Fumigation for pest control in stored product protection – outlook

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Fumigants hold their place in storage of feed and food especially for pest control. High volatility and penetrability through bulks of stored goods and quick lethal effect on organisms within these products render gaseous substances suitable tools in the frame of integrated pest control. If insect pests have bypassed all human precautions and prevention efforts, large bulks of stored products can be disinfested by use of appropriate fumigants and fumigation techniques. No other approach leads to such instantaneous and feasible pest control without moving the produce, without building up undesired residues.

Not many suitable chemicals are left for this use. Many compounds showed undesired medical side effects like carcinogenicity in the case of nearly all halogenated compounds. Others like methyl bromide are environmentally not safe and will presumably be skipped due to their ozone depleting or otherwise detrimental potential.

Which compounds are left at present or can be foreseen as promising future candidates for use in pest control:

<table>
<thead>
<tr>
<th>Fumigant</th>
<th>Registered</th>
<th>Location</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphine</td>
<td>×</td>
<td>World</td>
<td>grain, other products, wood, empty space</td>
</tr>
<tr>
<td>Methyl Phosphine</td>
<td></td>
<td>Patent, UK</td>
<td>as phosphine, controls phosphine resistant insects</td>
</tr>
<tr>
<td>Methyl Bromide</td>
<td>until 2005/2015 in Europe and USA only end of 2000</td>
<td>World/Article 5 countries</td>
<td>grain, other products, wood, empty space</td>
</tr>
<tr>
<td>Hydrogen Cyanide</td>
<td>×</td>
<td>G</td>
<td>empty space</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>×</td>
<td>G,F,UK,I,other Europe, AUS,USA,Israel</td>
<td>grain and other products, wood</td>
</tr>
<tr>
<td>Carbon Dioxide under high pressure</td>
<td>×</td>
<td>G, J, USA</td>
<td>spices, drugs, herbs, other products, wooden pallets</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>×</td>
<td>G, I</td>
<td>grain and other products, wood, artefacts</td>
</tr>
<tr>
<td>Sulfuryl Fluoride</td>
<td>×</td>
<td>USA, SWE, G</td>
<td>wood protection, artefacts</td>
</tr>
<tr>
<td>Methyl Formate</td>
<td>–</td>
<td>Research Aus</td>
<td>dried fruits</td>
</tr>
<tr>
<td>Ozone</td>
<td>–</td>
<td>Research F, G</td>
<td>empty space</td>
</tr>
<tr>
<td>Carbonyl Sulphide</td>
<td>–</td>
<td>Research and patent AUS; research USA, G</td>
<td>grain, empty space other products</td>
</tr>
<tr>
<td>Sulphonyl Fluoride</td>
<td>–</td>
<td>Patent G</td>
<td>empty space</td>
</tr>
</tbody>
</table>

* planned
The list is not comprehensive

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At present, tremendous efforts are undertaken to maintain fumigation technology as part of pest control. Peters (1942), Monro (1961) and Bond (1984) wrote their books on fumigation against pests simply as technical descriptions ‘how to do it’. From the late 80ies on, the political dimension of this pest control method changed and
amongst others Bond (1989), Reichmuth (1989, 1990, 1995, 1998) Banks (1994) and Bell (1995) stressed that chemical pest control and especially fumigation with toxic chemicals is an endangered technology. The Methyl Bromide Issue revealed a dramatic need for safer fumigation techniques but also effective fumigants which can be safely and without harm to the environment applied for disinfection, disinfection and sterilisation. For the first time in pest control, there was a world-wide approach in one group of specialists (MBTOC committee) for several years to obtain a clear view as to whether methyl bromide (MB) could simply be discarded and replaced by another chemical or not. The answer was 'yes'. About 10% of the MB applications were considered as critical uses where alternative methods or chemicals were not detected or not at all feasible. The political pressure is still there to phase out the use and production of this gas as quickly as possible. There is no trust among politicians, that a modified use which would prevent the emission-like improved nearly complete recontainment, sorption and reuse has a real chance in the future. This may be linked with the general crisis of trust into promises of scientists and technicians concerning the safety and the risk of a technology. The dramas of the Titanic, Chernobyl, Sandoz, Apollo and other catastrophes undermined this consciousness of safety which was certainly wrong in the first place. Heavy failures are mostly linked in any kind with human carelessness and weakening concentration when working with dangerous substances or technologies. The danger evolves mainly when the precision of following accurately the instructions is not kept at the appropriate level. In so far, man himself is the weak point of this chain. Human nature can hardly be changed and only provisions can be taken to prevent such failures. In the case of the ozone layer there is not much slack to carry on as usual with some minor adjustments. That may have been the reason to decide the phase out.

On the other hand there is now considerable literature accessible MT0C report (Anonym 1994), Methyl Bromide ISSUE (Anonym 1996, Bell et al., 1998) to identify for nearly all areas of MB fumigations alternatives which will need financial and other support to be put into place.

The subject of pest control by fumigation has been given a new push either to improve the use of the other existing fumigants or to look for other old and neglected ones (carbonyl sulphide, alkyl formates) or new compounds (methyl phosphine, carbonyl sulphide, sulphonyl fluorides) which might offer a broad or at least limited potential.

The new developments of the past four years since the previous IWCSPP conference comprise:

- Several approaches of better gas recontainment (in USA, Chile, G)
- Development of a new phosphine generator (in Chile)
- Propagation of modified phosphine fumigation (in UK, USA; AUS; Chile)
- Research into the corrosion potential of phosphine (Canada)
- Launching of SO₂F₂ for control of wood boring insects (in Germany)
- Preparation of SO₂F₂ as empty space fumigant in spp control (in G; UK)
- Investigation of COS as alternative spp fumigant (in AUS; USA; G)
- Investigation of MITC as fumigant (in F)
- Investigation into methyl phosphine as supplement for phosphine (in UK)
- Physical techniques like application of heat, cold and irradiation as alternatives for fumigants (in Canada; USA; G; DK)

The new developments are regularly presented during the International Working Conferences on Stored Product Protection (IWCSPP), the International Conferences on Controlled Atmosphere and Fumigation in Stored Products (CAF), the Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions and other meetings on this subject. The literature is cited in the proceedings.

Only a few focal points should be stressed in this paper without going into too much details on chemical compounds.

The use of the necessary or appropriate amount of gas for an efficient pest control still is one of the critical issues of fumigation. Always, the concrete situation requires the analysis of the present pest and stadium, the infected produce and object, qualities of the structure of the object, crevices, gas tightness, sealability, distance to living quarters and neighbourhood, temperature, humidity, sensitivity of electronic or other parts and pieces within an object which might be sensible towards the selected chemical, the necessary time schedule for thorough pest control.

When looking into the literature there is a tremendous gap of required dosage between the theoretical ct-products to achieve a given mortality from laboratory data (example MB) to the recommended fumigation schedules (Anonym (1982), Howe and Hole (1967), Bond (1984), Anonym (1994), Monro (1961)). The investigation and understanding of this discrepancy may offer a way to reduce the use of large amounts of fumigants. Off course, plenty of the gas is lost in practice during the treatment due to leakage (Banks and Ripp (1984), Sharp (1982), Krath and Eisenstadt (1957), Reichmuth (1993)) and sorption (Banks and Pinkerton (1987), Banks (1986), Franz et al. (1992)). For flour mills, the loss of MB within two days comprises 50% to 90% of the initial dose (MacDonald and Reichmuth, 1996) (Figure 1).
As shown in Figure 2, this loss can roughly be described by:

\[ e = c_0 \cdot \exp\left[-\frac{n}{24} \cdot t\right] \tag{2} \]

with initial concentration \( c_0 \) as the theoretical concentration derived from the initial dose in g or kg MB per volume of the treated object, and leak rate \( n \) as approximate factor for the leakiness of a sealed fumigation object. This factor can regularly be determined by pressure testing of this object prior to fumigation by applying a constant pressure difference \( \Delta p \) to the atmospheric pressure \( p_0 \) for instance 10 Pascal (10 \( P_a = p_0 - p_at \), \( p_0 \) as initial pressure in Pascal above the atmospheric pressure), and determining the required air flow to hold this pressure difference \( \Delta p \) between the interior of the object and the ambient, or by determining the half life \( t_{1/2} \) of the pressure difference \( p_0 - p_at \), for instance the time of a pressure difference drop from 100 Pascal to 50 Pascal, and deducing \( n \) from this half life by use of the function:

\[ n = \frac{\Delta V}{V} = \frac{[p_0 \cdot \ln(2) \cdot \Delta t]}{[10^5 \cdot t_{1/2}]} \tag{3} \]

with \( \Delta V \) and \( V \) as part of the exchanged volume and the total volume of the treated object.

The factor 24 in (2) corrects the formula when \( t \) is calculated in hours instead of days. The deduction of formula (3) can be found in Reichmuth (1993).

The model fits nicely to practical situations, where often less than 2 mg/L of MB are left after only 24 hours of fumigation. In so far, an expansion of the treatment period beyond 48 hours would not increase the efficacy of the fumigation when the losses are as described. The aim has to be the improvement of gas tightness to avoid the indicated losses.

In Germany, objects to be fumigated have to pass a gas tightness check in advance (Reichmuth 1993). The maximum accepted loss rate \( n \) according to a pressure test at 10 Pascal is 2.4 volume changes per day. This demand can be fulfilled in most cases of fumigations of buildings but often requires some improvement in sealing. The necessary sealing procedures prior to fumigation are described in detail for instance by Neumann (1990) and Wohlgemuth (1990). Reichmuth (1993) tried to calculate the necessary initial dose after correcting for different degrees of leakage of the treated object. This leak rate was determined either by measuring the half-life of the pressure difference or the necessary throughput of air to obtain a pressure difference of 10 Pascal.

To install for instance a ct-product of 140 mg h/\( L \) within two days, which is sufficient to control most stages of insects at 25°C apart from the diapausing larvae, only a leak rate of \( n < 2.4 \) volume changes per day can be accepted if the initial dose is fixed to 15 mg/L (Figure 3). As integral of function (2) between the low border \( t_l = 0 \) and the respective upper border \( t_u = t \), the ct-product corresponds for each time \( t \) to the area under the respective curve of the gas concentration inside a fumigated structure (ref. Figure
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2): 
\[ c \cdot t = \frac{c_0}{(n/24)^{1/2}} \cdot \left[ 1 - \exp\left( -\frac{n}{24} \cdot t \right) \right] \]  

Figure 3 represents the different \( ct \)-products being obtained in objects with different leak rates \( n \). The graph shows clearly that above leak rates of 4.8 the final \( ct \)-product is almost achieved within the first 24 hours of exposure whereas with lower leak rates the \( ct \)-product is still growing further.

Figures 2 and 3 give an ideal illustration of this context. In practice, many changing factors like wind and temperature will influence the concentration characteristics in a fumigated building. Observations during plenty of fumigations in the field support the described tendency.

Nevertheless, the functions and graphs demonstrate that greater gas loss during the treatments will consequently lead to smaller \( ct \)-products inside the structure which in the example is exposed to 15 mg/L as initial dose of MB. For this case, an exposure period of 48 h would lead to a \( ct \)-product of 720 mg h/L, more than 5-fold the required lethal dose of 140 mg h/L. The division of 140 mg h/L as effective dosage for complete control by 48 h leads to 2.92 mg/L as theoretical constant concentration to be applied without any gas loss during 48 hours. Only 20% (2.92 mg/L) of the initial 15 mg/L in the example are therefore actually used to kill the insects. During the fumigation, the rest (80% of the dose!) is needed to compensate the leakiness of the object and is essentially emitted into the environment only. A better standard of gas tightness is desirable to avoid these tremendous gas losses; but the achievement of such higher standards is often quite costly.

One possibility to reduce these losses without a better sealing than 2.4 volume changes per day at 10 Pascal pressure difference offers the change of application technique (Unger et al., 1992). Instead of applying the whole amount of gas in the beginning of the fumigation, it is advisable to dose only for about 7 mg/L for volume of the whole building. Recirculation inside the building will help to quickly achieve an even distribution. After some hours of measuring the gas concentration drop gas losses are replaced accordingly by new MB from outside in order to install again the internal concentration of 7 mg/L. Thereby, a reduction of dose from 15 mg/L to 10 mg/L or less is possible without loosening the aim of complete pest control. On the other hand, a little more than the theoretical concentration is needed to ensure diffusion of the gas into cracks and crevices in concrete and wood to achieve complete insect control everywhere in the treated object.

\[ c = 15 \cdot \exp \left( -\frac{n}{24} \right) \]

**Fig. 2.** Methyl bromide concentration in a fumigated structure depending on the leak rate \( n \).
Fig. 3. ct-product for complete control of stored product insects during fumigation with methyl bromide at 25°C depending on the leak rate \( n \) of the structure.

Fig. 4. The initial dose of methyl bromide for fumigation of a structure depending on the degree of gas tightness expressed as leak rate \( n \) per day at a pressure difference of 10 Pascal for different ct-products and 48 hours of exposure period.
The final formula to determine the right initial dose $c_0$ for a fumigation with MB depending on the achieved gas tightness expressed as leak rate $n$ and the required c-product in a given exposure time can be derived from formula (4):

$$c_0 = n \cdot (c\text{-product}) \cdot 24 \cdot [1 - \exp(-n \cdot t/24)]$$  \hspace{1cm} (5)

Figure 4 presents some functions of $c_0$ for different c-products as parameter. Halving the leak rate $n$ by improving the degree of sealing of a building leads nearly to 50% reduction of the initial dose! This effect is lesser pronounced in the range of $n < 1$, where the steepness of the functions is flattening. Off course, depending on the species and stages to be controlled with MB, the dose should not be reduced below the effectiveness limit of about 3 mg/L as mentioned above.

On the other hand the sealing of buildings is a cost intensive procedure (Love 1983). Leak rates less than $n < 1$ are unrealistic and very hard to achieve. In so far there should be a compromise between the degree of sealing and the reduction of dose due to reduced losses of gas during the treatment and emission of some residual gas from the treated premise. The filtering and recapture of the gas is tremendously expensive and ineffective compared with the investment for better gas tightness of the building and consecutive reduction of plenty of the otherwise necessary dose.

The concern against toxic fumigants for pest control should be evaluated as to whether it is a problem of the gas or a problem of inappropriate use. If emission is a problem, emission should be reduced. If politicians have the opinion that man himself is the problem of bad use, the phase out of production and use is the logical consequence.

In the papers which describe the phase out of MB there is the additional mentionning of conditions which could allow a country to apply for exemptions of MB use as critical use. The condition is linked with 'feasibility' which comprises efficacy and cost. It would be very helpful if some hint could be given by Governmental authorities what feasible actually means in this context. In Germany there is a rough estimate available. If a so called alternative exceeds the MB-cost by more than 10-fold the alternative is not feasible. The first big scale machine for recapturing of MB in Germany, which was supported by the government, was estimated to cost 25,000 $ US additionally per fumigation. Under the perspective of the envisaged phase out, no German company seems to be volunteering for the production of more than this one prototype which up till now could not even successfully be used for economic and quick sorption and later desorption of the gas from the charcoal. According to the German definition this machine is not state of the art because it can not freely be purchased in Germany even though the principal of filtering plenty of gas with plenty of charcoal is trivial. In so far the routine use of such a machine can at present not be requested by German governmental authorities.

What are the expectations of the near future concerning the use of fumigants. The production of toxicology and residue data for registration of a new compound is so expensive and time consuming that the probability of this development is scarce. Some 'old' substances may be re-evaluated and brought back into the market if the set of registration data is available which must not be older than about ten years. Otherwise it does not meet the official governmental requirements and can not be considered as sufficient. GLP (production of chemical residue data according to the rules of good laboratory practice by licensed laboratories) and the presentation of extensive toxicology data are the main obstacles to obtain the registration quickly and with a low budget. The stored product pest control market even if the control of material destroying and hygienic pests is included—is not enough profitable to justify the immense costs of about 150 Million $ US for the development of a new chemical product.

Sulfuryl fluoride, as chemical with long history as termite control agent in the US, may be a candidate (see the publications on this subject within these proceedings!).

The optimisation of phosphine use will certainly be one important step world wide. There is severe concern, that the new developments like combinations with heat or release from cylinders bring along the temptation to shorten the period of treatment down to a few days. The research on this subject has ever shown, that time is the important lethal factor when handling phosphine for pest control (Winks 1982, 1984, 1985, 1986a, 1986b, 1987, Winks and Waterford 1986). The selection of resistant strains is very likely when not enough exposure time is ensured for nearly complete control. The quarantine authority in the US requires probit 9, which is at least LD$_{99}$ 90 (Finney 1952).

It can be envisaged that especially in countries with warmer climate the use of inert and modified atmospheres will proceed. At elevated temperatures of more than 25°C the lethal exposure periods are in the range of less than two weeks for the most tolerant species and stages and above all, sunshine may be used to produce gas or at least photovoltaic electricity for support of pest control.

Only intensive stewardship of the gas suppliers and fumigators will help to keep fumigation as the most effective pest control method. Reduced access will ensure the long lasting access.

References


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