Recent Developments in Fumigation Technology, with Emphasis on Phosphine

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Abstract

With the increasing use of phosphine as a grain fumigant and the spread of phosphine resistance, it is vital that phosphine toxicity be understood and that steps be taken to use the gas effectively. This paper outlines some of the components of phosphine toxicity and describes some of the characteristics of phosphine resistance. The paper also describes some new methods of application as well as recent developments in old methods.

FUMIGATION remains one of the more effective methods available for the disinfestation of stored products. Although it is now quite an old technique, there are a number of new developments that may have a significant impact on the way it is used in the future.

Phosphine Toxicity

For many years, the approach to setting dosage rates for fumigants and other agricultural chemicals has been to choose a level that will kill the most tolerant stage of the most tolerant species likely to occur in the fumigation enclosure. The use of methyl bromide, for example, has been based on this philosophy (Brown 1959). It is therefore not surprising that early uses of phosphine were similarly based, although users knew that the gas evolved slowly and that the fumigation consequently took longer. While studies on the toxicity of methyl bromide to insects showed that, for the most part, the toxicity followed the relationship in which the product of concentration (C) and time (t) was a constant for a particular level of response, e.g. the LD_{99}, the toxicity of phosphine displayed a significant departure from this relationship (Howe 1973). In a number of studies it was shown that exposure time was the more important variable of dosage (Winks 1984).

Although early studies of phosphine toxicity on particular stages of insects showed that exposure time was the more important variable of dosage, the magnitude of the deviation from the relationship $C \times t = k$, generally obtained for adults, did not account for the importance of exposure time in practical fumigations. The importance of exposure time in practice lies in the variation in tolerance of immature stages. Indeed, the key to successful fumigation with phosphine lies in understanding the large variation in tolerance of the immature stages and that this tolerance changes with time of development (Fig. 1). With the dosages commonly used in practice, an adequate concentration must be maintained for long enough for eggs to approach or reach the larval stage, and pupae must approach or reach the adult moult. It follows from this that, if the rate of decay of concentration is greater than the rate of decay of tolerance of the most tolerant stages (eggs and pupae), there is a probability of survival. Thus, if the dose of phosphine (the amount absorbed) does not reach a toxic level before the phos-

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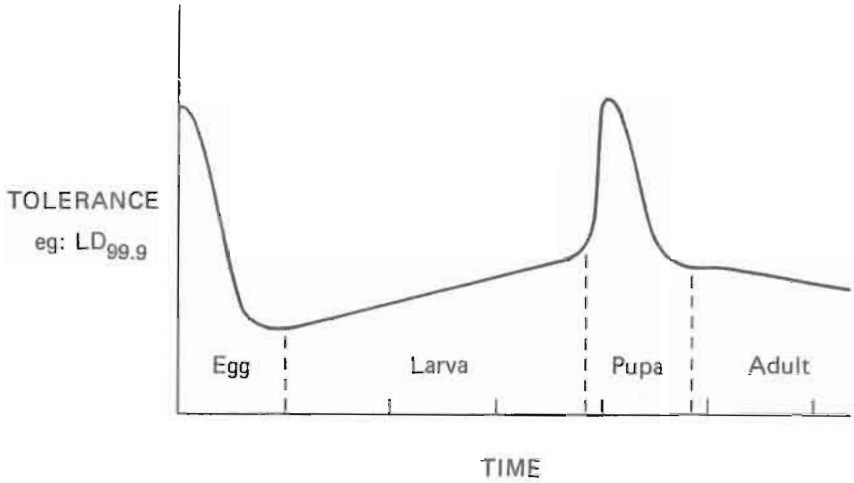

Fig. 1. Schematic representation of the change in tolerance to phosphine of the different stages of stored product insects with time.

phine concentration decays to zero, the insect will survive. This can be represented schematically as in Figure 2, which describes the response of pupae. The effective dose is that necessary to kill, and may describe an individual or a population. The time scale, in terms of tolerance or absorbed dose, will vary with species and with temperature.

Sealing the fumigation enclosure will lower the loss rate of phosphine and thus retain sufficient gas for long enough for an effective dose to be absorbed (Fig. 3). Because of the low application rates that are commonly used, it is necessary for the tolerant stage to develop to a less tolerant stage, whereupon it either succumbs to the dose absorbed from a more or less constant uptake rate, or that the uptake rate increases as development towards the next stage proceeds. Thus, to achieve a high probability of success, the minimum exposure period should be approximately equal to the maximum development period of the most tolerant stage. It is essential, of course, that at the minimum exposure period there is still sufficient gas left in the enclosure for the insects to absorb. It follows from this that the critical concentration is that at the minimum exposure period. If we take, for example, a maximum pupal development time of 10 days, then if there is sufficient gas left after 10 days to kill young adults, the probability of success will be high.

From this it can be argued that the critical concentration is that needed to kill the most tolerant adult, while the critical exposure time is the maximum development time of the slowest-developing tolerant insect stage within the enclosure. This is true, of course, whether we are talking about susceptible or resistant insects. Since the rate of development of the tolerant stages cannot be increased readily, the key to successful fumigation lies in reducing the rate of decay of the concentration. This may be achieved either by improving the level of sealing of storages, or by using different methods of application that will allow continuous input of gas.

With a constant concentration, one would expect that, as the tolerance of, for example,

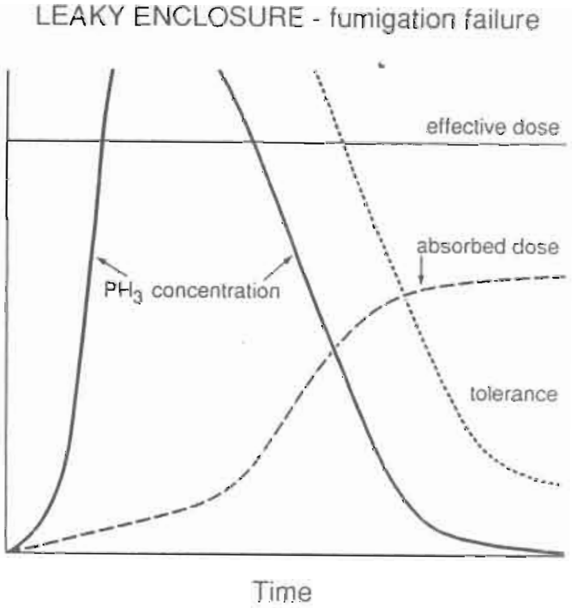

Fig. 2. Schematic representation showing that in a leaky fumigation enclosure the absorbed dose does not reach a lethal level when the concentration decreases faster than the tolerance of stages like eggs and pupae.

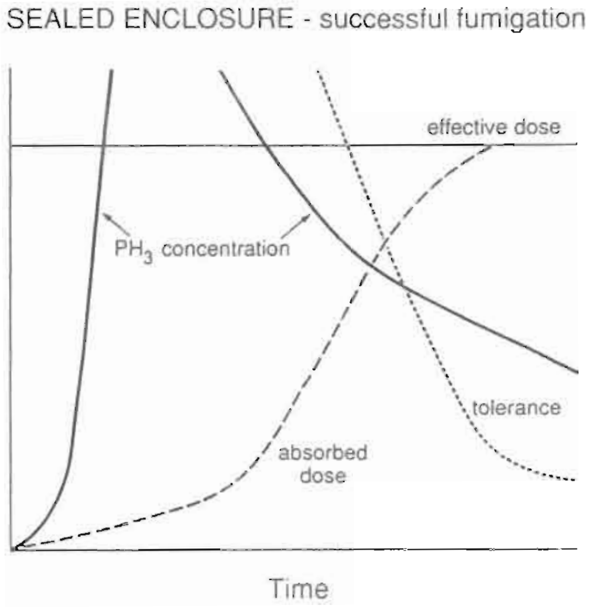

Fig. 3. Schematic representation showing that, in a well-sealed enclosure, the absorbed dose reaches a lethal level because the rate of decrease of the concentration is less than that of the tolerance of eggs and pupae.

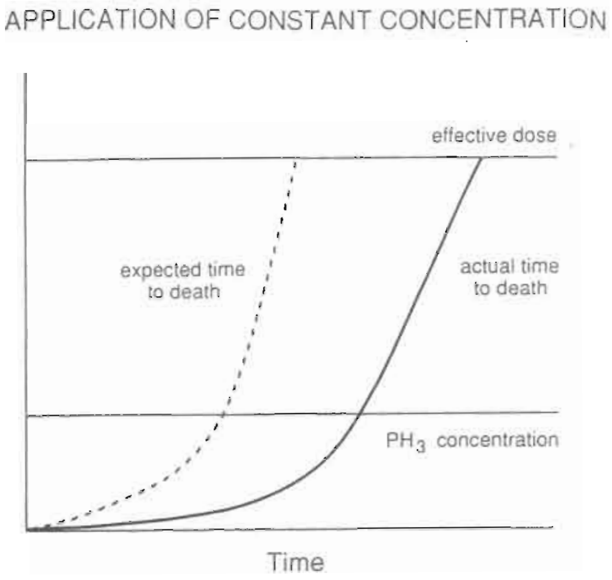

Fig. 4. Schematic representation showing that the absorbed dose can be expected to reach a lethal level after a period of exposure to a constant concentration. Studies show, however, that the actual time to death is greater than expected from the development times of a species.

the pupal stage decreased, the amount absorbed would increase more or less exponentially (Fig. 4); i.e., it is influenced only by the rate of change of tolerance. Thus, it could be expected that the time to death of an individual or a population would be governed simply by the time of development of the most tolerant stage and would be more or less predictable from the biology of the species. The data we have, in contrast to those of Reynolds et al. (1967), suggest that phosphine delays the rate of development, and that a prediction of time to death derived from the biology of the species would be too short to achieve complete kill of the population. If there is delay of development when insects are exposed to a constant concentration in the laboratory, it is reasonable to expect that there will be similar delays in the field which would further exacerbate the problem of short exposure times because of poor sealing or because the fumigation is terminated early for operational reasons.

It is sometimes suggested that if the level of sealing is not adequate then all that is required is a higher dose. In a leaky store that is about half full, a typical situation for many sheds or godowns, even with high application rates the likelihood of success is quite low (Fig 5.). It should be noted that the concentrations shown in this Figure 5 are calculated average concentrations and grossly underestimate the problem. While the high application rate would succeed if the calculated concentrations were achieved throughout the storage, with the leakage rate involved, there would be many large pockets of much lower concentrations in which the fumigation would fail. On the other hand, the C × t product calculated for a well-sealed storage with a leakage rate of 5% per day, suggests that, providing the temperature is at least above 15°C, the application rate could be reduced quite significantly.

Resistance to Phosphine

Insects would seem to have a greater propensity to become resistant to phosphine than to many, if not most, other toxicants. In the laboratory, we have produced resistance in every strain of every species that we have attempted to select, including standard reference strains that have been in culture for over 20 years. Moreover, with a limited number of selections we have, in many cases, produced stable levels of resistance; i.e., there has been no regression of the resistance for over 10 or more years. One cannot help but wonder about selection programs that appear to be so efficient that we

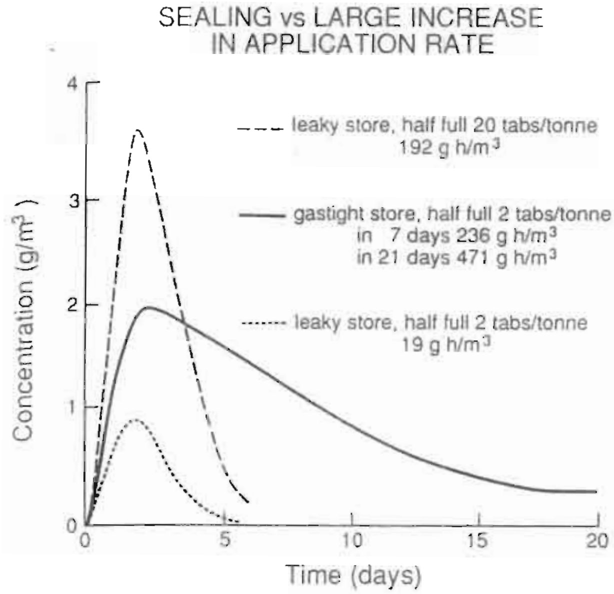

Fig. 5. Calculated concentration profiles showing the dosage achieved by adding additional fumigant to a leaky fumigation enclosure compared with the dosages achieved by sealing the same enclosure.

achieve apparent homogeneity so quickly. It is difficult to believe that we are dealing with a low-frequency resistance gene that has occurred as a result of random mutations. A further fact that has emerged is that we seem to reach an upper limit of resistance quite quickly. Under normal circumstances these facts would not augur well for the future of a chemical as a control agent. However, there are mitigating facts that put phosphine into a different category to contact insecticides such as organophosphates:

- the levels of resistance are not so high as to preclude the continued use of phosphine; and
- the magnitude of resistance varies with concentration (Fig. 6) (Winks and Waterford 1986).

The magnitude of resistance is calculated as the ratio of an appropriate lethal dose for the strains being compared, e.g. the LD_{99}, and may be expressed as a ratio of lethal concentrations for fixed exposure periods or a ratio of times to absorb a lethal dose at a fixed concentration. An examination of the curves of Figure 6 shows that the level of resistance varies with concentration, and indeed this should be expected with any combination of poison and target organism where dosage is comprised of more than one variable. It should also be noted that if one were to measure resistance using traditional approaches, such as a range of concentrations at a fixed exposure period, the measure of resistance or 'resistance factor' would be greater than if a range of exposure times were chosen at a fixed concentration. This characteristic of phosphine is due to the fact that the exponent n, the toxicity index, for phosphine in the relationship $C^nt = k$ is less than 1. As the magnitude of this exponent decreases, the difference between measurements at fixed concentrations and fixed times increases so that there can be a perception of quite high levels of resistance. This is so for adults of strains of *Sitophilus* spp. and *Rhyzopertha dominica*, with their much lower exponents than those for *Tribolium* spp., when tested following the guidelines of the FAO Resistance Test Method, i.e., with a range of concentrations at a fixed exposure period.

Although changing tolerance confounds traditional analysis of Ct relationships in immature stages, the limited data available suggest that the changing tolerance has the effect of a very low exponent of toxicity, which again would have the effect of producing a high level of resistance or relative tolerance if fixed exposure tests of, for example, 20 hours were used. Pupae of *Sitophilus granarius* provide a good example of this.

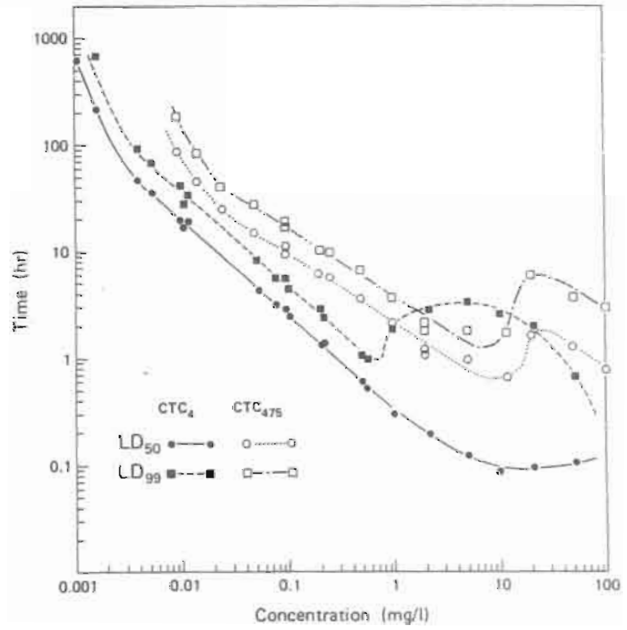

Fig. 6. The relationship between the time required for an LD_{50} and LD_{99} at each of a range of fixed concentrations of phosphine to which adults of a resistant strain of *Tribolium castaneum*, CTC_{475}, and a susceptible strain, CTC_4, were exposed (from Winks and Waterford 1986).

Complete control of phosphine-resistant strains can be achieved with phosphine by choosing the dosage parameters carefully. On the basis of our present knowledge, this will mean choosing concentrations to minimise resistance and retaining the concentration for longer periods. Following the more traditional approaches of adding more chemical will only exacerbate phosphine resistance.

Clearly, there are only two options for using phosphine that will minimise selection for resistance on the one hand and permit the control of resistant strains on the other:

- use of gastight enclosures; or
- use of methods of application that will provide a constant concentration throughout the enclosure even if it is not gastight.

The continued use of phosphine other than in either of these two ways is courting disaster, particularly as the usage of this fumigant increases. Even in conditions of severe economic constraint it would seem more sensible to pay the cost of implementing one of the two alternative options than to pay the cost of no longer being able to use the fumigant.

New Methods of Application of Phosphine

Multiple dosing. In an attempt to increase the time of exposure in godowns, TDRI (now ODNRI) developed a method of adding a second batch of fumigant to the enclosure when the concentration dropped below a certain level (Friendship et al. 1986). This method is based on adding strings of aluminium phosphide sachets to the headspace of the enclosure through a port in the side of the godown. While the objectives are in keeping with our understanding of phosphine toxicity, the method should be used only in sheds or godowns that achieve a reasonable standard of gastightness. In structures that are not gastight, there will be pockets of low concentration around, for example, doors and windows, especially under windy conditions, that will decrease the probability of success. Although this method of application has some novel features, it does nothing to ensure that there will be a uniform concentration throughout the grain mass and relies for success on a randomness of factors that contribute to gas loss. Where there is some uniformity of gas loss factors, e.g., wind direction, the probability of success decreases. In addition, prolonged exposure periods, that may be necessary for resistant strains, may render the method uneconomical.

SIROFLO. SIROFLO is a method of applying phosphine for which patents are pending and thus only limited information can be presented. The method is based on the dilution of a low concentration of phosphine into an air stream that is introduced into a storage, thus producing a small positive pressure (Fig. 7) (Winks 1986). The pressure thus produced assists distribution and offsets factors that contribute to gas loss from the storage. The method currently relies on the use of a 2% gas mixture of phosphine in carbon dioxide available from Commonwealth Industrial Gases, but we are also developing a controllable on-site generator in conjunction with Wellcome Australia and Detia. The details of the generator are also covered by patent. The fact that with both sources of gas the process becomes completely controllable is one of the key attributes of SIROFLO. Both the concentration and the exposure time can be varied easily before and during a fumigation to cope with the many factors that influence the outcome. In the absence of well-sealed enclosures, it is currently the only method of using phosphine that could

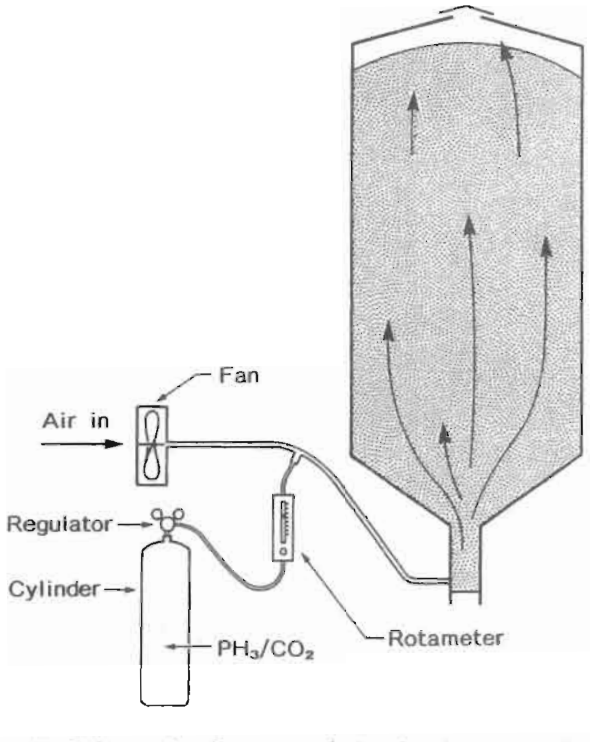

Fig. 7. Schematic diagram of the SIROFLO method for applying phosphine to vertical silos.

be relied upon to control phosphine-resistant strains, i.e., to have adequate control over the exposure time. Indeed, much of the laboratory development of SIROFLO has been with phosphine-resistant strains, and it has successfully controlled two infestations of resistant *Rhyzopertha dominica* in the field.

Unlike recirculation systems, which have both positive and negative pressures and thus require high standards of gastightness, SIROFLO is a flow-through process and in this way a positive pressure is maintained throughout the enclosure. Although it offsets most of the factors that give rise to gas loss, there are still certain minimum requirements. The method is currently being implemented in vertical silos in Australia and in some horizontal storages, although the latter are still in the development phase. These trials are primarily aimed at optimising distribution systems and flow rates.

In Australia, the greatest interest in the SIROFLO process is as a grain protection method. Grain can be stored for long periods using the process without using normal protectants. Moreover, the costs of protection are substantially less than the costs that are associated with the current grain protectants. The method is also more acceptable than conventional fumigation methods in terms of both worker safety and environmental considerations.

Licensing Agreements for SIROFLO with Wellcome Australia, Detia Freyberg and Commonwealth Industrial Gases (a member of the British Oxygen group) are expected to be finalised during 1990, whereupon the method will become available progressively in countries outside Australia.

Cylinders and on-site generators. While both cylinders and on-site generators of the type mentioned in the previous section have obvious advantages in the context of a method such as SIROFLO, they are also advantageous as a source of gas in methods of fumigation where there is a benefit associated with developing the full concentration rapidly. Such methods have advantages in recirculatory fumigation systems. In such systems, the most effective approach to introducing gas is to be able to meter its input in accordance with the flow rate of the fan so that the full dosage is introduced in the time equivalent to one air change of the enclosure. This should achieve uniform distribution of the fumigant in the shortest possible time.

On the subject of recirculatory fumigation, there is a perception that phosphine fumigation in silos equipped with recirculation can be done in a shorter time. Times as low as a few days have been suggested. This is totally inconsistent with our knowledge of phosphine toxicity and while short exposure times might achieve an illusion of success by killing adults and larvae they will not kill eggs and pupae. Such practices are, in fact, an effective way to select for phosphine resistance. The only reduction in exposure time that is possible in the context of effective fumigation is associated with the time required to introduce the full dosage of gas. Thus, cylinders and, in due course, on-site generators, will provide the added advantage of reducing the fumigation time by about a day over blankets for example. It is, of course, essential to understand that the exposure times required for phosphine fumigation are not from when the fumigation is started but from when uniform distribution of gas can be expected. While the two times may have been similar for methods using admixture of tablets they are vastly different for methods based on surface application followed by convective distribution.

'Old' Methods Revisited

In-transit shipboard fumigation. The use of fumigants, particularly phosphine, in ships holds during a voyage has been under evaluation by scientists of the U.S. Department of Agriculture Laboratory at Savannah, Georgia for some years now. The results of the earlier trials were not particularly successful, and in some cases the trials failed to achieve even a cosmetic fumigation (Zettler et al. 1984). Recently, this group conducted trials in which a recirculation system was installed before the grain was loaded. Flexible perforated ducting was laid around the floor of the hold and on the grain surface. By comparison, the recirculation system achieved complete distribution in about 5 days of a 25-day voyage whereas the earlier method, which they refer to as the 'tubing-probe method', took 20 to 21 days to achieve distribution in the same 25-day voyage (Robinson 1988). This use of ducting was an attempt to improve the poor distribution obtained in earlier trials.

Clearly, in-transit ship fumigation should be considered only when all else has failed and should be contemplated only in vessels with gastight holds, i.e., no access to other parts of the ship, and when some provision has been made to recirculate the gas.

Fumigation under gas-proof sheets. Although gastightness has been recommended or implied in all such methods for a very long time (Brown 1959), it is only recently that methods have been developed that will achieve such standards reliably in sheeted bag stacks and enable them to be tested. Details of these developments are given elsewhere in these proceedings.

Worker Safety and the Environment

During recent years, greater attention has been directed towards the safety of workers when fumigants are used, and in many countries, greater attention has been focused on the release of fumigants into the atmosphere. These concerns are not directed exclusively at fumigants but reflect greater concern for industrial chemicals, worker safety and environmental pollution generally.

In the context of worker safety, there remains a need for more efficient monitoring systems. Since health authorities do not generally recommend static sampling of workspace atmospheres it imposes a requirement to develop efficient personal monitors that are also relatively inexpensive. Ideally, a personal monitor that is activated when some level is exceeded is needed. However, such a device should accommodate the concept of a time-weighted average exposure and upper limits of concentration. Currently, such sophistication is available only in intelligent instruments incorporating a range of detectors suitably driven with black boxes filled with electronic components a long way removed from the concept of a cheap personal monitor. Until a suitable personal monitor is available, there will be a tendency for people responsible for operational procedures to treat time-weighted averages of threshold limit values (TLVs) as ceiling limits, with consequent additional operational constraints.

In a number of countries around the world, environmental considerations are becoming more acute. Discharging fumigants like methyl bromide into the atmosphere is causing concern. Environmental agencies are raising questions about the dispersal and fate of fumigants. Moreover, they are invoking levels that are considerably below the TLVs applicable to workspace environments. It is argued that such TLVs are set with normal healthy members of the workforce in mind, not young children or the elderly, and a lower environmental level would therefore seem to be more appropriate. Thus, when grain storages are close to houses there is a possibility that these lower levels might be found in and around these houses. There is therefore a need to understand more precisely the factors that influence the dispersal of fumigants in the atmosphere. Secondly, there is a need to consider the development of suitable scrubbers that will remove fumigant from silo exhausts and destroy it. In densely populated areas, this approach may be the only way that we will be able to continue to use fumigants in the future.

The Future of Fumigants

Fumigation will remain one of the more valuable control strategies for the preservation of grain and other stored commodities for many years to come. It is still the cheapest method available for disinfesting grain. Phosphine, I believe, will remain one of the more important fumigants available for this purpose. However, unless steps are taken to employ it effectively, resistance will spread and it will remain of use to only those countries that have the capacity to employ longer exposure periods. It is important to realise that where the capacity does not exist to prolong exposure periods the only hope is alternative and less convenient or effective fumigants. Other methods of disinfestation will be more costly.

It is to be hoped that, by the time of the next Conference on Controlled Atmospheres and Fumigation, methods of usage of phosphine will have improved dramatically. It is vital that, in some of the developing countries where such a method is most needed, efforts be made to use the fumigant properly. The argument that these countries cannot afford the costs of sealing or alternative methods of application is untenable. These are the very countries that cannot afford to lose a fumigant like phosphine, for to do so is to risk losing more grain to insects. I wonder what the cheaper cost is?

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