FACTORS INFLUENCING DOSAGE AND CHOICE OF TOXICANT IN STORED-PRODUCT FUMIGATION

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In making recommendations for the fumigation of stored products a number of important constraints must be taken into account, covering both matters of general application and problems which could arise in a specific field situation. In particular, attention must be given to factors which may become limiting i.e. could predetermine the failure of a treatment or prevent the application of an effective dose of a particular fumigant.

Let us consider the basic requirements for a successful stored-product fumigation. At their simplest they could be defined as the ability to produce a gas concentration at all the points of infestation, sufficiently high and for the necessary length of time to have full lethal effect (that is to attain an effective concentration-time product), without damage to the commodity. Within limits it has been usual to consider the product of the average gas concentration and the time of exposure as having a relatively constant effect on the insect.

BIOLOGICAL CONSIDERATIONS: Since the ability to produce a given concentration of fumigant at any point depends much on the particular field situation this part of the problem will be discussed later. First must be considered the factors which determine the dose of toxicant necessary at the point of ingestion by the pest. Experience shows that one of the insect developmental stages is generally more difficult to kill than the others. After laboratory testing to determine which stage this is, it has been usual to assume that the field dose will be calculated to control this most tolerant stage, in the expectation that this will ensure control of that species in all its stages of development.

In a fumigation over a short period such as is common with methyl bromide this may be a perfectly satisfactory approach from the biological point of view, so long as the dose indicated is economically reasonable. This may depend on the physical possibilities of the situation. In seeking to control the most tolerant stage of the pest the temperature of fumigation will play an important part in determining the dose and it should be noted that the temperature of a bulk of infested material may differ markedly from the air temperature outside.

At lower bulk temperatures, for example below 10°C, to attain the required concentration-time product, which for methyl bromide may be 2 - 4 times greater than that effective at 25°C[1], it may be necessary either to prolong the period of exposure so that fumigant loss becomes a significant factor, or to increase the initial dose until damage to the commodity could result. In these circumstances full practical control may be difficult to achieve.

It is also necessary to know to what extent periods of exposure to low gas concentrations can be included in determining the effect of a given concentration-time product. There is evidence that some insects can survive concentrations of methyl bromide of up to 2 mg. per litre indefinitely[2]. Clearly that part of a concentration-time product (c.t.) consisting of periods below or around this concentration level cannot be treated as equivalent in lethal effect to shorter periods at higher concentrations.

One of the ways in which increased tolerance to fumigants may show itself is in an increase in this "threshold" concentration below which no effect is apparent. Under these conditions, if the average gas concentration achieved by a certain treatment schedule proved too low or only marginally high enough, an increase in the concentration-time product achieved by lengthening the time of exposure would be of limited effect.

Turning to another major fumigant, phosphine, which is likely to increase in importance because of its excellent penetration capabilities, lack of residue problems and generally high toxicity to insects, research has indicated that, taking the pest population as a whole, even more striking deviations from the concept of a constant effect concentration-time product can be expected. The susceptibilities of different stages in a species are known to vary widely, sometimes over a range of 50 - 100 times. It has been shown both with *Sitophilus granarius* [3] and with *Ephestia elutella* [4] that with cultures containing all stages, short periods of exposure to high phosphine concentrations (less than 2 days) resulted in survivals whereas longer exposure of 5 days and upwards were successful with extremely low concentrations, at c.t. products far below those failing to control at the higher concentration. These results have become widely known but only more recently has it been possible to explain this behaviour other than on the basis of the slow lethal action of phosphine. Howe[5] postulates that because the tolerant phase, for example newly laid eggs of *Sitophilus granarius*, can continue to develop in a non-lethal phosphine atmosphere, if the period of fumigation is long enough it will reach a susceptible stage which is then killed. This suggests that it becomes unnecessary to plan rates which will control the most tolerant stage if the time under gas is sufficient for further development. This mechanism can also explain the ineffectiveness of phosphine at low temperatures i.e. below 10°C, since development to a susceptible stage becomes impractically long. The development of resistance to a fumigant such as phosphine might show itself with subtlety in an extension of the life span of the normally tolerant phase, whereas an increased dose requirement to kill a particular stage might not be very apparent. Under these conditions even a considerable increase in dosage rate in compensation could be unsuccessful.

In practical fumigation conditions, for example with goods in transit in containers or rail-cars, safety or economic considerations may rule out the use of a long fumigation period with phosphine since the goods cannot be held up and the airing and unloading will then be out of control of the fumigator. In these circumstances methyl bromide, though not necessarily the most easily distributed or the most economic fumigant, may prove the better choice.

From the foregoing it is apparent that the calculation of the dose required at the point of ingestion requires a number of interacting factors to be taken into account. Where several species must be controlled compromises may have to be made but these must be considered in conjunction with the factors which determine how much of an applied dose of fumigant actually reaches the pest.

PROPERTIES OF THE FUMIGANT: Among the factors influencing distribution and loss of gas it is necessary to separate those which are typical of the fumigant's behaviour and commodity interactions from the variables such as air movement and leakiness of structures which cannot generally be predicted. One factor, temperature which as already stated has a major effect on the ingested dose requirement, also has considerable influence on fumigant/commodity interactions and hence penetration of the gas.

The boiling point of a fumigant largely determines to what extent diffusion of its molecules will be hindered by the commodity at ambient temperature and pressure. As the temperature of a vapour approaches and exceeds the boiling point of the compound its molecules move much faster and therefore are able to penetrate more quickly. Conversely a vapour which at ambient temperature is much below its boiling point becomes more easily condensible in pore structures or adsorbed on surfaces and hence loses its power of penetration. Figure I shows this relationship between the boiling point of a compound and its penetrative ability in an empirical manner. The figures plotted are based on practical observations and illustrate well the marked effect the physical characteristics of a fumigant have upon the relationship between the dose applied and the dose reaching the target. The influence of the boiling point can be clearly seen but other factors such as chemical affinity and solubility in water or oil also play a part in determining whether a fumigant vapour will be held by a commodity and hence penetrate less well. The displacement of the points for hydrogen cyanide and ethylene oxide well to the left of the line can be explained respectively by the high solubility of HCN in water and the chemical reactivity of ethylene oxide with protein. The diagram also demonstrates the excellent penetration of phosphine and the inability of dichlorvos and other high-boiling-point compounds to act as penetrative agents.

Even before considering the overall loss of fumigant by adsorption on the commodity it can be seen that with certain fumigants, particularly those with boiling points above 80°C, the ratio between the doses which will be experienced by insects buried in a bulk and those freely exposed at the surface can be quite large unless forced circulation or other manipulation such as fumigation under reduced pressure can be adopted. These dynamic means of improving the distribution of gases are not commonly available however, especially in developing countries.

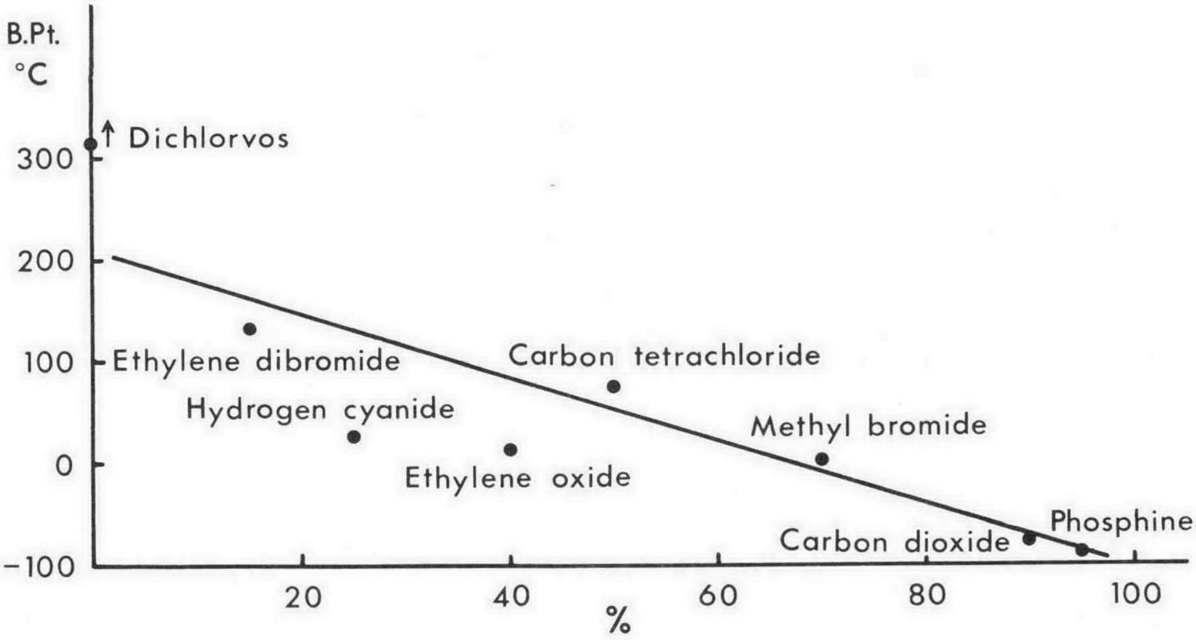

FIGURE 1. Concentration-Time Product at centre of 140 lb. bag of flour as percentage of free-space CTP

Biological investigations in which the vapour toxicities of various compounds are directly compared must therefore take account of these physical factors in assessing whether a chemical is likely to be successful as a fumigant. This is particularly important if mixtures of compounds are being examined for a synergistic effect, since the relative concentrations of the vapours present at any particular site will rarely reflect the proportions present in the dose applied.

VACUUM FUMIGATION: Where goods are very densely packed and a short time only is available for treatment, penetration of the gas can be assisted by fumigation in chambers under reduced pressure, the so-called vacuum fumigation process. The effect of removing the air from the chamber and hence from within the interstitial spaces in the commodity is to reduce the number of collisions in space between fumigant and air molecules so that the fumigant moves much more freely through the bulk. The amount of sorption by the goods is not changed however and for this reason it is normal to use only fumigant compounds with low boiling points in reduced pressure work, as other compounds tend to be difficult to remove afterwards, especially from the centre of packages where air-washing processes are relatively ineffective[6].

The advantages of treatment under reduced pressure are generally utilised by a shortening of the period required for treatment rather than in the use of a lower dosage. Phosphine cannot be used because of its tendency to spontaneous combustion when the pressure is reduced, but because of its excellent powers of penetration at atmospheric pressure there is nothing to be gained; in fact removal of the oxygen of the air would probably result in the insects becoming more tolerant[7].

EFFECTS OF DIFFERENT COMMODITIES: So far the attributes of the fumigant have been considered but the commodity itself can have a very considerable effect on the dosage which must be applied to control an infestation. Because of the affinity of the fumigant for the commodity, only a part of the applied dose remains in the vapour phase, the amount sorbed being no longer available for control by the respiratory route. As a result of physical forces i.e. adsorption, an equilibrium is rapidly established between the amount sorbed and the vapour concentration. If chemical reaction also takes place this will gradually decrease the amount physically held and hence the free vapour concentration, but this effect is not generally sufficient by itself to merit adjustment of the dose in compensation. However the physical losses can be great, especially with fumigants having high boiling points. Only in the case of phosphine, where adsorption on most commodities is extremely low, can the effect of loss on the commodity be ignored in calculating the starting dose.

Fortunately the amount of fumigant to be added in compensation for these losses can be determined in preliminary small-scale experiments. It can be expressed for example as a weight addition per ton of commodity and is sometimes referred to as the "sorption" or "loading factor". At its simplest, excluding leakage a dose of fumigant can be divided notionally into two portions, that which will remain available as a gas (S) and that which will be lost by sorption (M). This can be expressed as:

$$\underset{\text{Dose}}{D} = \underset{\substack{\text{Space}\\\text{Factor}}}{S} + \underset{\substack{\text{Commodity}\\\text{Factor}}}{M} \qquad (\text{I})$$

Taking into account the volume V of the fumigated space (or volume of commodity if it occupies the whole space) and the weight of commodity to be treated (W) the expression can also be written:

$$D = SV + MW \quad (2)$$

where S = gas concentration, oz. per 1000 ft^3

V = volume $\frac{ft^3}{1000}$

M = commodity factor, oz. per ton

W = load, tons

D = dose in oz.

Thus for no load ($W = 0$) the dose D is equivalent to the gas concentration to be achieved in the empty space multiplied by its volume. The value of S can be the average concentration of gas required to control the pest, in which case D will be the total amount of fumigant applied. Alternatively for more general use, equation (2) can be expressed in unit terms so D becomes the dose required to produce a concentration of 1 oz. per 1000 ft^3 or mg. per litre ($S = 1$). By measuring the effect of one or more known weights of commodity on the average space concentration in chamber tests, the amount of extra gas to be added to the dose D to maintain the necessary concentration S, can be determined and expressed in terms of ounces per ton or grams per tonne of commodity, hence the factor M in equation (2).

The effect of difficulty of penetration can also be taken into account in such calculations, at least for predetermined packaging conditions, by making the concentration S that achieved at the most difficult point, for example the centre of a case.

Table I shows some of the factors which have been derived in this way for use in fumigating container-loads of various commodities with methyl bromide in the United Kingdom[8]. As indicated earlier the temperature must be taken into account in these calculations both in its effect on the lethal concentration required and in the loss on the commodity. The doses given are for fully loaded containers of about 1250 cu.ft. capacity and are calculated so that the pest is exposed to a minimum concentration-time product of 200 mg.hr. per litre above 10°C and 300 at temperatures below 10°C. The most difficult to penetrate commodities are given a 48 hour exposure. These levels are those which should control a variety of stored-product insect species, but the dose can be increased by a factor of 50% or more if control of more tolerant pests such as some species of mites or *Trogoderma granarium* larvae becomes necessary. The table shows that with the more sorptive commodities in Classes 4, 5 and 6 the dose may be three or four times that used for an empty container whereas commodities in Class I require no extra loading factor.

Unfortunately, with some dense or highly sorptive materials like oil seed cakes, such calculations, particularly at low temperatures, can indicate dosage rates which are unrealistic in economic

TABLE 1. Dosage Schedules For 1250 ft^3 Transit Containers Pounds Pounds Methyl Bromide Per Container

Class	Below 10°C	Above 10°C	Period Hours
1. Rice, Barley, Peas, Beans Cocoa Beans, Dried Fruit, Empty Containers	2	1	24
2. Wheat, Maize, Oats	3	2	24
3. Rice Bran, Pollards	3	2	48
4. Sorghum, Brazil Nuts, Walnuts	4 1/2	3	24
5. Groundnuts, Oilseeds, Jute Sacks	4 1/2	3	48
6. Oilseed Cake and Meal, Fishmeal	8	5	48

terms or which could lead to contamination of the product by taint or by the production of excessive chemical residues. In these limiting circumstances it may be necessary to accept treatment at a lower dose, sufficient only to retard the infestation, or to use another fumigant.

Take-up by cereals after the application of heavy dosages of liquid fumigants such as ethylene dichloride and carbon tetrachloride can lead to considerable amounts of residue at the end of a treatment, and care must be taken to ensure that they are removed by thorough aeration before use. Recent post-fumigation analytical studies[9,10] have indicated that these compounds can remain in association with bulk cereals for some months after treatment if they remain undisturbed and the use of more readily removable compounds would be desirable. However, there are advantages in the penetration by gravity of these heavy chemical vapours which are not easily obtained with the more volatile fumigants and alternative means of distribution may need to be installed before these can be employed.

Ethylene dibromide, which has long been used as a component of grain fumigants, has a particular affinity for the surface layers. It is widely used in warm climates, for example in India, but has recently been shown to be capable of producing tumours in rats and mice[11]. Its residues in feed had earlier been implicated in effects on laying hens[12]. Unless further studies show that there is no possibility of ingestion of any residue of ethylene dibromide by man, its continued use as a fumigant will be increasingly difficult to defend.

CONCLUSIONS: To summarise, studies on the effects of fumigants on stored-product pests are increasingly showing the necessity for reappraisal of traditional attitudes towards control requirements. In preference to the use of dosage levels which will eradicate the most tolerant pest stages it may be possible to adopt measures designed to attack the pest at a more susceptible point and behavioural studies may well be rewarding in this context. Biological testing must be continually supported by physical studies which can further elucidate the factors contributing to the fate of the fumigant, both from the points of view of control efficiency and of safety in use.

With increasing awareness of the importance of pure and wholesome food, future emphasis must be on control measures which will contaminate as little as possible. The fumigants have an important part to play here, but as with other chemical pest control agents, they must be applied in a manner designed to ensure their most effective and economic use. Only by integrated studies of all the relevant factors by scientists of several disciplines are these aims likely to be achieved.

REFERENCES:

[1] Heseltine, H. K., Thompson, R. H. "Fumigation With Methyl Bromide Under Gasproof Sheets" U. K. Ministry of Agriculture, Fisheries and Food, Slough, (1974) 41.
[2] Reynolds, E. N., Welch, J. J., Goodship, G. "Pest Infestation Research 1964" H.M.S.O. London (1965) 47.
[3] Howe, R. W. J. stored Prod. Res. 8 (1973) 241.
[4] Bell, C. H., Glanville, V. J. stored Prod. Res. 9 (1973) 165.
[5] Howe, R. W. J. stored Prod. Res. (1974) In the Press.
[6] Burns Brown, W., Heuser, S. G. J. Sci. Fd. Agric. 4 (1953) 48.
[7] Bond, E. J., Robinson, J. R., Buckland, C. T. J. stored Prod. Res. 5 (1969) 289.
[8] Heseltine, H. K. Proc. Mtg. of Standing Committee on Fumigation, European, Medditeranean Plt. Prot. Org. Paris (1974).
[9] Scudamore, K. A., Heuser, S. G. Pesticide Sci. 4 (1973) 1.
[10] Heuser, S. G. Pesticide Sci. 4 (1973) 409.
[11] Olson, W. A. et al. J. natn. Cancer Inst. 51 (1973) 1993.
[12] Bierer, B. W., Vickers, C. L. J. Amer. vet. med. Ass. 134 452.