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A NEW POSITIVE PRESSURE SYSTEM FOR COMBATING DILUTION DURING PHOSPHINE FUMIGATION OF BULK GRAIN

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ABSTRACT

Phosphine must be used effectively to prevent the development of resistance in stored grain pests by guaranteeing the required concentration and exposure period. Where resistance exists, phosphine can still be used to give control by the use of longer exposures and higher concentrations, as appropriate. The treatment of grain in silos should not normally present control problems but the treatment of floor-stored grain bulks presents difficulties due to sealing deficiencies. A practical system for treating these has been developed. This utilises dosing from cylinders of phosphine in nitrogen downstream of a centrally-placed circulation fan. The fan is used to generate uniform distribution but, more importantly, to provide a pressure gradient within the bulk. Grain near to the fan is at a slight negative pressure and the flow from the fan is distributed by piping to locations at the periphery of the bulk where they create a small positive pressure. The recirculation flow rate can be increased to replenish the concentration where it is depleted by the effect of wind pressure on the bulk. The system aims to reduce sensitivity to climatic effects and, consequently, phosphine loss by outleakage and inleakage of air and dilution of phosphine. Gas flow modeling, using computational fluid dynamics, was used to predict leakage and optimise the system.

INTRODUCTION

Resistance to phosphine

Resistance to phosphine (PH₃) in stored-product insects is a reality with twelve species being implicated to date. This is an unfortunate drawback since PH₃ has, for almost five decades, been shown to be an ideal fumigant for the disinfestation of stored grains and other commodities. The mechanisms involved in the mode of action and, at least some, of the resistance mechanisms are understood (Chaudhry, 1997). There have been many surveys and descriptions of individual resistance levels, some of which have been reviewed by Chaudhry (1997). We have now arrived at a position where dosage schedules designed for the control of susceptible strains have become unreliable in some situations due to resistance. At its worst, the problem is so widespread that almost every store surveyed has resistant populations, as is the case in Morocco (H. Ben Halima, pers. comm.), though in some countries the problem is less severe albeit with a significant incidence of resistant strains. Manufacturers of PH₃-releasing formulations must bear a partial responsibility in that, often, there has been poor product stewardship. It is important that new cylinderised formulations should be used carefully to prevent them from contributing to the selection for resistance rather than being used to overcome it. The emergence of this problem comes at a time when we will see more PH₃ fumigation due to the demise of methyl bromide (MB) as a fumigant for most uses under the Montreal Protocol. This has a twofold effect. Firstly, there will be more PH₃ fumigations and, therefore, more low standard fumigations leading to resistance selection. Secondly, MB itself will not be available to exert an unintentional but important counter-selection pressure. In addition, there is continual scrutiny of the effect of PH_3 on the operator, along with moves to increase fumigation exclusion zones and to reduce occupational exposure standards. This latter proposal goes against the need for higher concentrations and longer exposure periods to combat resistance (Price and Mills, 1986).

Improving fumigation methods

In some situations, for example the fumigation of stacked packaged commodities under gas-proof sheets, there is a general optimism that a properly constructed and sealed stack can enable gas concentrations and, particularly, exposure periods for the control of resistant strains to be achieved, though, even here, care is necessary. There is already interest in applying vacuum tests on sealed stacks to verify the level of seal (Navarro, 2000). The same methods cannot be applied to unsealed silos, which suffer gas loss mainly through the chimney effect. SIROFLO[®] and SIROCIRC[®] continue to be trialed in order to combat leakage in this situation (Hou Jun *et al.*, 2000). The Central Science Laboratory, U.K., has dealt with the problem of silo fumigation by re-circulation with continual dosing (Wontner-Smith *et al.*, 1999). This method was demonstrated to produce higher concentrations while using less PH₃ per tonne than the SIROFLO technology, which utilises a flow-through of PH₃. It is also poses less safety problems. However, the problem of the effective fumigation of horizontal grain storages remains.

Phosphine distribution in horizontal storages

Good PH₃ distribution can be a problem. Records from farm stores show that initial grain temperature varies throughout a bulk. Temperature gradients will give rise to interstitial gas movement and, over time, the temperature gradients in dry grain can be expected to reduce as the grain tends towards the same temperature. These internal gas movements are unpredictable and cannot be relied on to generate uniform distribution of PH₃ to all points in a bulk. The introduction of a steady pressure gradient within the bulk will dominate the natural air movements and ensure effective delivery of PH₃ throughout the bulk. Pressure gradients of less than 1 Palm⁻¹ can be effective. Research has been carried out using recirculation methods to produce a more uniform gas distribution by a form of 'closed loop' fumigation as used in silos (Noyes, *et al.*,

2000) or the Phyto-Explo system used by Chakrabarti et al. (1994) in a floor store.

Leakage from horizontal storages

Previous studies by Banks and Annis (1984) identified the principal mechanisms of air exchange between a sealed grain bulk and the surroundings. The present study seeks to confirm the relative importance of these mechanisms with a view to minimising their effect on the loss of PH_3 from a grain bulk.

Gas flow within a porous medium (bulk grain) only takes place when a pressure gradient exists between two points or boundaries. At low gas flow rates the interstitial gas quickly comes into temperature equilibrium with the grain so its density is held constant. The density of ambient air outside the bulk boundary varies as its temperature changes through the day. This density difference gives rise to a pressure gradient across the bulk boundary. It will cause flow to take place through any holes in the boundary.

Barometric pressure changes result in expansion or contraction of the interstitial gas volume. These changes will result in pressure differences that will cause flow across the bulk boundary.

Wind interacts with buildings containing grain bulks and can potentially generate substantial pressure gradients across the exposed face of the grain mass. Atmospheric pressures above and below those in the grain bulk are generated by high wind on structures such as sheds (Hoerner, 1965; British Standards Institute, 1972).

Floor stores are notoriously difficult to seal, particularly when fitted with a ventilation system. It is difficult to get storekeepers to incur expense for an occasional treatment. To get an effective level of seal it is often necessary to line walls and bulkheads with a polyethylene sheet before filling.

Implications for the selection for resistance

Even if attempts at sealing take place, the situation arises where a generally adequate treatment suffers from localised leakage of PH_3 in a bulk, which generally experiences a good treatment. Of greater importance, in terms of insect survival and possible selection for resistance, is the local dilution of PH₃ by ingress of air. This can lead to a wide range of concentrations and even shorter exposure periods near to leaks. Some of these doses will be selective. Of these, some will be selective in favour of heterozygous resistants, which are very similar in tolerance to susceptible insects (Li and Li, 1994; Mills and Athie, 2000). This, in turn, will increase the frequency of the resistance gene(s). The very fact that a resistance with an incompletely recessive major gene develops at all is indicative of either, at worst, generally low standards or, at best, variable standards in a particular fumigation. Once there are a significant proportion of homozygous resistant individuals present the selection can continue so that the population becomes wholly resistant. It may be that we should not be using PH₃ in substandard storages in order to prevent the development of resistance as suggested by Zettler (1993). In many situations this is not a viable option, especially where grain weight loss is occurring or where there is the urgent need in order to market the grain. These storages need to be brought up to the required standard or new fumigation methods introduced. Variable gas concentrations in a generally well sealed storage can be corrected if we apply the same effort that we apply to describing and understanding the resistance problem in the laboratory.

The loss of PH₃ can be partly overcome by the use of continuous or automated dosing of cylinderised formulations of PH₃ in liquid carbon dioxide (CO₂) (ECO2FUME[®]) or in compressed nitrogen (N₂) (FRISIN[®]) to lengthen exposure periods. These are certainly of benefit but their use alone (Bell, *et al.*, 1991) without a consideration of application technology cannot prevent the problem of localised dilution. To tackle this problem requires a new direction and a sophisticated engineering solution. This was the aim of Winks and Russell (1994) in testing SIROFLO in unsealed horizontal storages but they concluded that oscillating concentrations resulted from 'chimney forces' causing ingress of air down the shed walls when the ambient air was cooler than that in the bulk during the night.

The aim of the present work is to develop a new fumigation method, which aims to guarantee, as far as is possible, the necessary parameters for a successful fumigation of horizontal storages even in windy conditions. A multi-disciplinary research team, which harnesses gas flow modeling using a Computational Fluid Dynamic (CFD) model, engineering and fumigation expertise is working towards this goal. This method is targeted to prevent the development of resistance by achieving the correct fumigation parameters to control susceptible strains (Hole *et al.*, 1976) and resistant strains (Price and Mills, 1986). It will enable the implementation of a strategy to control resistant insects (Mills and Athie, 2000) where they are suspected after failed fumigations or are known to occur after the application of a rapid test for diagnosis (Savvidou *et al.*, 1994).

MATERIALS AND METHODS

Computational Fluid Dynamics (CFD) model

The purpose of computational modeling was to obtain a detailed view of the gas flow within the grain bulk under controlled conditions and so help to interpret the experimental results. The CFD technique was used to model the gas flow and predict the gas velocities, pressures and temperatures throughout the store. The technique, which is well established, subdivides the store geometry into cells in which the differential equations, which describe heat and mass transfer are solved numerically. The CFD package CFX 4.2 (CFDS, 1997), was used to create the cells and solve the linearised equations. Body-fitted coordinates are used to reproduce complex shapes.

The dimensions of the store, the covering sheet, and the inlets and outlets were known and reproduced in the CFD model. The number of cells used for a 250 tonne capacity, sloping-fronted store was approximately 750,000. Small cells, about 30 mm thick, were placed near leakage points. The grain was treated as a porous medium with a void ratio (porosity) of 0.4. Leakage was modeled by ascribing a porosity of 0.005 (cf. grain = 0.4) to the cells adjacent to the leakage points. The value for the porosity was derived from small-scale grain bin trails carried out by ADAS Consulting Ltd, and corresponds to an average leakage gap of 0.15 mm.

Physical properties of the grain bulk: The properties of the grain, in this case wheat at 13% m.c. (w.b.) (ASAE, 1995), are given in Table 1. The model is applicable to any grain type if the corresponding properties are known. It is assumed that these are constant and uniform throughout the store within the operative range. The properties of the gases involved, N_2 , CO_2 , O_2 and PH₃, have

been taken from Bejan (1993), whilst diffusion coefficients can be found in Bird *et al.* (1960).

The equation relating pressure gradient to gas flow velocity in the grain was taken from ASAE Standards 1992, because it applies in the low velocity regimes encountered in this work. However, because the natural alignment of grain kernels produces less resistance horizontally (Kumar and Muir, 1986), a 15% difference in resistance between horizontal and vertical directions was assumed.

 TABLE 1

 Physical properties used in the CFD model

Volume porosity	0.4
Bulk density	757.16
PH ₃ Diffusion coefficient	1.592_10 ⁻⁵

Boundary conditions: The plastic sealing sheet covering the grain was modeled as a thin membrane impervious to gas flow. Assuming no wind effect on the store, the pressure at all leaks was set to a standard atmosphere.

The store and bulk: The trial described was the culmination of a series of trials in the same horizontal storage at the Central Science Laboratory. The dimensions of the store are given in Fig. 1. The store was fitted with a ventilated floor and the left hand wall was the concrete plenum chamber for this system. The lateral ducts were sealed with Bromotek laminated sheet from Lawson Mardon Packaging Ltd., UK and aerosol adhesive at the slides in the plenum chamber and the tightfitting doors from this were closed. The right hand wall was of corrugated metal sheets, the joints of which had been carefully sealed with silicone sealant. Wooden bulkheads formed the front and rear wall of the bulk to a height of 3 m. These were sealed internally with 125 μ m polyethylene film, taking particular care in the corners and over the floor in the bay for approximately 1 m. Feed wheat (250 tonnes) was put into the store and fumigated in other experiments involving different bulk shapes and recirculation systems. For the present trial it was graded into a slope, being 2.5 m deep at the rear and 1.5 m deep at the front.

The recirculation system: Two polypropylene spark-proof speed controlled fans were mounted in a 600 mm diameter chamber that also formed a suction and delivery manifold. Two fans were used to make it possible to remotely reverse the flow in the system when required.

The fans were calibrated by measuring the total flow from the delivery manifold outlets with a vane anemometer at a range of fan speeds.



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x Sampling positions

Positions of the circulation system

Fig. 1. Plan of the grain bulk (10 m x 13.5 m) used in trial with 8 blowing and sucking ducts showing the re-circulation system and sampling positions. (Not to scale).

The manifolds each had 8 outlets connecting to 100 mm i.d. flexible polypropylene pipe (land drainage pipe). All 16 pipes were connected to 1.5 m long injection or suction tubes. These tubes were perforated along their entire length and open at the bottom end and were inserted into the grain using a vacuum cleaner at the locations shown in Fig. 1. The tubes from one manifold were linked to a ring of tubes near the center of the bulk and those from the other manifold were connected to the tubes at the periphery of the bulk. The system could be run to produce sucking (negative pressure) in the centre and blowing (positive pressure) at the perimeter or vice versa. These pressure differences were intended to result in a continuous flow between the edges and the centre of the bulk. The whole recirculation system was located under a 125 μ m polyethylene joined with aerosol adhesive sheet over the bulk to minimise the chance of leaks to atmosphere from the recirculation ducts. Round the perimeter, the sheet was glued to the wall sheets, where possible, and pushed into the grain elsewhere. These latter locations were a possible source of leakage.



Fig. 2. Three-dimensional schematic of the grain bulk showing the locations of the blowing and sucking ducts.

Phosphine dosing and measuring: The bulk was dosed from cylinders of FRISIN[®] (1.7 % v/v or 2.4 % w/w PH₃ in compressed N₂). A dosing tube led from the cylinder regulator to a flowmeter to control the flow rate and thence into the fan suction and was quickly distributed to the edges of the bulk and back to the fan. A record was kept of the amount of FRISIN, and hence phosphine, used in the trial. Phosphine concentrations were monitored in the locations in Fig. 1 at the bottom and surface. The concentrations were monitored through nylon 6 gas sampling lines which were taken to a mobile laboratory and connected to a Hewlett Packard 5890A gas chromatograph (GC) fitted with a photo-ionisation detector, an automatic gas sampling loop, two 16-position gas sampling valves and a 1 m x 3.2 mm OD glass-lined stainless steel column packed with Porapac QS. Samples of gas were drawn automatically down each sampling line in turn using a diaphragm pump and the concentration analysed against a cylinderised standard of PH₃ in N₂.

Pressure, temperature and wind monitoring: Continuous pressure monitoring in and around the bulk was intended to confirm the leakage mechanism in relation to variations in climatic conditions (wind and temperature). A series of

air pressure profiles through selected sections of the bulk were intended to identify the recirculation paths as a check to the CFD model.

An electronic micro-manometer using a pressure transducer (Furness Controls Ltd., FCO 44) with a working pressure range of +/- 20 Pa was used. The single transducer was multiplexed to monitor up to 6 separate points within the trials area. The principal locations investigated were top and bottom of the bulk and the windward and leeward faces just outside the bulk. Pressure measurements were made differentially to a sealed reference chamber located under the sealing sheet on top of the grain bulk. This reference chamber was equilibrated with atmosphere for a short period during each multiplexer cycle (every 60 min). The ambient pressure measurements were made using a static probe to minimise the dynamic effects of wind. The measurements were made at 10 sec intervals and averaged over a 2 min period. Recordings were made at 2 min intervals. The barometric pressure was regularly recorded during the trial.

Air pressures within the grain bulk were mapped with the fan running at full speed prior to the trial to discover the pattern of the recirculation flows and to identify regions of the bulk, which were at risk from in-leakage of outside air. Measurements were made using the electronic micro-manometer and a pressure probe thrust into the grain bulk from top to bottom in 0.5 m increments. Evidence from these measurements was used to identify the best places for the recirculation suction and injection ducts.

Ambient temperatures and the temperatures at position F at the surface and bottom in the grain were monitored using copper-constantan thermocouples. Air speed inside the building above the grain bulk was also monitored using a cup anemometer. Air speed and temperature data was recorded using a Yokogawa HR2300 hybrid chart recorder.

Running the trial: The trial was run so as to observe the effects of manipulating the fan speed and the rate of gas input in order to assess the effect on the PH₃ concentrations in the bulk and the pressures at locations monitored. The fan was switched on at an initial flow rate of $4.85 \text{ m}^3 \text{ min}^{-1}$ and the initial gas flow was set at 3 L min⁻¹ (0.0774 g PH₃ min⁻¹). The PH₃ concentration was monitored for a period of about 3 days for a range of fan speeds with the system blowing to or sucking from the periphery. The input rate for PH₃ was also varied. The lapsed times from the start, for changing these parameters are given in Table 2.

The trial ran for a total of 623 h (26 d) with the fan switched off after 574 h and the PH₃ flow at the end. The decay in the PH₃ concentration was also monitored. A total of 50.85 kg of FRISIN equivalent to 1.23 kg of PH₃ was used or about 4.9 g/tonne in order to run the trial for enough time to monitor the effects of changes in recirculation rate, fan direction and gas input rates. The trial was not designed to achieve any particular exposure period but was run until the effect of experimental variables could be assessed under stable wind conditions as far as possible.

TABLE 2

Dosing and recirculation parameter changes at various lapsed times from the start of the fumigation

Lapsed time (h)	Phosphine input rate (g min ⁻¹)	Recirculation rate (m ³ min ⁻¹) + is blowing to perimeter - is sucking from perimeter
0	0.0774	+ 4.85
71	0.0774	+ 3.59
148	0.0451	+ 3.59
168	0.0322	+ 3.59
219	0.0322	+ 1.83
338	0.0322	- 1.81
383	0.0258	- 3.28
457	0.0258	- 0.97
506	0.0258	+ 0.82
574	0.0258	0
623	0	0

RESULTS AND DISCUSSION

CFD predictions

The 250 tonne store with retaining walls on three sides and a sloping front face, is shown schematically in Fig. 3. The store is assumed to be symmetrical and one half only has been modeled. Figure 3 shows a recirculation system with a suction pipe in the grain bulk centre and injection pipes in each corner. Since the positions of leaks were not known, a 'worst case' leakage condition was assumed. Leakage paths were assumed to exist at all edges of the covering sheet and at all edges of the rear retaining wall. The recirculation rate was 4.79 m³ min⁻¹ (into the whole store). The results show that the pressure distribution created by the recirculation system itself leads to gas exchange between the store and its environment. Figure 3 shows the volume of grain in which the PH₃ concentration is less than 0.1 g m⁻¹, which amounts to 10.5% of the total volume. To maintain a phosphine concentration of 0.3 g.m⁻¹ in the injected gas, 0.206 g min⁻¹ of PH₃ must be added. Reducing the recirculation rate reduces the leakage rate but does not reduce the affected volume. Hence, reducing the recirculation rate reduces the quantity of phosphine to be replaced.

There is evidence from the experimental results that the leakage shown in Fig.I3 at the sheet side was present in the tests, due to the difficulty of sealing the sheet against a corrugated wall. However, tests with an SF₆ based leak detector suggest that the edges of the sheet are generally well sealed. Figure 4 shows the result from a simulation with the same recirculation rate as before but with leakage paths assumed to exist at the edges of the rear retaining wall only. The volume of grain in which the PH₃ concentration is less than 0.1 g!m⁻¹ amounts to 1.4% of the total volume, and the additional PH₃ required is now only 0.034 g!min⁻¹. It is interesting to note that the pressure distribution and hence the flow pattern near the floor, has changed significantly.



Fig. 3. Predicted leakage into a 250 tonne grain store employing a phosphine recirculation system consisting of one central suction pipe and two injection pipes. The affected grain volume is shown by the 0.1 g m⁻³ concentration iso-surface. Leakage is due to the pressure distribution created by the recirculation system, recirculation rate 4.79 m³ min⁻¹. Leakage paths are assumed at all the sealing sheet edges, and at the side and floor joints of the rear retaining wall.

Figures 3 and 4 show that the effects of a 1 m sec⁻¹ wind blowing over the store have been included in the simulation. The pressures created by the wind were calculated in a separate model. The pressures at the leaks, relative to a downstream datum, were less than 0.5 Pa and the predicted effect of a 1 m sec⁻¹ wind on leakage rates is negligible. The 'wind effect', which is evident in the experimental records as a decrease in PH₃ concentration, is more likely to be due to barometric pressure changes, which have been measured at +/- 300 Pa or more, rather than wind alone. A change in barometric pressure will cause gas to enter or leave the enclosure by virtue of a change in specific volume. The recirculation system transit time is approximately 2 h at 4.79 m³ min⁻¹, hence PH₃ concentration recovers fairly quickly. This time would be longer in the most extended flow paths.

The provision of injection pipes at the centre of each side of the grain bulk, in addition to those in the corners, has the effect of reducing the injection pressure and the flow pattern but not the overall leakage rate. This seems to be because the negative pressure at the central extraction pipe remains largely the same. Reducing the negative pressure at the centre by using a distributed array of suction pipes appears to be a more effective means of leakage control and this was used in the trial.



Fig. 4. Predicted leakage into a 250 tonne grain store employing a phosphine recirculation system consisting of one central suction pipe and two injection pipes. The affected grain volume is shown by the 0.1 g m⁻³ concentration iso-surface. Leakage is due to the pressure distribution created by the recirculation system, recirculation rate 4.79 m³ min⁻¹. Leakage paths are assumed at the side and floor joints of the rear retaining wall.

Findings from the model

(i) CFD modelling of a floor store with recirculation has simulated the interactions between outside wind and internal gas flows, and predicted the PH_3 concentrations in the bulk.

(ii) Leakage into and out of the store is caused partly by the recirculation system itself. This can be minimised by the correct distribution of extraction and injection pipes.

(iii) The quantity of PH_3 required to replace losses as a result of recirculation can be minimised by using a low recirculation rate.

(iv) Assuming a reasonably well sealed store, rapid changes in barometric pressure are more likely to cause changes in PH_3 concentration than wind pressure.

(v) After adverse weather, PH_3 concentration throughout the bulk will recover most quickly using a high recirculation rate.

Phosphine concentrations and dosage rate

The trial aimed to produce a concentration in the grain of 0.1 g m⁻³ (c. 70 ppm) to demonstrate the logistics of the system. It should be noted that increases in the dosing rate will ensure higher concentrations and any exposure period can be

accommodated provided that the supply of source gas does not run out. A manifolded bank of cylinders would ensure this does not happen.

The concentration-time curves are given in Fig. 5 for the best, worst and average concentrations.



Fig. 5. Highest, Lowest and average concentrations of phosphine in the bulk against time.

During the first 120 hours the winds were far too strong for any fumigation to be successful. Following this there was a period of normal weather where wind speeds were no more than moderate and this lasted for the rest of the trial. During this time the system worked well when the system was used to deliver gas to the periphery. This permitted a reduction in the circulation rate from $4.85 \text{lm}^3 \text{lmin}^{-1}$ to $1.83 \text{ m}^3 \text{ min}^{-1}$ and a reduction in the dosing rate from 3.0 L!min^{-1} to $1.0 \text{ L} \text{ min}^{-1}$ or 0.0774 to 0.0258 g PH₃, (Table 2). With the exception of one position, concentrations substantially greater than $0.1 \text{ g m}^{-3} \text{ min}^{-1}$ were obtained everywhere except for a brief period where the flow of FRISIN was interrupted after 220 hours.

Between 220 hours and 340 hours the circulation system was set at 1.83!m³!min⁻¹ and concentrations in excess of 0.1 g m⁻³ where obtained everywhere including the weakest position. This appears to be the optimum flow rate for this bulk producing minimum leakage due to the circulation system

while still providing an even distribution of gas. When the flow rate was reduced to $0.82 \text{ m}^3 \text{ min}^{-1}$ a less even distribution of gas was obtained.

A reversal of the direction of flow was used at a range of flow-rates but, as expected, this allowed a less even distribution with some high and low concentrations caused by air being sucked in from the edge of the fumigation enclosure (Table 2 and Fig. 5).

Leakage control

It had been envisaged that it would be possible to generate a variable positive pressure at the edge of the bulk to balance pressures due to wind and thus minimise gas exchange with the bulk. Extensive pressure measurements failed to show the existence of systematic pressure gradients from windward to leeward of the bulk. There was evidence from the average PH_3 concentration that systematic increases in the circulation rate resulted in increased leakage of PH_3 . This effect may be explained by a leakage path over the top of the bulk under the sheet to the centre surface which is at negative pressure and a balancing out-flow at the sheet edge where the pressure is positive. Larger scale bulks may allow the cover sheet to make a better seal at the grain surface so minimising this recirculation path.

Understanding the leakage mechanism

The measured variation in PH_3 concentration from earlier trials had no clear simple link with climatic variations. The recirculation rates were measured and found very low. There was evidence that density differences between the air within the bulk and ambient was generating a pressure gradient that could cause vertical flow either upwards or downwards through the bulk. Dynamic pressures due to the wind did not appear to be generating pressure differences, which would cause the levels of PH_3 loss that had been observed during periods of high wind. Changes in barometric pressure could not be exclusively linked to leakage events.

The introduction of a sealed reference for the pressure measurements revealed a far from steady or smooth movement in barometric pressure. During calm periods there was very little short-term fluctuation in the pressure but during windy periods the pressure cycled through as much as 20 Pa (typically 8-12 Pa) with a period of about 4-5 min. Exchange between the air in the bulk and the surrounding atmosphere takes place as a result of small but repeated volume changes in the air. When the pressure rises the air in the bulk is compressed and, if it is assumed that the boundary of the bulk is rigid, a small volume of outside air must move into the bulk diluting the PH₃. When the pressure falls again the reverse occurs, the air in the bulk expands and some of it moves out through the bulk boundary taking some of the PH₃ with it. This process accounts for the leakage seen during windy periods.

A period of time under stable conditions was examined in detail (Fig. 6) to compare the diurnal pressure variations and the resulting phosphate concentrations at the worst position (G, top) where there appeared to be a leak in the building structure.



Fig. 6. The effect of pressure and temperature difference on phosphine leakage.

Future possibilities

The dosing system appears to have advantages over SIROFLO in that it uses less gas to achieve higher concentrations (Wontner-Smith et al., 1999), an important factor when dealing with tolerant pest species or resistant strains. It is also more efficacious at the bulk periphery. This is vitally important since fumigations are normally single events with the aim of controlling the entire pest population to avoid expensive re-fumigation. Ingress of air at the periphery produces a PH₃ concentration gradient from very low to fully effective concentrations. Intermediate concentrations will be selective doses for the various resistant genotypes so that fumigation failures have serious long-term consequences in terms of resistance development as well as being immediate, often economic, failures. It is not an economic option to ensure the survival of some susceptible genes in the population, even if this were technically feasible. We must continue to aim for complete control with the risks of increasing the resistance problem. This system requires further development in order to optimise the blowing duct spacings for different bulk shapes and it is hoped that this can be pursued in a further project.

For bulks of several thousand tonnes we see the need for multiples of this system, each one dealing with a sector of the bulk, perhaps with a series of fans up the mid-line of the bulk. A dosing economy could be achieved by the incorporation of the CSL automated dosing system PH_3 (Wontner-Smith *et al.*, 1999). This would dose individual fans on demand based on the feedback of concentrations measured at key locations in the grain or in a duct downstream of the fan. It may be that a combination of SIROFLO and this system would be more beneficial than each used singularly.

CONCLUSION

The new PH_3 dosing system will preserve PH_3 concentrations at all locations, even at the bulk periphery, under conditions of moderate winds but it will not cope with strong winds. It will be necessary to extend the exposure period beyond that recommended at present in order to ensure an effective treatment under stormy conditions. The additional time required will be the subject of further research.

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REFERENCES

- ASAE Standards (1995) Thermal properties of grain and grain products. ASAE Standards, D243.3
- Banks, H.J. and Annis, P.C. (1984) Importance of processes of natural ventilation to fumigation and controlled atmosphere storage. In: Proc. 2nd Int. Symp. on Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages. (Edited by Ripp, B.E.) 11-22 April 1983, Perth, Australia, 299-323.
- Bejan A. (1993) Heat Transfer. Published Wiley.
- Bell, C.H., Chakrabarti, B. and Mills, K.A. (1991) New application methods for the use of phosphine to disinfest bulk grain. H-GCA Report No. 41, Home-Grown Cereals Authority, London, 63 pp.
- Bird, R.B., Stewart W.E. and Lightfoot E.N. (1960) Transport Phenomena. Wiley.
- British Standards Institution (1972) Code of basic data for the design of buildings, Wind Loads, British Standards Institution *CP3*. 5, Part 2, 49 pp.

CFDS (1997) CFX 4.2 User Manual, CFDS. Harwell Laboratory, Oxfordshire, UK.

- Chakrabarti, B., Watson, C.R., Bell, C.H., Wontner-Smith, T.J. and Rogerson, J. (1994) Fumigation of a 7000 t bulk of wheat with phosphine using the Phyto-Explo system to assist gas circulation. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R) Canberra, Australia, 17-23 April 1994, CAB International, Wallingford, Oxon, UK, 1, 64-67.
- Chaudhry, M.Q. (1997) A review of the mechanisms involved in the action of phosphine as an insecticide and phosphine resistance in stored-product insects. *Pesticide Science* **49**, 213-228.
- Hoerner, S.F. (1965) Fluid Dynamic Drag. Published by the author, Midland Park, New Jersey, xiv + 440 pp.

- Hole, B.D., Bell, C.H., Mills, K.A. and Goodship, G. (1976) The toxicity of phosphine to all stages of thirteen species of stored product beetles. J. stored Prod. Res., 12, 235-244.
- Hou Jun, Newman, C., Winks, R.G., Russel, G. and Ryan R. (2000) Results of trial of new phosphine recirculation technology - Beijing Central Grain Depot, China. In: *Proc.* 7th Int. Working Conf. on Stored-product Protection, (Edited by: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., and Lianghua, G.), Beijing. Sichuan Publishing House of Science & Technology, Chengdu, China, 1, 429-433.
- Kumar, A. and Muir, W.E. (1986) Airflow resistance of wheat and barley affected by airflow direction, filling method and dockage. *Transactions of ASAE*, **29**, 1423-1426.
- Li Yan-sheng, and Li Wen-zhi, (1994) Inheritance of phosphine resistance in Sitophilus oryzae (L.) (Coleoptera: Curculionidae). In: Proc. 6th Int. Working Conf. on Stored-Product Protection (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.) Canberra, Australia, 17-23 April 1994, CAB International, Wallingford, Oxon, UK, 1, 113-115.
- Mills, K.A. and Athie, I. (2000) The development of a same-day test for the detection of resistance to phosphine in *Sitophilus oryzae* (L.) and *Oryzaephilus surinamensis* (L.) and findings on the genetics of the resistance related to a strategy to prevent its increase. In: *Proc. 7th Int. Working Conf. on Stored-product Protection*, (Edited by: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., Lianghua, G.), Beijing. Sichuan Publishing House of Science & Technology, Chengdu, China, 1, 594-602.
- Navarro, S. (2000) Pressure tests for gaseous applications in sealed strorages: theory and practice. In: Proc. 7th Int. Working Conf. on Stored-product Protection, (Edited by: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., Lianghua, G.), Beijing. Sichuan Publishing House of Science & Technology, Chengdu, China, 1, 385-390.
- Noyes, R.T., Phillips, T.W., Cupurus, G.W. and Bonjour, E.L. (2000) Advantages in recirculation technology in the U.S.A. In: *Proc. 7th Int. Working Conf. on Storedproduct Protection*, (Edited by: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., and Lianghua, G.), Beijing. Sichuan Publishing House of Science & Technology, Chengdu, China, 1, 454-461.
- Price, L.A. and Mills, K.A. (1986) The toxicity of phosphine to the immature stages of susceptible and resistant strains of some common stored product beetles, and implications for their control. J. stored Prod. Res., 24, 51-59.
- Savvidou, N., Mills, K.A., Bell, C.H. and Pacheco, I.A., (1994) The development of a sameday test for resistance to phosphine and its application to fumigation strategies. In: *Proc. Brighton Crop Protection Conference - Pests and Diseases*, Brighton, U.K, 1994, 449-456.
- Winks, R.G. and Russell, G.F. (1994) Effectiveness of SIROFLO^R in horizontal storages. In: Proc. 6th Int. Working Conf. on Stored-Product Protection (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R) Canberra, Australia, 17-23 April 1994, CAB International, Wallingford, Oxon, UK, 2, 1237-1244.
- Wontner-Smith, T.J, Savvidou, N., Mills, K.A., Cardwell, S.K. and Bell, C.H. (1999) Strategies for the use of phosphine to combat infestation problems affecting bulk grain. Home-Grown Cereals Authority Project Report No. 181, January 1999, Home-Grown Cereals Authority, London, 72 pp.
- Zettler, J.L. (1993) Phosphine resistance in stored-product insects. In: Proc. Int. Conf. on Controlled Atmospheres and Fumigation in Grain Storages. (Edited by Navarro, S., and Donahaye, J.), Winnipeg, Canada, June 1992, Caspit Press Ltd, Jerusalem, 449-460.