden materials are infested by pests of quarantine significance. SF, SF + MITC mixture, hydrogen cyanide, phosphine, methyl iodide and EDN are identified as potential alternatives to MB.

Phosphine is used for the in-transit fumigation of New Zealand export *Pinus radiata* logs destined for China. It is now routinely used as a quarantine and pre-shipment measure and has partially replaced methyl bromide for this purpose. The current dosage specification requires at least 200 ppm v/v of phosphine to be maintained for 10 days. Due to sorption of the gas by the logs, top-up of phosphine is required 5 days into the voyage to prevent the concentration falling below 200 ppm. In-transit tests have shown an even gas distribution throughout the loaded ship holds. High concentrations of CO_2 also occur within the ship holds during the fumigation period that may increase the insecticidal action of the fumigant.

Perishables

This is a very complicated domain, since every species has its own pest and a particular sensitivity to the treatment. The main quarantine treatments apart from MB are physical, cold for a long time at low temperatures like for the Mediterranean fruit fly and others, or heat like for mangoes or papayas.

Many systems exist with combinations of various individual treatments, but each one is specific. For example, CATTS (Controlled Atmosphere/Temperature Treatment System) is a combination of short duration high temperatures under low oxygen, elevated carbon dioxide atmospheric environment.

It is strange that phosphine, traditionally used for stored products with a long exposure time at temperature >10°C or 15°C, shows very good efficacy at 0°C for fruit pests. Since the arrival of ability to inject phosphine, in cylinders or generators, it has become possible to get an instantaneous high concentration of phosphine without ammonia, which may taint or damage the fruits. For example, it is the case with high moisture content dates and chestnuts. A preliminary trial to fumigate fresh fruits (apple, nectarines, pears, grapes and plums) at -0.5°C to +1°C using the Horn Diluphos system indicated that 36-72 h fumigation with 1500 ppm phosphine showed complete mortality of all insects tested at all developmental stages (eggs and larvae) without causing damage to the fruit (Horn et al. 2005). These results are not official ones, and phosphine is not yet an approved alternative to MB for perishables.

Ethyl formate in mixture with CO2 (Vapormate®) seems to have good properties for fruit and vegetables. Nevertheless, due to high concentrations often needed to kill all insects, some phytotoxic effects may occur. Nevertheless, the high moisture content Deglet Noor dates can be treated with $420 g/m^3$, 12-hour exposure time, without any injury with 100% *Carpophilus* mortality. In this case, it is a real alternative to MB. It is registered in Israel for this usage.

COS, carbonyl sulphide, has been tried for perishables and flowers. It is very fast-acting, at above 15°C, mainly on surface insects, but it may be phytotoxic on certain species.

Gamma irradiation has been shown to be an efficient method to treat some fruits. Generally, doses from 0.05 to 0.2 kGy are sufficient for quarantine security. The advantage of irradiation is that the treatment is fast, non phytotoxic, residue-free and fruit can be treated in the final packaging. But the capital costs of irradiation are high, irradiation can render the pest stages sterile rather than dead, and, lastly, it has poor consumer acceptance in some markets.

Other non chemical methods are used. For example, the system approach for fruit flies, includes at least two independent measures which may be applied throughout various stages of the process, specifically during the growing period and harvest; post-harvest and transportation; and entry and distribution within the importing country.

The alternatives to MB for quarantine treatment is a broad very complicated field, because each plant species has its own pest and a sensibility to the stress caused by the treatment. In addition, if it is a chemical, it has to be registered, with residue tolerances. GRAS compound, like EF, or combination treatments with CA and temperature variation have the most promising future, if they can work at probit 9.

CONCLUSION

The banning of MB was considered unacceptable at one time. It was used everywhere as the fumigant of choice, effective on almost all pests and fast-acting whatever the temperature. We know that a universal alternative does not exist, which means that a huge amount of alternatives have to be adopted or found. The existing alternatives were not used at all, or very little for different reasons, mainly for longer exposure times in function of the temperature, but also for efficacy reasons in the quarantine sector. Researchers and companies, since 1992, have made a lot of effort to find new fumigants able to replace MB, like ethyl formate, carbonyl sulphide, ethanedinitrile or methyl iodide. Phosphine, an old fumigant used for dry commodities at temperature >15°C, was surprisingly tried on fresh fruit at very low temperatures. Controlled atmospheres and heat were modernised in their implementation.

Durable commodities have a lot of existing alternatives, and techniques were improved to better use them. Phosphine is a good example of the efforts made by researchers for a better understanding and by pesticide companies to produce it as a gas with different systems, creating a safer and quicker fumigation. Controlled atmospheres are now in common practice with shorter exposure times than before.

Structure fumigation has two true good alternatives, SF and heat, but their implementation is more complicated than MB and the cost is much higher. That leads one to manage the treatments more carefully than before and could lead to better results.

Quarantine remains a very difficult problem. Quarantine gathers together a lot of products of very different natures: wood, seeds, fruits, vegetables, leaves, plants, etc. For each one, the pests are different. Efficacy and non phytotoxicity are the target with one more important constraint, the mortality rate must be higher than 99.997%. In addition, the alternative has to be accepted by the import country. At last, if the alternative is a chemical compound, it has to be registered and as the market is very small and the cost is getting higher and higher, there is no easy solution.

Many niches without alternatives to MB remain, mainly in the quarantine sector and that is an opportunity for research. Nevertheless, with the financial crisis, research may miss this opportunity. The choice for the decision-makers is very difficult: keep MB, that costs nothing in the short term and disregard the ozone layer, or ban MB without research, that costs almost nothing in the short term and disregard quarantine pests? Neither is the valid solution; we need to take this opportunity to start good research in all of the fields covered by MB but it will have to be financed immediately.

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