THE USE OF A CYLINDER-BASED FORMULATION OF 2-3% PHOSPHINE IN LIQUID CARBON DIOXIDE

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Abstract

The use of phosphine as a fumigant has always relied upon solid commercial formulations containing metal phosphides which react with moisture to release the gas. After treatment, it is recommended that all residues are removed but this is not always accomplished, often traces of undecomposed material remain in the commodity and sometimes grain loads are rejected on account of a persistent characteristic smell.

Trials showed that the cylinder-based formulation of 2.5-3% phosphine in liquid carbon dioxide can be used effectively to fumigate grain held in farm bins or floor stores. To maintain gas levels throughout exposures of up to 21 days, dosage levels of phosphine may need to exceed those currently recommended for bulk grain held in smaller floor stores, but for grain bins, dosage levels around 5-6g phosphine per tonne are sufficient. An initial high rate purge gives no advantage to the treatment and best results are obtained by using an even application rate througout the chosen exposure period.

Introduction

Grain is stored in the U.K. in glavanised steel bins and concrete silos on farms, in purpose built floor-stores on farms or at commerical premises and in aircraft hangers and other non-standard buildings which are used by farmers and grain merchants alike. This diversity coupled with biological complexities due to the wide differences in tolerance between different species and strains and between stages of the same species of insect, creates difficulty in devising a general set of recommendations for the use of the fumigant phosphine to control infestation. Furthermore, the exposure time needed varies with the temperature, together with the concentration range over which phosphine acts efficiently. In practice, it is difficult to maintain a high enough level of phosphine troughout a bulk of grain for periods in excess of 10 days.

A cylinder-based formulation containing 2-3% phosphine in liquid carbon dioxide was developed in collaboration with British Oxygen Company Ltd (BOC) and was initially evaluated in a pilot-scale study in the laboratory, in a gas-tight bin containing 6 tonnes of grain (Chakrabarti and Wontner-Smith, 1987). This paper reports the results obtained in 4 larger scale trials, the first two in bolted metal farm bins and the third and fourth in different floor-stores. The purpose of the trials was to investigate whether the use of the cylinder-based supply of gas would provide a more efficient means of treating grain than current methods without greatly increasing costs and whether it would enable tolerent insect stages to be controlled.

Materials and methods

Gas supplies

The batch of phosphine/carbon dioxide (PH_3/CO_2) mixture supplied in size J cylinders by BOC Special Gases Division and used in the first trial were analysed as reported previously (Chakrabarti and Wontner-Smith, 1987) and were found to contain 30-33 g/m^3 (2.1-2.3% w/w) phosphine. Subsequent batches contained 2.6% w/w of phosphine.

The Bioassays

Sitophilus granarius was the test insect chosen because of its high natural tolerance to phosphine particularly in the pupal stage. Prior to a trial, grain infested with older larvae and pupae reared in the laboratory was separated into similar 10g batches using a Boerner divider and was placed in cadmium-plated cages. After transfer to the trial site, cages were inserted at various depths together with 2mm bore nylon gas sampling lines using rods and cage-holders. Thermocouples were attached to selected cage holders to measure grain temperatures. To assess the total number of insects per cage, control cages were kept in the laboratory at 20^o-25^{o}C and 60% R H. Two or more cages were also kept at the site of the trial in untreated grain to act as a control.

After exposure at the site and removal from the grain, the bioassay samples were incubated in the laboratory at 25^{o}C and 60% RH and examined weekly for emerging adults. The mortality in samples was based on adults emerging from fumigated cages as percentage of those emerging from the site control.

Gas sampling

A Hewlett Packard 5880 gas chromatograph (GC) installed in a mobile laboratory was used to monitor phosphine concentrations during the fumigations. The GC is equipped with a flame photometric detector and 32 stream selection valves and can be programmed to monitor gases at upto 31 positions at regular intervals while unattended.

1. First trial in a farm bin

The bin chosen for this trial was one of two free-standing bins of galvanised, corrugated steel construction, mounted side by side on a concrete plinth. It measured 5.3m high at the eaves and 7.4.m in diameter and contained 175 tonnes of home-grown wheat. Each of the two bins had a 20 cm diameter auger hole at the base and was joined at the rear to a common aeration system served by a blower. The passage of air to a plenum chamber under the perforated bin floor was regulated by an external lever-operated internal flap which was closed for the trial.

For dosing, a copper pipe 3m long, 15mm o.d., blanked at the end but with the last 0.5m length perforated with a 3mm hole at 10cm intervals, was inserted via a blanking plate into the auger hole underneath the plenum chamber. The protruding end of the copper pipe was connected to a length of semi-rigid, 9mm o.d. "Wadelon" nylon tubing which in turn was connected to a gas cylinder rested on an electronic platform scale. Nylon gas sampling lines, insect cages and thermocouples were inserted at different depths at the bin centre and 0.5m away from the edge of the bin near the hatch (Table 1). After lines were led out of the bin via the hatch, the grain surface was covered with a PVC fumigation sheet and light-weight iron chain was placed round the periphery of the sheet. Aeration duct and auger hole were also taped round with polythene sheeting.

The dose was calculated on the basis of the concentrations of phosphine in the cylinders and the planned initial dosage rate of 5g/tonne of this gas. Due to an unexpectedly low amount of gas in two successive cylinders, only one half of the dose could be applied on the first day. The remainder was applied on the next day and a total of 41.08kg was applied, slightly higher than the calculated amount. On each occasion it took only 10 minutes to apply the gas.

The GC recorded drops in concentration below $0.05g/m^3$ at several points after six days. During this time phosphine had progressively moved upwards from the bottom towards the grain surface. Therefore a bleed of the gas mixture from the cylinders at the rate of about 8kg/day was started to maintain a concentration of at least $0.1g/m^3$ at all points. It was difficult to maintain a steady flow because of ice forming at the delivery point from the cylinder to the nylon tubing, preventing smooth flow of the gas. Fumigation was continued for 16 days when the amount dosed as bleed was 51 kg of the $PH3/CO_2$ mixture. The total dose for the period was 92.08 kg of the mixture equivalent to 11.3g/tonne of phosphine.

The concentration-time products (CTPs) at different positions with insect mortalities are given in Table 1. The temperature of the grain varied from 9^o-11^oC. Temperature fell to -50^oC or even lower in the aeration system at certain times during dosing.

The test was conducted under extremely windy conditions, for much of the fumigation period, at the coldest time of the year. Furthermore, the design of the ventilation ducting allowed quite high levels of gas leak to the neighbouring bin. In spite of these difficulties the fumigation was successful in eradicating a resident infestation of *Cryptolestes ferrugineus* in the bin and no survivors were recorded from the bioassay (Table 1) with the highly tolerant grain weevil.

2. Second trial in a farm bin

The trial facility featured two bins, each measuring 6.1m high at the eaves and 5m in diameter mounted side by side on a concrete base, other features being the same as in Test 1. The bin selected for the trial contained 145 tonnes of feed wheat. Both the internal flaps leading to the bin from the blower were shut and the access covers on the duct leading to the selected bin was unbolted and removed. The flap was sealed using spray-adhesive and impermeable thin laminated sheet. The cavity was then packed with bubble-pack polythene, covered with another laminated sheet and the metal cover was loosely placed on top of it. Other preparations were performed as in the first trial.

For dosing, the perforated pipe was replaced by a 3-way jet connected via a flow meter and needle valve to the cylinder. To achieve a dosage rate of nearly 5g/tonne of phosphine, 24.2 kg of the mixture was dosed under the plenum chamber in 45 minutes. Two days after dosing when gas concentrations started to fall, a maintenance flow was established. Starting with a very low flow of 0.8 kg/day, it was progressively increased to 1.2 kg/day and eventually to 3kg/day after 12 days which stabilised the concentrations at all points for the rest of the trial period.

Gas concentrations were monitored from dosing until after unsheeting at the end of the treatment, 17 days later. The temperature of the grain during fumigation ranged from 6^{o}-11^{o}C.

The CTPs along with bioassay data are presented in Table 1. Within 12 hours of dosing, phosphine had distributed well to all points, concentrations ranging from 0.7 to 8.3 g/m^3. The very high concentrations measured throughout the trial in the auger spout into which gas was introduced, provided further indication that the principal source of gas loss was to the ventilation system, as no comparable levels were recorded in the bottom layers of the grain. However, it is clear in this bin that with a continuous application rate of 2-3 kg of the PH_3/CO_2 mixture per day, an adequate concentration of gas can be achieved at all points for as long as required. A total of 8.9g of phosphine per tonne of grain was applied over the 17 days exposure period.

It is worth noting that complete control of normal strains of most pest species other than *S. granarius* would have been obtained in this trial within 10 days. However, fluctuations in the gas levels during the pin-pointing of the maintenance flow rate required for the bin did permit some survival of the bioassay *S. granarius*.

3. Trial fumigation of grain in a temporary floor-store, built inside an aircraft hanger.

A bulk containing 270 tonnes of milling wheat was stored in an area measuring 13m x 10.2m and 2.9m high, contained in a corner of a hanger by wooden bulkheads on two sides. The other two sides were of corrugated galvanised metal erected 1m away from both the side walls and the hanger door respectively. Though the height of the wall was 2.9m on all sides, the grain was unevenly stored with at least two high peaks, rising about 1m above the wall. It was learnt that the grain was admixed with pirimiphos methyl at harvest and a further dose was applied on the surface layer following the discovery of a mite infestation. A composite surface sample contained 19.3 mg/kg of pirimiphos methyl. There were four ducts for aeration, width wise, at 3m intervals under the grain, made of 102mm diameter perforated plastic drainage pipes. All the wooden bulkheads were covered with laminated polythene from outside with 0.5m spare on the concrete floor and a metre spare on the grain surface. All the ducts were sealed at the door end and at the other end 1.5m long, 3mm o.d. stainless steel tubes were inserted in the ducts as dosing probes and sealed properly with nylon bags and masking tape. These stainless steel tubes were connected to 9mm o.d. "Wadelon" tubings which in turn were connected to individual cylinders through the flow meters and "Whitey" needle valves. Only one of the cylinders was placed on an electronic balance for continuous monitoring while weights of the other three cylinders were recorded at intervals.

Gas sampling lines were placed along a diagonal at three different depths and on the surface (Table 2). Other sample lines were inserted where it was suspected that concentrations of phosphine would vary. The lines were extended to the mobile laboratory and connected to the GC. Bioassay samples and thermocouple wires were placed alongside gas sampling lines (Table 2).

The grain surface and retaining walls were then sheeted with heavy gauge laminate which was extended 1 metre on the floor and weighted down with chains. The grain temperature ranged fromn 6° to 8.5°C.

Because of the high rate of loss anticipated from the grain bulk, it was decided to dose at a steady rate throughout the exposure period to give a total dosage of 5g or more phosphine per tonne and to extend the exposure period beyond 16 days. To achieve this, a flow of 300ml of the gas mixture per minute was set from each cylinder, equivalent to $1.73m^3$ or just under 100g of phosphine per day. Dosing from the cylinders was continued upto 18 days with an intermittent flow.

Despite the high CTPs recorded at some points, the maximum residue limit (MRL) of 100 μg phosphine per kg of grain was in no danger of being exceeded (Table 2). The maximum expected anywhere in the treatment would be 15ug/kg, based on measurements of up to 7μg for CTPs up to 350 gh/m^3.

4. <u>Trial fumigation of grain in a purpose built floor-store.</u>

In this store, 500 tonnes of wheat were contained in an area 28m x6m and 3m high. The far end and one side were of strengthened corrugated metal sheets, the other side was of rendered brick wall. The grain surface was fairly uneven and at the front sloped to floor level. The average depth was about 2.5 m. Three metal ducts were laid lengthwise under the grain bulk at 2m intervals and fed by blowers fixed 3m up the outside end-wall.

To provide an expansion chamber in the dosing system, three small empty gas cylinders as used with a breathing apparatus, were connected to the cylinders of PH_3/CO_2 mixture, between the regulator and the flow meter. The regulator chosen was specifically designed for use with liquid carbon dioxide, and it was hoped that the controlled vaporization of the PH_3/CO_2 mixture into the expansion chamber would prevent any interruption during dosing at low flow rates.

As in the previous trial gas sampling lines were placed along a diagonal at different positions and depths (Table 2) along with bioassay samples and temperature probes. The grain surface was covered with 30μ laminated sheets joined by rolling edges together and stapling. The edges around the bulk were carefully buried into the grain. All three cylinders of PH_3/CO_2 were weighed and as before, one was left on an electronic balance to monitor gas output. The grain temperatue during the trial varied from 7° to 10°C.

Due to the size of the grain bulk and the knowledge gained from the previous tests,it was decided from the beginning to dose at a rate of one litre of mixture per minute from each cylinder.

As each cylinder contained about 30 kg of the mixture, it was calculated that at this rate, each should last for about 10 days. With the new dosing system the fluctuation of the gas flow was restricted to 700 - 1000 ml/min and adequate concentrations of phosphine were achieved and maintained fairly well at all positions.

The fumigation was continued for 16 days which needed a cylinder-change and a total dose of 102.75 kg of PH_3/CO_2 mixture was applied. On the basis of 500 tonnes of wheat, the dosage amounted to 5.3g of phosphine per tonne. The CTPs ranged from 150 - 1187 gh/m^3 (Table 2). The post-fumigation samples were aired off at room temperature for a week before residue analysis and these contained

1 to 24 μg/kg of phosphine (Table 2). Higher CTPs do not seem to have resulted in high residues.

Discussion and Conclusions

These four trials with a phosphine/carbon dioxide mixture have shown that the method is practical and effective and offers a number of advantages over the use of conventional metallic phosphide preparations. Taking into account the grain temperature, insect species and weather conditions, a dosing regime can be established with a cylinder-based preparation for farm bins as well as bulk stores.

In trials 1 and 2 the two farm bins were initially treated with a high dose of phosphine, equivalent to 5g/tonne dosage rate. These high concentrations were however soon lost, which clearly indicated the weakness of current fumigation methods when gas is generated only at the start of a long exposure period. The best strategy seems to be to maintain an even flow of gas throughout the chosen exposure period.

It is vital for the success of a treatment to have a reliable dosing system which will maintain a constant rate of flow of gas unattended for the duration of the fumigation. The modified system used in trial 4 gave a much better consistency of flows but further development work is desirable. It should be possible for an even gas flow rate to be maintained until cylinder(s) run out so that operating costs can be minimised. Anticipated costs per unit volume of phosphine using the cylinder based supply may be somewhat higher than for existing formulations but may be offset by reduced operator cost. The method is much safer for operators as any contact with the fumigant is avoided, all preparations for dosing being completed before the gas flow is started. In addition, despite high CTPs recorded in Trial 4, the maximum residue limit (MRL) of 100 μg phosphine /kg was in no danger of being exceeded.

While it is true that bioassay insects survived in three trials, the method offers the prospect that the tolerant weevil *S. granarius* can be controlled together with strains that have developed resistance to the fumigant and it is the only means of guaranteeing the presence of gas over the long exposure periods that are needed.

Reference

Chakrabarti, B. and Wontner-Smith, T. (1987) Investigations on the use of 2% phosphine in carbon dioxide as a potential new fumigant mixture. Slough Laboratory Report No.19.

Table 1

Positions of sampling lines with CTPs and bioassay data from two tests in bolted metal bins loaded with wheat

Position	Depth from surface m	Test 1 CTPs gh/m^3	Test 1 % Kill of Insects	Test 2 CTPs	Test 2 % Kill of Insects
Centre	5	---	---	376	---
"	4	---	---	464	100
"	3	455	100	232	96.9
"	2	347	100	241	93.9
"	1	260	100	152	93.9
"	Surface	175	100	250	92.4
Side	5	---	---	523	---
"	4	---	---	363	98.5
"	3	400	100	208	92.4
"	2	165	100	240	96.9
"	1	135	100	206	93.9
"	0.5	---	---	208	---
"	Surface	134	100	202	84.7
Midway,	4	---	100	---	---
Centre and	3	---	100	---	---
hatch	2	---	100	---	---
	1	---	100	---	---
East	0.5	---	---	147	---
West	0.5	---	---	159	96.9
North	0.5	---	---	108	93.9
South	0.5	---	---	92	100
Auger hole		3591	---	8620	---

"---" No gas sample or bioassay evaluations were carried out at those positions

Table 2

Positions of sample lines with CTPs, bioassay data and phosphine residues in two trials in floor-stored grain

		Test 3			Test 4		
Positions	Depth from surface m	CTPs gh/m^3	% Kill of Insects	PH_3 residues µg/kg	CTPs gh/m^3	% Kill of Insects	PH_3 residues µg/kg
Far end, corner	3.25	---	---	---	---	---	---
	3	33	---	3	---	---	---
	2	---	97.9	---	---	---	---
	1.5	62	---	---	576	---	24
	1	---	97.9	---	---	---	---
	0.5	33	---	2	175	100	3
	Surface	36	100	---	150	100	12
Centre, along diagonal	3	357	---	7	898	100	12
	2	---	100	---	---	100	---
	1.5	76	---	---	326	---	24
	1	---	100	---	---	100	---
	0.5	41	---	3	---	---	
	Surface	47	100	---	201	100	6
Near end, along diagonal	3	128	---	4	---	---	---
	2	---	100	---	203	100	2
	1.5	120	---	4	---	---	---
	1	---	100	---	196	100	2
	0.5	109	---	4	---	---	---
	Surface	74	100	5	146	96.1	1
Far end, centre along the wall	3	308	---	---	---	---	---
	2.5	---	---	---	1187	---	15
	2	100	---	---	---	100	---
	1.5	73	100	---	---	---	---
	1	---	---	---	443	---	5
	0.5	47	100	---	---	---	---
	Surface	---	100	---	155	100	19
Near end, centre	3	650	---	---	---	---	---
	2	---	100	---	537	100	5
	1.5	120	---	---	---	---	---
	1	---	100	---	---	100	---
	0.5	90	---	---	---	---	---
	Surface	---	---	---	239	100	9
Near end, left hand corner	2	---	100	---	---	---	---
	1.5	70	---	---	---	---	---
	1	---	100	---	---	---	---
	Surface	---	100	---	191	---	16

Table 2/contd

Positions of sample lines with CTPs, bioassay data and phosphine residues in two trials in floor-stored grain

Positions	Depth from surface m	Test 3 CTPs gh/m^3	Test 3 % Kill of insects	Test 3 PH_3 residues µg/kg	Test 4 CTPs gh/m^3	Test 4 % Kill of insects	Test 4 PH_3 residues µg/kg
On a peak	3	---	100	---	---	---	---
	2	---	100	---	---	---	---
	1	---	89	---	---	---	---
	0.5	3.8	---	---	---	---	---
	Surface	36	100	---	---	---	---
In duct, far end		1040	---	---	---	---	---
Side wall, centre	2.5	---	---	---	473	100	17
	Surface	---	---	---	186	100	15
Centre of the slope	1	---	---	---	551	---	5
	Surface	---	---	---	277	97.4	17
Near brick wall, halfway on the	1	---	---	---	226	---	5
	Surface	---	---	---	185	---	3

"---" No gas samples, bioassay evaluations or residue analyses were carried out at these positions.

L'UTILISATION POUR LA FUMIGATION DU GRAIN D'UNE FORMULE A 33 % DE PHOSPHINE DILUEE DANS DU DIOXYDE DE CARBONE LIQUIDE PRESENTEE EN BOUTEILLE SOUS PRESSION

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RESUME

L'utilisation de la phosphine comme fumigant a toujours été réalisée commercialement par l'emploi d'un générateur de gaz à base de phosphure metallique qui réagit avec l'humidité atmosphérique pour produire le ph_3. Après traitement, il est recommandé d'enlever tous les résidus, mais ceci n'est pas toujours fait et, souvent, des traces de matières non décomposées restent dans la denrées et il arrive parfois que des lots de grains doivent être rejetés en raison d'une odeur caractéristique persistante.

Des essais ont montré qu'un réservoir de forme cylindrique contenant 2,5-3 % de phosphine dans du CO_2 liquide peut être employé avec efficacité pour la fumigation du grain stocké à la ferme ou en organismes stockeurs. Afin de maintenir une quantité de gaz uniforme pendant le temps d'exposition allant jusqu'à 21 jours, la dose de phosphine peut dépasser le niveau conseillé pour les stocks de grains en vrac mais, pour les grands silos, un taux d'environ 5-6 g de phosphine par tonne est suffisant. Une purge préalable ne présente aucun avantage et les meilleurs résultats s'obtiennent en veillant à appliquer un taux uniforme tout au long de la période d'application.