

USE OF A CYLINDER-BASED FORMULATION OF PHOSPHINE AS A CONTROL STRATEGY FOR FLOOR-STORED GRAIN

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ABSTRACT

The use of 3% phosphine (PH₃) in carbon dioxide (CO₂) has been investigated as a virtually residue-free method of treating bulk-stored grain. Coupled with the strategy of drying and cooling grain after harvest, it offers a safe and efficient alternative to solid phosphide formulations and can eliminate the need for prophylactic admixture of grain with insecticidal dusts or sprays, provided that insect populations are monitored by an appropriate trapping technique. The use of continuous gas flows from a cylinder supply is shown to provide a means of sustaining sufficient levels of gas for a long enough period to treat the small (less than 1,000 tonnes capacity) floor store at low temperatures. In contrast, solid formulations lose efficacy as the size of the store is reduced because of sealing problems, surface area increasing in relation to volume as size decreases. The cylinder-based mixture also provides a means of using phosphine to treat "hot spots", localised areas of infestation or spoilage, in large bulks, thereby economising on the cost of an entire bulk treatment. In this capacity the mixture fills a gap left since the withdrawal of liquid fumigants.

INTRODUCTION

The optimal strategy for the storage of grain in cool temperate climates is to load freshly harvested grain into a clean store, then to reduce moisture content (m.c.) to below the level permitting mould growth to prevent spoilage, and finally to cool the grain by ambient aeration to below the minimum temperature for insect development. Under ideal circumstances, no other pest control measure is required, but local conditions, climatic aberrations, and trade transport can provide a means for infestations to arise. Thus, there remains a place for chemical control, though not necessarily as the prophylactic use of pesticide admixture with grain. This practice gained popularity in the 1970s and, although still very much in use, would be unlikely to be instituted today with the current end user-driven policy of

minimising pesticides in foodstuffs.

Grain can be harvested, dried, and cooled, but cannot then be left safely unattended until required, particularly if stored until after the following spring. It is necessary to monitor the condition of the bulk by installing a grid of temperature probes and positioning traps between probes to detect insects. Several new designs of grain pest traps are now available (Cogan *et al.*, 1991a,b). If temperatures increase or insects are detected action can be taken, possibly by surface application of a contact pesticide, but more completely by fumigation.

Since the increasing unpopularity and eventual withdrawal of liquid fumigants from the fumigation arena, there have been difficulties in obtaining satisfactory control of infestations with phosphine (PH₃), the only fumigant available for regular use in bulk grain. Furthermore, phosphine requires long periods of exposure to work effectively, and resistance has developed in several pest species, making it essential that treatments be carried out under closely controlled conditions. Sometimes, but not always, the reason for a failure can be attributed to poor quality sheeting, very low temperatures or insufficient exposure time, or to other instances where recommendations for treatment have not been followed adequately. However, some cases of failure have not been obviously related to such defects, and may have arisen simply because existing methods developed for phosphine usage do not extend to some of the current storage situations.

At the outset of the current project, problems were encountered both in the treatment of very large grain bulks of several thousand tonnes and in quite small storages. For large bulks, there was also a lack of an effective method of fumigating a localised infestation, the only alternative with phosphine being to fumigate the entire bulk - a costly procedure.

For storages smaller than 1,000 tonnes capacity the problem was, and still is, one of gas containment, the surface area of any shape of bulk storage becoming relatively large in comparison to volume as size is reduced. There is also the general problem of having to recommend treatment in grain stored at temperatures below 10°C when it is known that it would be difficult to retain gas for a sufficient period to control tolerant pests using standard sealing methods.

The tests described here follow those reported recently elsewhere (Chakrabarti *et al.*, 1991) and demonstrate that the use of a continuous flow system for PH₃, based on a 3% v/v mixture of PH₃ in carbon dioxide (CO₂) in cylinders, has advantages over conventional dosing methods for treating typical farm stores. The system also makes it possible to treat localised infestations in very large bulks, and enables fumigation with PH₃ to provide the final component of an integrated strategy for the protection of grain in store.

MATERIALS AND METHODS

Following a standard sampling procedure, in each trial a diagonal was traced across the grain bulk using string from the far back corner of the bay to the start of the slope near the front. At each of these two positions - at the centre of the diagonal that coincided with the centre of the bulk, and at the start of the slope at the front centre - nylon gas sampling lines were inserted to the bottom of the bulk, to the midpoint between bottom and surface, and to just below the surface. Further lines were placed to provide sampling points at 1-m intervals if the grain was 3 or more metres in depth. The highest point of the grain bulk was treated as an additional sampling position if it did not coincide with the centre. All lines were run from the bulk to a mobile laboratory stationed nearby. Samples of grain were taken to check the grain m.c. and for use as controls for subsequent analysis of residues.

Up to 50 cages containing 3-5-week old immature stages of a standard stock of *Sitophilus granarius* reared at 25°C, 60-70% relative humidity (r.h.) in the laboratory were inserted in the grain alongside the gas sampling positions and elsewhere to supplement the information obtained on gas distribution and treatment efficacy. Cages were held in threaded cage holders linked to rod spacers that permitted the insertion of cages at metre intervals to depths of up to 4 metres. Thermocouples were attached to the rods to obtain a representative profile of the temperatures within the bulk.

Efforts were made to seal the bulk prior to dosing. The ventilation ducts beneath the bulk were sealed off as far as possible by gluing polythene sheets across the ends or by sealing the individual hatch plates along the main plenum duct if present, leaving a corner free for inserting dosing lines. Plenum ducts were sealed by sheeting the fan itself from inside and outside the duct. Lightweight laminated sheets having low permeability to PH₃ were placed on the grain surface and pushed into the grain round the sides of the bulk to achieve a good seal. The sheets were overlapped, glueing, taping, or stapling all joins. Dosing lines were then run to the aeration ducts from cylinders located outside the bulk or away from the grain, and the sealing of the aeration ducts themselves or their hatches in the plenum chamber was completed.

A total of four trials are reported here: the first two on a 500-tonne bulk of wheat in Cambridgeshire: one with existing PH₃ formulations and the other with the CO₂ mixture, the third on 10,000 tonnes of wheat in Worcestershire, and the fourth on another 500-tonne bulk in Warwickshire.

In the first trial, the bulk was dosed by burying two new 6-m length Detia bag blankets (each releasing 1.1 kg PH₃, equivalent to 100 Detia sachets) across the centre of the bulk prior to sheeting, and by inserting conventional Detia sachets into the aeration ducts below, sealing each in turn to provide a dosage rate of 7 g/tonne, slightly higher than the 6-g rate normally recommended. In all tests with the cylinder-based mixture, the dosage rate was set at about 5 g/tonne. The third trial explored the potential of

using PH_3 as a spot treatment method and compared the effect of multiple and single-point continuous flow systems, dosing two separate parts of a 10,000 tonne bulk at a rate of 5 g/tonne PH_3 for a hypothetical treatment zone at a 3-5-m depth and its surrounding area, amounting to a total of 100 tonnes of grain.

In all trials with the cylinder-based mixture, gas flows were monitored by both weight and flow rate, and gas was obtained from standard size J cylinders supplied by BOC Special Gases Division. Each cylinder was fitted with a standard CO_2 regulator from which the dosing line was run via a gas flow meter to a 1-m perforated stainless steel dosing probe. Excluding the localised treatment trial, gas was introduced into ventilation ducts at roughly 3-m intervals along the bulks by inserting dosing lines and probes up to 4-m into the duct. Lines used for dosing comprised nylon "Wadelon" pressure tubing having a 9-mm outer diameter and 2-mm wall thickness. Each cylinder was weighed before use and flow rates were set by adjustments of the Platon flow meter needle valves throughout the desired exposure period.

The dosing procedure was modified for each trial. The Cambridgeshire trial featured three gas cylinders feeding a common expansion chamber from which four dosing lines were run. The Warwickshire trial featured the use of separate reservoirs for each cylinder. In the "spot treatment" test on the 10,000-tonne barley bulk in Worcestershire, a manifold was used to supply the four dosing lines for the multiple dosing point treatment, while the single-point dosing line was run from the cylinder via its own reservoir. Each dosing line terminated in a 1-m stainless steel probe perforated at 10 cm intervals for the last 50 cm, which was inserted to a depth of 3-m in the grain.

Gas concentrations were monitored throughout the 16-day exposure periods. The bulk was then unsheeted and allowed to aerate. Hand-held electronic detectors were used in conjunction with Dräger and other detector tubes to investigate whether PH_3 levels had fallen to below the occupational exposure standard (OES) before moving on to the grain to remove lines and test insects and to take samples of grain from the top, middle, and bottom of the bulk at selected positions, depending on the distribution of measured gas concentrations. These samples were analysed at the laboratory by the method of Scudamore and Goodship (1986) to check that PH_3 residues did not approach the maximum residue limit (MRL) of 100 $\mu\text{g}/\text{kg}$.

RESULTS

The cylinder-based application technique provides a means of sustaining sufficient levels of gas for a long enough period to successfully treat floor stores of less than 1,000 tonnes capacity without any increase in the amount of PH_3 applied. Figs. 1 and 2 and Table 1 show the comparative performances of solid and cylinder-based formulations on the same bulk. In spite of the higher dosage applied with solid formulation, gas levels fell below 0.1 mg/l at all positions within 8 days, whereas at the prevailing grain

temperatures of 6-17°C, exposures of up to 16 days duration were known to be required.

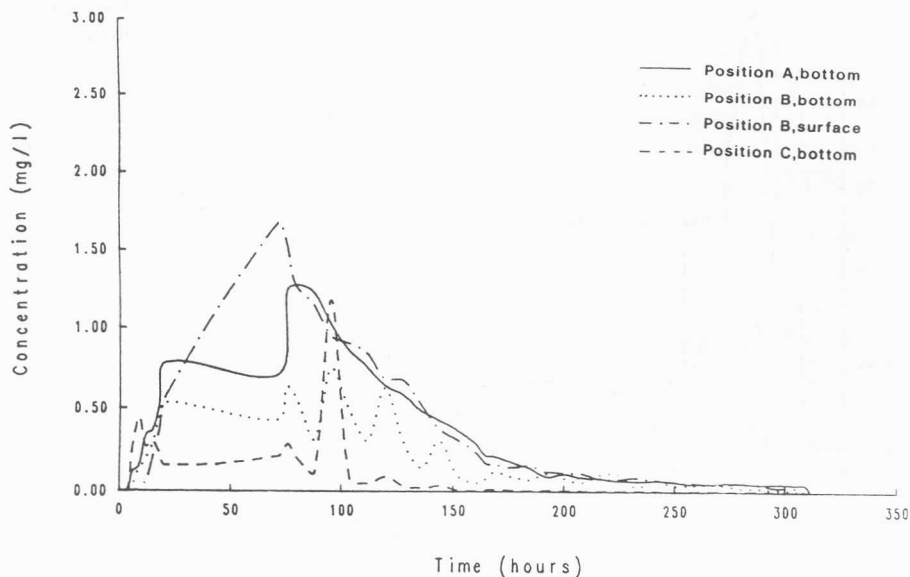


Fig. 1: Gas concentration profiles at the Cambridgeshire site using Detia bags.

After airing the bulk and restarting the treatment with application of PH_3 as a 3% v/v mixture in carbon dioxide from cylinders, concentrations remained above 0.1 mg/l for 16 days at most positions, apart from a dip during the establishment of the maintenance flow rate from days 4 to 9 (Fig. 2).

This was reflected in a small survival of test insects at one position only, whereas with the solid formulation several sampling positions yielded survivals (Table 1).

The subsequent trials highlighted the importance of having a separate reservoir attached to each cylinder to facilitate a steady flow of gas under low and fluctuating temperature conditions. Difficulties were encountered in maintaining an even flow to several outlets from a common reservoir which necessitated frequent visits to the site for adjustment of flow rates. This was apparent in the Worcestershire trial for the multiple dosing system. Nevertheless, the trial illustrated that the cylinder-based gas supply enabled the successful treatment of localised areas of a large grain bulk, offering a realistic replacement to the now prescribed liquid fumigant mixture for the treatment of "hot spots". On this occasion, in the presence of very low grain temperatures, little gas remained near the surface while very high concentrations were recorded at 5-m depths (Table 2).

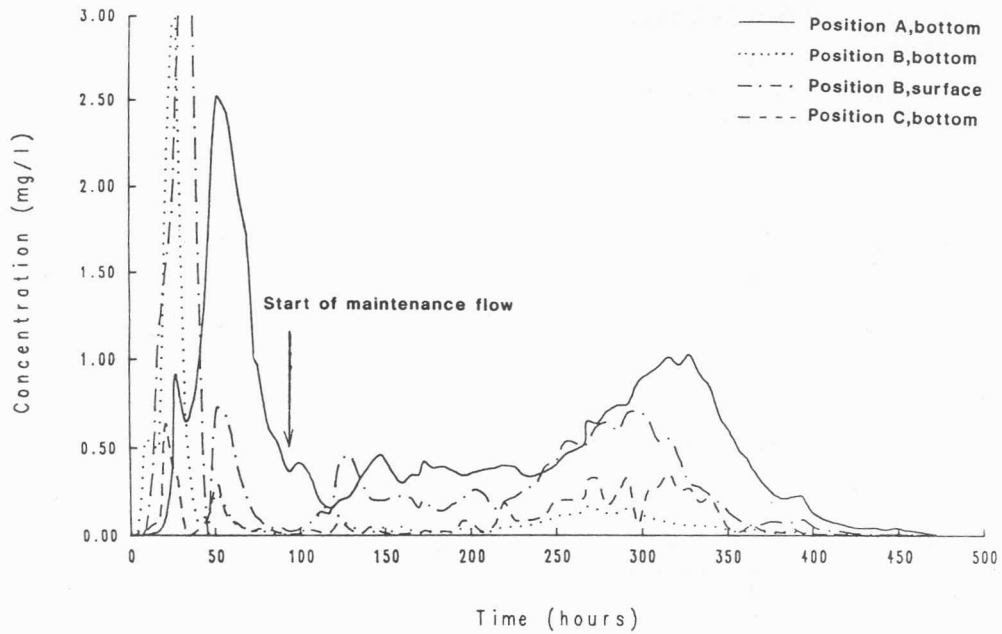


Fig. 2: Gas concentration profiles at the Cambridgeshire site using the phosphine/carbon dioxide mixture.

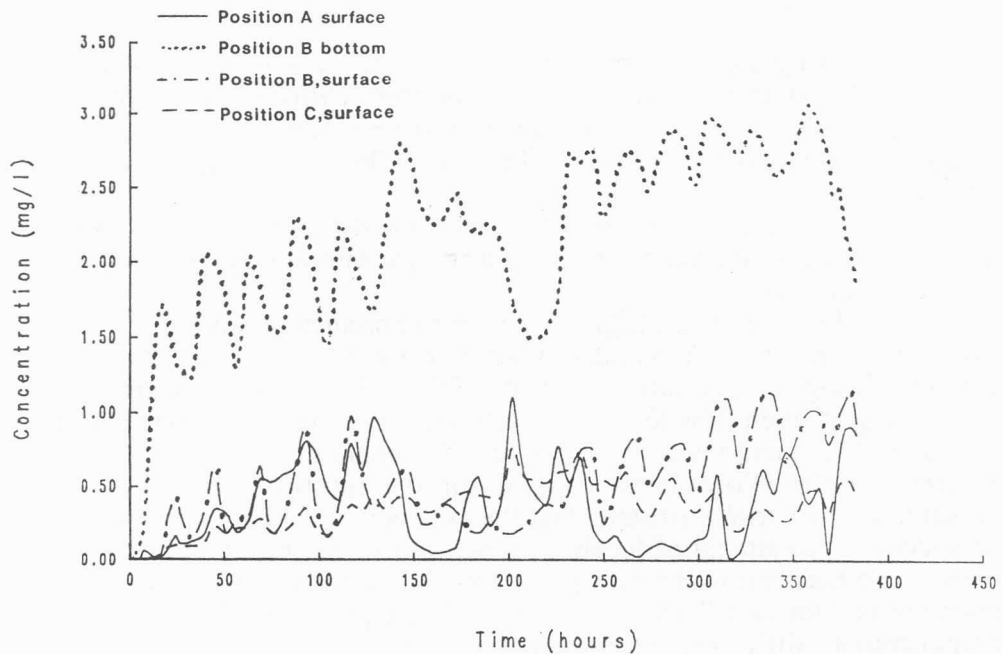


Fig. 3: Gas concentration profiles at the Warwickshire site using the phosphine/carbon dioxide mixture.

Table 1: A comparison of Ct products, residues and kill of immature *Sitophilus granarius* in two trials using different methods of applying phosphine to a 500-tonne bulk of wheat in Cambridgeshire.

Position in grain	Depth (m)	Bag blanket		PH ₃ /CO ₂	
		Ct product (mg.h/l) (Residue, ppb PH ₃)	% Kill* of <i>S. granarius</i> (and grain temp. °C)	Ct product in mg.h/l (Residue, ppb PH ₃)	% Kill* of <i>S. granarius</i> (and grain temp. °C)
Rear corner	Surface	128 (0)	100 (7)	318 (5)	100 (6)
	1.0	130	100 (13)	264	100 (11)
	2.5 (bottom)	122 (2)	100	297 (4)	100
Centre	Surface	143 (2)	96 (7)	169 (2)	100 (6)
	1.0	110	100 (14)	152	100 (15)
	2.0	88	100	93	100
	2.5 (bottom)	72 (2)		50 (0)	
Front corner	Surface	47 (4)	94 (7)	215 (3)	100 (6)
	1.0	23	100 (12)	121	100 (10)
	2.0 (bottom)	30 (2)	91	56 (5)	97
Back centre	Surface	154		214	
	1.0	160 (3)		188 (0)	
	2.0 (bottom)	277		114	
Highest point of bulk, near front centre	Surface	136	98 (8)	412	100 (7)
	1.0	141	100 (16)	453	100 (17)
	2.0	153 (2)	98	484 (2)	100
	3.5 (bottom)	211	100	739	100

* Kills of *S. granarius* corrected for mortality in controls held on site.

The Warwickshire trial illustrated the extent to which a constant flow of gas throughout the treatment was effective in achieving an even distribution of gas (Fig. 3). The maximum residue level of PH₃ recorded was less than a quarter the MRL of 100 µg/kg although Ct products in excess of 400 mg.h/l were achieved at several points. Again survival was recorded from only one position, this an exposed corner of the bulk where windy conditions prevailing for much of the trial resulted in a Ct product of less than 150 mg.h/l.

DISCUSSION

Phosphine is a fumigant with many advantages and has come into world-wide use for the treatment of bulk commodities. However, attempts to extend its use into new situations arising because of changes in storage practice or loss of previously used control agents are identifying a number of problems. Some pests are tolerant of exposure to PH_3 at particular stages of development (Bell, 1976) and their control requires lengthy exposure periods, especially at low temperatures. This problem may be compounded further by the presence of resistance in pest populations.

Table 2: Results of the Worcestershire trial, investigating the use of the cylinder-based mixture of phosphine in carbon dioxide as a means of treating localised areas of a large bulk to control infestation.

Area and sampling position	Depth (m)	Mean grain temp. ($^{\circ}\text{C}$)	Corrected % mortality of immature <i>S. granarius</i>	Ct product (mg.h/l)	Phosphine residue (ppb)
Area 1, 4 dosing points					
At central dosing point	Surface		20	4.1*	0
	3.0		100	57	2
	5.0		100	262	7
0.5m from centre	Surface	7.6	21	0.3	0
	3.0	2.3	100	45	0
	5.0		100	273	2
1.5m from centre	Surface		14	0.4*	
	1.0	6.0	41		
	3.0		96	18	
	5.0	2.2	100	155	7
Area 2, single dosing point					
0.5m from centre (1)	Surface	6.3	98	42	1
	3.0		96	27	2
	5.0		100	434	11
0.5m from centre, opposite (1)	Surface		82	6.5	
	3.0		100	252	
	5.0		100	1,368	
1.5m from centre 2m from (1)	Surface		2	1.3*	
	1.0	5.5	46		
	3.0		93	9.3	
	5.0	2.0	100		

* Ct product at 0.5 m depth

The picture emerging from the field trials conducted in this project is that conventional methods of treating small bulks of grain with PH_3 are likely to be unreliable in achieving an adequate degree of control, especially at low temperatures. This problem is tied up with leakage being largely dependent on the surface area of the enclosure when measures have been taken to achieve a good seal. As the size of the enclosure increases, the surface area to volume ratio reduces progressively. Hence, if the volume is increased eightfold (a doubling of linear dimensions), the surface area is only increased fourfold and leakage of the enclosed gas volume will proceed at only half the percentage loss rate. This effect may be the critical factor for bulks of 500 tonnes or less when exposures have to be extended beyond two weeks.

An alternative approach is therefore needed for dosing the small store. One such approach is the development of a means of continuously introducing fumigant throughout the exposure period to replace gas leaking out. The current tests on a cylinder-based supply of 3% (2.6% w/w) PH_3 in CO_2 have shown that simple methods exist to enable this to be done. The "Siroflow" system already in use in Australia incorporates a cylinder-based 2.6% mixture of PH_3 in CO_2 that is introduced into grain stores via a fan driven airstream (Winks, 1990) but the present tests show that introduction of gas directly from cylinders can be equally successful.

The cylinder-based mixture also provided a realistic means of treating successfully a localised area of a very large bulk. There is a need for further testing to establish the optimal position of dosing probes in the presence of steep temperature gradients surrounding the infestation centre, but in principle a continuous supply of gas should solve the problem.

It proved possible to remain within the existing recommended dosage level of 5-6 g per tonne even for small stores by setting the appropriate steady gas flow to run continuously throughout a 16-day exposure. At this rate of introduction of gas there was never any problem of frosting up of cylinders even in the coldest weather. However, controlling gas flows through separate needle or ball valves, or flow meters was not completely satisfactory, as there was a continual tendency for flows to fall off, necessitating frequent adjustments. The provision of gas reservoir in the dosing line resolved the problem only partly. The best result was obtained, especially for the lowest flow rates, by using a metering valve and leaving flow meters fully open.

Phosphine fumigation can thus provide the necessary reserve control measure to an integrated control programme designed on the basis of good hygiene and drying and cooling grain coming into storage. Should circumstances arise whereby fumigation becomes a necessary option, the careful monitoring of trap catches and increases in grain temperature would provide information on the scale of the treatment needed and on its timing. Clearly, the presence of a small number of insects at the weekly assessment of catch in cool grain is not a sufficient basis to recommend treatment

(Pinniger, 1988). However if catches of 6 or more beetles occur in traps grouped together in a part of the 4-5-m grid, then as recommended to UK intervention stores (Cogan, P. M. personal communication), further investigation is required. A subsequent increase in catch or gain temperature would then trigger active control measures, such as fumigation with PH₃.

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