ON CRITERIA FOR SUCCESS OF PHOSPHINE FUMIGATIONS BASED ON OBSERVATION OF GAS DISTRIBUTION PATTERNS

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Abstract: Recent changes in the basis of practical use of phosphine have created a need to re-evaluate the distribution of gas produced during fumigation. This evaluation must be made against an awareness that survival of insects may increase the risk of selection of strains resistant to phosphine. Using examples from recent Australian full-scale field trials, illustrations are given of various defects in fumigant retention distribution and application that may lead to inefficient use of material and survival of insects. The ratio of minimum to maximum concentration is used as an indicator of distribution in unsealed systems with uniform admixture of phosphine releasing agents and sealed systems with surface application.

Based on the gas distribution patterns in the examples presented, a set of criteria are proposed by which the success of a treatment can be judged, and a commercially successful result and a completely successful one, i.e. one in which complete insect kill may be expected, can be differentiated. In increasing order of stringency the criteria are (a) the grain be found free of insects by inspection after treatment, (b) the average maximum concentration of phosphine be >50% of that expected theoretically, (c) the concentration at the end of the exposure period be greater than the minimum effective against insects and (d) that the ratio of minimum to maximum concentration exceed 0.25 after not more than 25% of the exposure period.

1. INTRODUCTION

Phosphine has been used routinely for grain fumigation in many parts of the world for more than 25 years. Until recently, it was general practice to add phosphine-generating material, typically Phostoxin tablets, in a way designed to provide as even a distribution of the formulation as possible throughout the grain bulk (Munro, 1969). The formulation was either placed in the grain stream during the loading of large silo bins or was distributed by probing into the grain bulk in both large flat storages and farm bins. Attempts were sometimes made to restrict gas loss by sheeting the surface of treated bulks and sealing access doors and other penetrations in the the storage fabric. Nevertheless, phosphine was regarded as a fumigant suitable for poorly sealed enclosures and high application rates, up to 10 g t⁻¹, were recommended in such cases in an attempt to compensate for losses through leakage from the system. Furthermore, some dosage schedules for stored grain recommended exposure periods of only 2 days (e.g. Anon., 1972).

This approach is now recognised to be unsound (Winks *et al.*, 1980). As a result in Australia, there have been important changes in the basis of the way in which phosphine fumigations are carried out. These changes have substantial practical consequences:

(i) Recommendations for phosphine use in large structures now state that the structure must be well sealed and, at a dosage of 2 g t⁻¹, set a minimum exposure period of 5 days (7 days if *Sitophilus* spp. are present) at > 25°C for a completely effective fumigation. In addition, it is now recognised that it is not possible to achieve a good fumigation in the face of a high gas loss rate from the system merely by inceasing the rate of phosphine applied (Winks *et al.*, 1980).

(ii) There is increasing use of surface application techniques. In these the phosphine-generating material is applied onto the grain surface or the headspace above the grain (e.g. on the conveyor catwalk).

(iii) There is also a tendency towards the use of reduced dosage rates (down to 0.5 g t⁻¹) made possible by low rates of gas loss from sealed systems. These reduced rates are usually combined with much increased exposure periods to the fumigant to take advantage of the increased sensitivity of the insects infesting the grain to phosphine under these conditions (Reynolds *et al.*, 1967; Heseltine, 1973).

The changes from use of poorly sealed to well sealed systems, from uniform admixture to surface application, bring with them substantial changes in the patterns of phosphine gas distribution occurring during treatments. Good distribution patterns are important to the success of phosphine fumigations. Accordingly, there is a need to re-evaluate the effectiveness of particular fumigation systems in the light of currently accepted requirements. Underexposure of a region to phosphine may result in survival of some insect pests, giving an unacceptable result in a particular fumi-More importantly, if inadequate fumigations are carried gation. out, strains of pests resistant to phosphine may be selected. This may lead, at first, to the need for increased exposure periods and dosage and finally to phosphine being rendered ineffective.

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It is thus remarkable that despite the long history of use of uniform admixture and the importance of proper distribution of gas, there are still very few detailed data available on the distribution patterns occurring in large scale fumigations (but see Schuyler, 1963; Mori *et al.*, 1966; Conway and Mohiuddin, in press). There is also little information on the more recently developed surface application procedure (but see Snider and Allen, ca. 1977; Cook, 1980; Banks and Sticka, 1981; Winks, 1981; Zettler *et al.*, 1982).

This paper provides examples of the gas distribution patterns found in some large scale fumigations. It contrasts the results from uniform admixture in unsealed systems and surface application techniques in sealed storages, and illustrates particular defects in the two processes. These defects are discussed in terms of a broader study on particular modes of failure of phosphine fumigations brought about by defective gas distribution. A method of analysis of gas distribution data is presented that provides a means of determining particular defects in technique. Finally, a set of criteria is proposed which can be used to define the degree of success of a treatment, distinguishing between what is regarded as a commercially adequate result and a treatment in which no insects survive. Data is presented that can be used to justify why some current practices should be discouraged and others adopted, sometimes at substantial cost in modification of structures and changes in procedures.

2. BACKGROUND TO EXAMPLES

2.1 Choice of examples

With a dosage nominally capable of controlling insects, factors that may lead to fumigation failure are:

(i) Excessive overall loss of fumigant;

(ii) Inadequate fumigant dosage in localised regions;

(iii) Excessive delay between application and fumigant reaching some regions resulting in an inadequate exposure period.

All these factors may occur simultaneously.

Examples of each of these types of failure are evident in the data from uniform admixture of phosphine-generating preparations in unsealed, large, tall, narrow bins, and in the data from on surface application in sealed storages. These two combinations are taken as paradigms of two extreme forms of phosphine application: that where the initial distribution of gas generator is good but the sealing is poor and that where the initial distribution is poor but the sealing good.

Although there is a wide variety of other combinations of application process with enclosure size, degree of sealing and shape, no data for these various combinations is given here as the same types of failure will occur as in the examples given. The physical processes involved in distributing the gas are the same in both small and large storages and similar defects in distribution may be expected although they may vary in their magnitude with the size of system. If non-uniform application of the gas generator gives an adequate fumigation in a particular situation, it is assumed that uniform admixture also will do so in the same situation. With surface application and other non-uniform techniques, the main limiting factor is the rate of dispersion of the gas from the region where it is generated. The distance required for the gas to travel is much greater in these cases than with uniform admixture of formulation to the grain.

2.2 Data sources

Data for the examples given below are taken from various field trials carried out in Australia since 1973 by CSIRO Division of Entomology, usually in collaboration with a state grain handling organization. General details of the trials are given in Table 1, the trials being referred to by locality. All trials were carried out on wheat of < 12% moisture content at grain temperatures >20°C.

In each case, the fumigation was of a standard such that it gave what would have been regarded as a commercially successful Phosphine concentrations were measured with various inresult. dicator tubes (Drager, Auer, Kitagawa, Gastec). It should be noted that this method of phosphine analysis can be subject to substantial error (sometimes > +30%, (Leesch, 1982)) if not corrected for the variation in sensitivity of the tube batches under the particular conditions of usage. Readings from later trials (Harden, Bordertown, Newcastle, Meandarra) were corrected for sensitivity and temperature, (Banks and Sticka, 1981), but those from other trials were uncorrected. A large number of sampling points was used in each trial (Table 1). They were distributed to give both a good estimate of the general distribution of the gas and to monitor critical areas, such as close to the floor or wall-to-roof joints. Average concentrations of a storage were calculated from the observations at particular points weighted by the gas volume of the region that

TABLE 1.

Details of field trials used to provide illustrative data.

Trial designation (Locality of trial)	Bordertown	Cunningar	Harden	Meandarra	Newcastle	Walleroo A	Walleroo B
Storage type	Steel bin	Concrete cell	Shed	Concrete cell	Steel bin	Concrete cell	Concrete cell
Storage dimensions	24 m high, 21.6 m diameter cylindrical, roof pitch	30.5 m high, 10.9 m diameter cylindrical, 28° roof pitch	12.9 m high, 121 m long, 30.8 m wide, 30° roof, 2.5 m wall	30.4 m high, 12.0 m diameter cylindrical, 28° roof pitch	9.4 m high 2.2 m diameter cylindrical, 26° roof pitch	32.1 m high, 10.7 m diameter cylindrical	32.1 m high 10.7 m diameter cylindrical
Degree of sealing	Sealed, pressure test (full, 500- 250 Pa) 480 secs	Roof vents open	Sealed, pressure test (full, 125 - 62.5 Pa) 300 secs	Sealed, pressure test (full, 1000 - 500 Pa) 660 secs	Sealed, pressure test (full, 500 - 250 Pa) 84 secs	Cell top open, aeration duct unsealed	Cell top open
Load (wheat, tonnes)	6800	2215	16470	2460	294	2140	2100
Phosphine application system	Surface application	Into grain on loading	Surface application in 'blankets'	Surface application	Surface application	Into grain on loading	Into grain on loading
Phosphine releasing preparation	Phostoxin pellets	Phostoxin tablets	Detia sachets	Phostoxin tablets	Phostoxin tablets	Phostoxin pellets	Phostoxin pellets
Total phosphine added (kg)	2.99	6.1	26.4	1.92	0.27	2.7	2.7
Number of sampling points used	46	28	51	28	44	60	48

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they were sampling. The weighting factors were approximate only, but it was found that because of the large number of sampling points used, the average value is not very sensitive to the magnitude of the weighting factor used for individual points.

The ratios of the minimum to maximum concentration found in a system are a measure of evenness of phosphine distribution. This ratio shows when a significant concentration has been achieved at all points in a system and is thus an indication of the time at which the exposure period for the entire system can be taken to have started.

Phosphine concentration data are given as a percentage of that expected if all the phosphine potentially available was present in the gas space in the enclosure (i.e. without leakage or any sorption into the grain or on other materials therein). Since the concentration at a point at a given time under particular conditions will be approximately proportional to dosage applied, data presented in this way can be converted into concentration terms for any applied dosage. It is then possible to assess if a particular rate of application satisfies some set dosage parameter (e.g. a *Ct*-product value or a minimum effective concentration level). The actual values of these parameters are not discussed in detail here.

3. EXAMPLES

3.1 <u>Uniform admixture in poorly sealed systems</u> - deficiencies in fumigant retention and distribution.

(i) <u>Excessive loss of fumigant</u>. In the past, phosphine has been used in structures that were so poorly sealed that the maximum concentration of phosphine achieved was only a small fraction of that theoretically available from the applied formulation.

Figure 1 shows the average concentration in an open cell in which the aeration duct at the base was unsealed. The estimated theoretical concentration curve, calculated on the basis of total gas volume, is shown. In this case the fumigant was not used efficiently[†] and was lost very rapidly by leakage.

A similar situation (Fig. 2) was observed in a concrete cell which was not well sealed and in which the roof ventilators were kept open in order to vent dust-laden air displaced during the

[†] We consider 'efficient' use in this context to be that more than 50% of the theoretical phosphine concentration be observed at some time during the treatment.



Fig. 1. Variation of average phosphine concentration with time in an open top concrete cell in which the aeration duct at the base had not been sealed off, showing inefficient use of fumigant (Walleroo A).

filling of the bin. Not only was there a loss rate resulting from the poor sealing of the system, but further substantial losses were caused by the protracted loading of the bin, which was carried out in four working periods spread over four days. The grain added during each successive period rapidly displaced the phosphine accumulated in the free space in the bin from the decomposition of phosphine-releasing material added on the previous days.

When fumigations are carried out in very leaky structures, as in these examples, the fumigant concentration may not be maintained at an adequate level until the nominal end of the exposure period and some survival of insects may be expected throughout much of the treated system.

(ii) <u>Inadequate exposure in localised regions</u>. Some fumigations are carried out under conditions where the gross leakage is slow enough to give an adequate average dose, but where some regions within the fumigation enclosure may receive insufficient dosage. In such cases, although the average concentration-time curve for the





Fig. 2. Variation of phosphine concentration with time in a concrete cell loaded over four days and with roof ventilators open (Cunningar), showing a low efficiency of use of the fumigant overall (average line, \blacksquare ----- \blacksquare) and low exposure to phosphine at points at the base of the cell (inset shows plan of sampling position).

funigation suggests that the treatment was successful, curves for specific regions may show this is not true. Figure 3 shows the concentrations of phosphine achieved in the treatment of an open topped concrete cell. Overall, the loss rate, though substantial $(13\% \text{ day}^{-1})$, was not sufficient to displace the funigant within the recommended 7 day exposure period. However, points both close to the grain surface (Fig. 3) and also at the base of the bin (not shown) received very low dosages. On several other occasions (e.g. Fig. 2) we have observed a similar rapid loss of phosphine from regions close to the bin base during treatment of large, tall, unsealed, concrete cells (approx. 2000 tonnes capacity).

Regions that receive inadequate dosage regimes in such cases may be quite restricted, in contrast to the situation given in the previous example. Nevertheless they may be an important haven within which some insects survive and produce a general infestation



Fig. 3. Variation of phosphine concentration with time in an opentop concrete cell with a reasonable average concentration $(\square ---- \square)$ but low exposure at points 15 cm below the grain surface (inset shows plan of sampling positions) (Walleroo B).

after further storage, and, thereby possibly contribute to selection for tolerance to phosphine.

3.2 <u>Surface application technique - deficiencies in fumigant</u> distribution

(i) Excessive delay in reaching some regions with low efficiency of utilisation. The surface application technique has a number of practical advantages that render it preferable to the systems involving addition of phosphine-generating preparations to grain during filling of cells or by probe. These include the ability to remove spent preparations, the ability to treat grain *in situ*, and the rapidity with which the fumigant application can be carried out. Indeed, in its simple form, it might rapidly replace other techniques were it not for some important limitations.

When fumigations are carried out with the fumigant preparation evenly mixed through the system, the gas needs to disperse only over relatively short distances to give significant concentrations throughout the system. In the absence of defects of the type cited above, the speed with which this occurs is rapid and the effective start of the exposure period is close to the time the preparation is added. In contrast, when the preparation is concentrated on the grain surface, the gas may need to disperse over substantial distances (up to 35 m downwards in some silo bins) to reach all parts of the bin. With natural mixing only, this may be slow. The effective start of the exposure period, i.e., the time at which all points in the system reach a significant fumigant concentration, may thus be many days after application. Furthermore, in tall, narrow structures, such as many concrete cells, the rate of dispersion of the gas may be so slow that a significant proportion of the gas applied is lost through leakage or sorption before concentrations begin to build up in the more remote parts of the system.

Data illustrating these problems is presented in Fig. 4a, which shows the average concentration-time curve and the change in minimum to maximum ratio with time during the fumigation of a large concrete cell at Meanderra. Here the gas reached all parts of the system only after about 14 days from application and after about 70% of the material applied had been lost by leakage and sorption.

Others (R. Sticka and B.E. Ripp, pers. comm.) have noted similar behaviour of the gas during fumigation of tall silo bins. They also have found that if the bin is not well sealed, the gas can be completely lost before it has time to disperse adequately within the system.

3.3 <u>Examples of successful treatments using surface application</u> technique in sealed systems

In the example shown in Fig. 4a, although the overall gas retention was adequate and there was no observed formation of havens for survival of insects through localised air ingress, the treatment was not completely satisfactory. The rate of the dispersion of the phosphine from the point of release was so slow that it could not provide a significant concentration throughout the structure before most of the gas added had been lost. However, dispersion is affected significantly by the geometry and size of the system treated and in many situations the surface application technique gives an excellent fumigation in a sealed system.

Figures 4b, c, d, show further examples of the average concentration-time curves produced from surface application of phosphinegenerating material in sealed systems. These data are for a large shed (Harden) and small (Newcastle) and large cylindrical steel bins (Bordertown). The observed maximum concentration for each structure was > 55% of that expected and the loss rate was sufficiently low (< 12% day⁻¹) for there to be a substantial fraction of the original

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Fig. 4. Variation in average concentration of phosphine $(\bullet ---- \bullet)$ and minimum to maximum concentration ratio $(\bullet ---- \bullet)$ with time in sealed structures after surface application of phosphine generating material for (a) a large concrete bin (Meandarra), (b) a large steel bin (Bordertown), (c) a small steel bin (Newcastle) and (d) a large shed (Harden), illustrating variation in rate of dispersion of phosphine in different types of storage.

dosage present after more than 20 days from addition of the phosphinegenerating preparation. These data can thus be taken as examples of where the material applied was used efficiently and where sealing of the fumigated system results in good retention of the fumigant.

The ratio of minimum to maximum concentration eventually exceeded 0.3 (Fig. 4) thus confirming that there was effective natural mixing in the system and that there were no havens observed where survival could be expected. In one case (Fig. 4a), data was not collected for long after phosphine had dispersed throughout the storage but it can be expected that the forces that were sufficient to even out an initially very uneven concentration pattern would have continued to operate adequately to maintain the approximately uniform pattern observed in examples in Figs 4b, c, d.

4. PHOSPHINE DISTRIBUTION CRITERIA FOR A SUCCESSFUL FUMIGATION

The data used in the examples was drawn from various large scale treatments, each of which was effective enough for it to be regarded as commercially successful. Yet, as we have seen, many of the treatments did not use the applied fumigant efficiently and, in several cases, there were regions of the treated system that did not receive an adequate dosage regime for complete kill. In others, the phosphine concentration built up in some regions only long after application of the fumigant material. These deficiencies can be incorporated in a set of criteria classifying the success level of a treatment and ranging from what is regarded as a 'commercial success' to a practical definition of a perfect result.

In the case of a 'commercial success', insect numbers must be reduced to a level where they are not detected by the subsequent handler or purchaser of the grain or where an acceptable period of storage is obtained before retreatment is required. In the perfect result there is no survival of pest insects, adult or immature forms, in the system after treatment and thus no chance of selection of strains resistant to phosphine.

We propose the following criteria for success of a phosphine fumigation, in increasing order of stringency. Each successive criterion includes, by implication, the previous ones. The trend is towards maximum likelihood of a perfect fumigation with applied dosage of fumigant.

(a) The grain bulk be found free of insects by conventional sampling at the end of the treatment period. This is one current

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definition of a commercially successful treatment, but is dependent on the intensity and method of sampling and may not detect either survival of immature stages or low numbers of adult insects.

(b) The average maximum concentration of phosphine in the system shall be not less than 50% of the expected quantity based on the dosage applied and the total gas volume in the fumigated system. This criterion implies that the gas is used efficiently and, indirectly, requires that the system is sealed sufficiently for the gas loss rate not to substantially affect the peak concentration.

(c) That an average concentration greater than the minimum effective against insects be present at the end of the exposure period. This criterion is an indirect constraint on the rate of loss of gas. It ensures that the period thought to be the exposure period is, in fact, so. Otherwise, under conditions of excessive leakage, the fumigant may have been lost before the end of the required exposure period. The minimum effective level has not yet been adequately defined but is here taken to be 0.01 g m⁻³ following Reynolds *et al.*, (1967) and Bell (1979).

That the ratio of minimum to maximum concentrations of (d) phosphine be not less than 0.25 after not more than 25% of the total exposure period and remain greater than that value for the remainder of the exposure period. This criterion is a measure of the evenness of distribution and how rapidly disperson occurs. We have chosen the value of 0.25 for the ratio of minimum to maximum as a realistic value consistent with the need to define an approximately even distribution. It implies that there are no regions either of excessively high concentration, showing inefficient use of the material added, nor ones with very low gas concentrations where insects may survive. The restriction on the fraction of the exposure period is to ensure that the distribution process is not so slow that when an even distribution is achieved the phosphine concentration has not already decayed to a small fraction of that applied.

On the basis of these criteria only two of the examples given here, Harden and Newcastle, may be judged to be completely successful fumigations. Two others, Meandarra and Bordertown, fulfil all criteria proposed except (d). The slow rate of mixing in tall narrow cells is a known problem (e.g. see Conway and Mohiuddin, in press) which restricts the use of surface application in these structures. Assisted natural convection using an external circulation assisted by the sun and very gentle forced convection have both been used successfully to overcome this problem (see Boland, in press; Cook, 1980).

5. CONCLUSIONS

The criteria given above can be used to judge the level of success of a fumigation. To provide as perfect a result as possible all four criteria for success should be met. As some of the examples show, it is possible to meet this standard even when using an application technique in which the fumigant material is initially applied in one restricted region. Clearly, some fumigations are currently carried out in situations that can give an incompletely effective though commercialy acceptable result. In such cases, a decision must be made either to continue such practices knowingly for short-term economic benefit at the risk of provoking the development of resistance to phosphine or to bear the cost of altering the techniques to produce a better fumigation and hence minimise the risks.

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