PROJECT REPORT No. 246

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DESIGN OF GAS DISTRIBUTION SYSTEMS FOR CYLINDER-BASED LOW VOLUME PHOSPHINE APPLICATIONS TO BULK GRAIN

by

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Contents

1. ABSTRACT.

The aim of the project was to develop a robust practical method of obtaining adequate concentrations of phosphine in all parts of farm and commercial floor-stored grain bulks. This has been achieved by a system based on the production of a peripheral positive pressure to balance the pressures caused by natural forces which cause ingress of air.

Trials were conducted on bulks of feed wheat of different shapes and different tonnages up to 370 tonnes and up to 4.5 m deep in a relatively well sealed bay. Cylinderised formulations of phosphine were used and dosed either via an automated dosing system or via a simple flowmeter. Initial trials utilised re-circulation using the in-floor ventilation system but this was abandoned since it produced an inconsistent distribution of phosphine and could not be used on unventilated bulks.

The principal of re-circulation by sucking dosed air from the centre of the bulk and delivering it to ducts that can be easily inserted around the periphery was then established. This has the effect of producing positive pressures around the edge of the bulk to prevent the ingress of air. A stepwise series of trials using this system when completely under a covering sheet showed that the optimum distance between delivery ducts for this particular store was about 5.25 m and an optimum economic dosing rate was established.

The design of the system was aided by Computational Fluid Dynamics (CFD) modelling which, though limited by uncertainty about the location of leaks in practice, proved useful in understanding the flows under different system designs and experimental conditions. It could give predictions of the percentage of the grain below a given concentration, the amount of phosphine required to replace losses and lateral and terminal flows through input ducts. It also showed that a modest 1 m s^{-1} wind did not affect to the efficiency of the system.

An understanding of the forces acting on the grain was obtained in trials by logging pressures and temperatures in the grain simultaneously with ambient conditions. This showed that gas density differences due to diurnal temperature changes and normal barometric pressure fluctuations caused gaseous exchange in the bulk. The high gas loss during high winds was due to relatively large but short-term atmospheric pressure fluctuations. The effect of varying the re-circulation rate was studied to provide an optimum for this store. In practice, the system cannot cope with short periods of strong wind but their effect can be overcome by extending the exposure period according to the duration of these conditions.

The system was trialed under commercial conditions in the same store and, while a uniform phosphine concentration was not possible, the variation was low and the system could guarantee the required minimum. This can easily be increased, according to the pest species or phosphine resistant strain present, by increasing the dosing rate.

These results form the basis for an efficient method of dosing phosphine in order to prevent the development of resistance and to control existing resistant populations. It is anticipated that larger bulks can be treated using multiples of the re-circulation system. It is expected that there will be an economy of scale possible in the efficiency of the system but further development is required to optimise the multiple system for different bulk shapes, grain depth, tonnages and economy of materials, labour and phosphine usage.

2. SUMMARY.

2.1 Introduction.

There is a potentially serious problem with resistance to the fumigant phosphine which has been used for over 30 years to fumigate bulk grain and bagged and packaged commodities in stacks. The resistance occurs in thirteen species of stored product insect pests and is widespread in many countries. Resistant strains have been known to exist in the UK for over 20 years but there is no recent survey data to give an accurate estimate of the incidence of these. However, there is likely to be sufficient genetic variation present within the grain trade to allow selection for resistance to occur in sub-standard fumigations. Resistant strains are known to require higher phosphine concentrations and longer exposure periods than for control of normal strains.

There is a decrease in the reliance on the admixture of organo-phosphorus insecticides for disinfestation of and protection of bulk grain due to health concerns and some have been withdrawn from the market. It is predicted that the use of phosphine will increase dramatically in both farm and commercial grain stores whenever cooling and drying strategies fail. At the same time, we are facing a reduction in use of the fumigant methyl bromide due to its implication in damage to the stratospheric ozone layer. In both developed and developing countries this will, inevitably, mean an increase in the use of phosphine, more low standard fumigations and more resistance. In addition, the often fortuitous counter-selection pressure provided by methyl bromide will not be available. Experts on fumigation, internationally, have warned of the reliance on phosphine, the only remaining grain fumigant, in the face of a growing resistance problem. However, dosages for the control of resistant strains using phosphine can generally be achieved with the use of new methods.

Fumigation of grain is used when there is an insect infestation detected and this commonly happens just prior to or when the grain is sold. The presence of such infestation can cause grain to be down-graded with loss of value and can cause trading problems and extra transportation costs. The problem is most acute in grain presented for export when total eradication is the aim. Phosphine fumigation is now being carried out prophylactically before grain is cooled and when insect numbers are low in order to help prevent a serious infestation from developing.

While a high standard of phosphine fumigation is possible in bins and silos, this can be difficult to achieve in floor-stored bulks which are inherently difficult to seal effectively. The general absence of any pre-sealing before the grain enters the store puts at risk the ability to attain the minimum exposure period required for full efficacy. The use of solid metal phosphide formulations in tablet and sachet form probed into the grain or, at worst, only into the surface layer cannot guarantee good gas distribution. This practice can also give erroneous estimates of free phosphine residues due to the unfortunate sampling of grain adjacent to a partially decomposed formulation. The biggest drawback of these formulations is that they give up their phosphine in only 2-4 days, according to temperature, and leakage of gas results in low concentrations or even complete loss of gas and an inadequate exposure period.

Previous projects financed by the H-GCA have shown the considerable advantages of using a cylinderised formulation of phosphine in carbon dioxide as a diluent. While cylinderised formulations are not currently cleared as pesticides in the UK, they are cleared in other parts of the world and are starting to appear in Europe. It is only a matter of time before they are available for commercial fumigators to use in the UK under harmonisation of registrations in the EU. Their main advantages are that any concentrations in the grain can be achieved by manipulating the flow of dosing gas and that gas can be introduced continuously in order to ensure sufficient fumigant during the entire exposure period.

They can also be used under the control of an automated dosing system for economy. They are safer to use and do not produce any solid phosphide residues and so, even at high dosage rates, the free phosphine residues are well below permitted limits. In terms of the actual kilogram cost of phosphine, they are more expensive than solid phosphide formulations. However, with careful sealing and the use of appropriate methods they have been shown to be competitive on cost since it is possible to use less phosphine per tonne of grain treated.

There is a pressing need to be able to consistently carry out phosphine fumigations with the goal of achieving total control of infestation in all life stages. This goal is at the core of any pro-active strategy to combat resistance. The alternative is to design fumigations which permit the survival of some insects in order to maintain genes for susceptibility to phosphine in a population. This classic resistance management strategy may be appropriate for some crop growing systems where an ‘economic threshold’ of pest incidence is possible. It is considered that this technically difficult strategy would not be acceptable to a grain trade seeking the highest control standards.

Unfortunately, some current fumigations are carried out to enable grain to be marketed and this may not necessarily require the total eradication of infestation. The control of the more susceptible active insect stages means that a survival consisting of eggs and pupae can be difficult to detect. While this approach can be attractive commercially, it is precisely this philosophy which can produce a selection pressure for resistance, when genes for its expression are present in a pest population. Even in a good fumigation there will be pockets of infestation, particularly at the bulk periphery, where ingress of fresh air produces dilution of phosphine and allows survival. This survival can cause immediate commercial problems and, if selection for resistance occurs, longer term consequences for the reliability of phosphine when it is used with current dosage schedules.

2.2 Objectives.

The overall brief for the current project was to produce a new dosing system and generate new recommendations and guide-lines for the practical application of phosphine for insect disinfestation of bulk grain in the UK. To achieve this end, a set of sub-objectives was identified to understand the problem and to progress, by practical trials, towards the goal. Firstly, to develop a design for a practical re-circulation system to achieve more even gas distribution in treatments of farm and commercial grain bulks. Secondly, to apply pressure logging methods to measure pressure distribution in grain bulks during fumigation in order to understand the physics of air re-circulation. Finally, to test the use of re-circulation to limit leakage at the bulk boundaries by balancing flow rates and external air pressures.

The project aims to ensure a general improvement of standards by the use of cylinderised formulations, the mixing of phosphine in the bulk by air re-circulation particularly targeted to protecting vulnerable areas in the grain. The system should be robust and controllable. It is expected that the careful application of this fumigation system will prevent the development of phosphine resistance. It can also be used to control resistant insects, where resistance tests have identified them, by the careful implementation of an appropriate dosage schedule.

2.3 The multi-disciplinary research approach.

A multi-disciplinary approach was taken to solve this complex problem. This involved the use of a model to predict the effect of different systems to show the way forward. This expertise was provided by the Silsoe Research Institute, BBSRC. Expertise on the physics of air movement, pressure measurement and the design of an engineered solution was supplied by ADAS Ltd., Silsoe. Chemical expertise on the application and measurement of phosphine in the grain and the environment was essential. Finally, biological expertise on the problem of phosphine resistance, toxicity of phosphine to insects and the use of a bioassay to demonstrate effectiveness was also necessary. This overall expertise in phosphine fumigation was supplied by CSL who also provided store and grain facilities and managed the project.

2.3.1 Modelling.

A complex computational model was designed using the principle of computational fluid dynamics to understand the gas flow in a bulk under controlled conditions. It could model the gas flows and predict gas velocities, pressures and temperatures throughout a bulk. The dimensions of the store, the covering sheet and the re-circulation inlets and outlets were reproduced in the model. The shape of the bulk, whether level, heaped or front-sloping, could be incorporated. The effect of wind on phosphine concentration was modelled. The model worked on wheat at 13 % m.c. but it is capable of working with any grain type if changes in parameters are programmed.

The plastic sealing sheet covering the grain was modelled as a thin impervious membrane. The model assumed likely leakage paths to occur at all edges of the covering sheet and at all edges of the bulk rear retaining wall. This proved useful though had the obvious limitation that, in practice, leakage points are unknown.

Tests in the store with a leak detector showed that the sheet edges were well sealed but it is possible that the phosphine concentrations were low in some locations due to other leaks in the vicinity, maybe from the floor/wall joint.

The findings from the model were very interesting and mainly applicable to the system in practice. The pressure distribution created by the re-circulation system itself leads to gas exchange between the bulk and the environment. The volume of grain below a defined concentration and the shape of this part of the bulk in relation to leaks could be predicted. It suggested that reducing the re-circulation rate reduces the leakage rate but not the affected grain volume. It could also estimate the loss of concentration of phosphine in air returning to the re-circulation fan. The significance of this, in practice, is that reducing the re-circulation rate will reduce the amount of phosphine to be replaced, a desired economy. The model predicted that the effect of a modest wind on leakage rates, when the system was running, were negligible. Also, assuming a well-sealed store, rapid changes in barometric pressure are more damaging to the phosphine concentration than is wind pressure. After adverse weather, phosphine concentrations throughout the bulk will recover most quickly by using a high re-circulation rate. Hence there is scope, certainly in multiple systems in large bulks, for linking the fan speed to an anemometer so that it will run faster for a set period after high wind ceases.

2.3.2. The experimental store and the trials.

A floor-ventilated bay in the Central Science Laboratory (CSL) Storage Research Unit at York capable of holding 400 tonnes of wheat and measuring 13.5 m by 10 m was used for all the trials. It was typical of many farm floor-stores, having a poured concrete plenum chamber of the ventilation system as one side. The other side was of sealed corrugated metal sheeting and the front and rear of the store consisted of wooden bulkheads. The wood was sealed with polyethylene film on the exterior and the lateral ventilation ducts were sealed in the normal commercial manner. In addition, the inside of bulkheads was sealed and the sheet extended 1 m over the bay floor before loading the grain as recommended in the H-GCA's 1999 Grain Storage Guide. A covering sheet was sealed with spray adhesive to the sheets at the front and rear on the bulk and it was pushed well into the grain along the sides, creating a slight leakage area. Different shapes of bulk, grain depth and different tonnages of feed wheat were examined.

In all trials, the grain and ambient temperatures were monitored and logged and the phosphine concentration in the grain was measured automatically by gas chromatography in a mobile laboratory located in front of the store.

Air pressure was measured with an electronic micro-manometer which could monitor up to 6 points inside and outside the bulk. In addition, a sealed reference chamber was located under the covering sheet. Ambient pressure measurements were made using a static pressure probe to minimise the dynamic effects of wind.

Phosphine was dosed in initial trials from cylinders containing the gas dissolved in liquid carbon dioxide (ECO2FUME[R]) and dosed by an automated system which measured the concentration in the grain and dosed as required. Later, the four main trials were dosed from cylinders containing a mixture of phosphine and compressed nitrogen (FRISIN[R]). The first two of these were dosed by the automated dosing system and the last two by using a simple needle valve and flowmeter.

Initial trials aimed to attain a low but effective concentration of phosphine for economy. Re-circulation was achieved by using a low volume centrifugal fan outside the covering sheet and utilising the in-floor ventilation ducts, initially sucking from a central floor duct and delivering to ducts at the ends of the bulk. This was refined for a second trial so that sucking was from the central floor duct with delivery to the surface in the four corners. While these systems were a considerable improvement over existing practice, they did not give the required degree of mixing and left some areas with low concentrations. They suffered the obvious limitation that they could only be employed on bulks placed over a ventilation system. The last initial trial employed a more powerful fan placed under the covering sheet. This was connected to four 1 m long perforated ducts, two sucking at the bulk centre and two delivering centrally to both ends of the bulk. This system was suitable for all floor-stored bulks. The results from this trial were much more encouraging with good concentrations in most locations. This concept was taken forward to design a suitable commercial system and to optimise the delivery locations to reliably achieve a slight negative pressure at the bulk centre and a slight positive pressure at the periphery. The positive pressure would tend to protect this area from the pressure effects of wind and diurnal temperature fluctuations.

Following the initial trials, a step-wise approach was taken to achieve the design and the optimum spacing of the peripheral delivery ducts. Three systems were tested (trials 1-3) with experimental manipulations to the re-circulation rate and the dosing rate. A final trial 4 was carried out as it would be in commercial practice with these system parameters held constant.

In trials 1 and 2, a new re-circulation system was designed with a manual speed-controlled low power axial fume cupboard-type fan housed in a specially fabricated polypropylene fan box with six outlets to be used or sealed as required. This rested on an integral inlet shaft sunk into the grain by using a vacuum cleaner. Pipes ran from the fan house and were connected by flexible polypropylene pipe to polypropylene perforated outlet shafts put into the grain periphery in the same way. In these and subsequent trials the dosing gas was changed to the mixture of phosphine in nitrogen.

Trial 1 employed four outlet shafts near to the corners of a 250 tonne bulk in a heaped profile with the peak towards the back wall where the grain was 3 m deep. The pipe for dosing phosphine was positioned in the fan inlet shaft. The trial was run for nine days and during this period the fan speed was adjusted to give total flows ranging from 3.5 to 6 cubic metres per minute. Air pressures within the bulk were initially mapped with the fan running at full speed to discover the three-dimensional pattern of re-circulation flows and to identify regions at risk from inward leakage of air. Even with the re-circulation at full speed an even distribution of gas was never achieved and areas of low peripheral pressure were linked to low concentrations. Clearly, a leak at these locations would allow air to be drawn in.

Trial 2 utilised the same system but with two additional delivery ducts inserted in the centre of the longer sides of the bulk to eliminate the negative pressures noted in trial 1. The first two days of the 9-day trial were very windy and low concentrations were seen throughout the bulk but, after the wind reduced, the concentrations quickly recovered throughout. The distribution of phosphine was much more even than in trial 1. However, areas of negative pressure were now seen at the centres of the front and back walls due to the total flow being shared between six rather than four delivery ducts. This indicated a need for two more delivery ducts at these locations. This was made possible by a more ‘user-friendly’ re-design of the system to be used in trials 3 and 4.

The fan box of the new system had eight inlets as well as eight outlets of a similar design to the outlets in the previous design. All the inlets and outlets were connected to 1.5 m perforated sucking or delivery ducts as before. These were of a smaller diameter (0.1 m ID) than the ones used in trials 1 and 2 since the flow through each was less and they could be more easily inserted and removed from the grain. A total of eight peripheral delivery ducts could be served, one near each corner and one at the mid-point of each side. The fan box, itself, was re-designed to hold two fans positioned to give opposite flow directions and both were connected to a manual speed controller. The fans were separated by a diaphragm to form separate inlet and outlet chambers. Thus, the direction of flow could be reversed in order to take phosphine to any 'dead spots' in the bulk by-passed by circulation paths. The 250 tonne wheat bulk was re-shaped so the grain depth was 2.75 m. deep at the back with a plateau over more than half of the bay sloping to 1.25 m at the front. The eight sucking ducts were positioned in a circle with one in the centre and the fan box to one side This system was easier to use and is expected to be attractive commercially.

Dosing was via a simple needle valve and flowmeter since it was decided that for a single dosing point this would be simple and adequately economical. The dosing pipe delivered phosphine 1 m below the grain surface in the centre of the sucking ducts. The trial was run over a period of 26 days on order to access the effect of changes to the dosing rate and the re-circulation rate and direction. The concentrations were monitored for about 3 days at each flow pattern. Pressures within the bulk were monitored at the full fan speed as in trials 1 and 2.

The system worked well in the normal re-circulation direction with no areas of negative peripheral pressure seen. Positive pressure extended to the full depth of the bulk at the rear even though they were over 1 m. above the floor. This was due to a flow through the ends of the delivery ducts which could overcome any leaks in or near the floor. Phosphine concentrations were planned to be in excess of 0.1 g per cubic metre, a concentration well above the toxic threshold for insect pests.

During the first five days, the wind was far too strong for any fumigation of this type to be successful. After this, a period followed to the end of the trial when winds were no more than moderate. The target concentration was reached everywhere with the exception of one position though this was corrected when the flowrate was increased to an optimum for this bulk of about 1.83 cubic metres per minute. A reversal in the flow direction resulted in a less even phosphine distribution due to air being sucked from the edges. However, the flow direction was reversed for 7 days with changes of flowrate during this time. It is likely that only a 30-60 minutes period of flow reversal per day would be beneficial in reaching 'dead-spots' and this could easily be automated.

The project required that the final system be tested under commercial conditions on a larger tonnage of commercially-owned grain using a store of different dimensions to the CSL store. This was not possible since the cylinderised formulations are not yet approved as pesticides in the UK. Obtaining trials clearance was too expensive for the project budget and so the CSL store was used but the fumigation was run as in commercial practice without experimental manipulations. The grain tonnage was increased to 370 tonnes with a peak behind the bulk centre. Exactly the same system was used as in trial 3 except that one sucking duct was located in the grain peak to ensure that it was treated adequately. The fan box was located in front of the peak. The optimum running parameters for the store and tonnage were used: 0.06 g phosphine dosed per minute via a flowmeter and a slightly higher recirculation rate of 2.9 cubic metres per minute.

The weather during the trial was exceptionally calm and a good distribution of phosphine rapidly resulted. After running the trial for 12 days, the flow of phosphine was considerably reduced in order to mimic the effect of a period of high wind. The phosphine concentration reduced but on return to near the original dosing rate it rapidly increased. Once again, a good positive pressure distribution was noted around the bulk periphery. The effectiveness of the treatment was assessed by the inclusion of a bioassay of a common pest, the Rust-red grain beetle, *Cryptolestes ferrugineus.* Caged naturally tolerant pupae of a phosphine-susceptible strain were inserted at all grain depths at two locations previously shown to have the lowest concentration, including the mid-point between two peripheral input ducts. The dosing gas was switched off after 15 days and the insect samples retrieved and emergence of adults beetles compared to untreated controls. All the fumigated pupae were killed showing that a typical infestation of this pest throughout the bulk would have been eradicated.

Grain samples taken after the fumigation at representative locations were analysed and found to contain free phosphine residues well below the permitted limit. Indeed, these would have been somewhat pessimistic since some of the grain had been fumigated in other trials. The residue would be expected to reduce drastically upon further airing.

It is important to note that these were experimental fumigations and so the minimum concentration target in the grain was in the normal toxic range, though chosen in order to conserve a limited supply of dosing gas. The system readily allows the target concentration to be increased in order to control more naturally tolerant pest species or resistant strains by simply increasing the phosphine dosing rate appropriately. The use of phosphine in trial 3 was approximately 4 g per tonne but this was required in order to achieve a much longer exposure period than would be normally be necessary. The use in trial 4 was approximately 2 g per tonne and gives a more realistic estimate of what would be used in practice over normal exposure periods for tolerant species. This amount is much less than normally used for solid phosphide formulations due to the savings from the prevention of unequal distribution and leakage. The cylinderised formulations are expected to be slightly more expensive in terms of cost per gram of phosphine. The overall cost of fumigant would not be excessive and, in any case, is a small proportion of the total cost of a fumigation which is mainly made up of labour charges.

2.4 Key results, conclusions and implications.

1. A practical method of re-circulation of phosphine in bulk grain has been developed which is robust enough to cope with most of the leakage and physical forces acting on a bulk. It can be used in both ventilated and unventilated storages. A paper describing was presented in October 2000 at the International

Conference on Controlled Atmospheres and Fumigation in Stored Products held in Fresno, USA where it was well received.

2.

This method of re-circulation involves suction from perforated ducts in the centre of the bulk and delivery to similar ducts at the edge. This has the effect of creating positive pressure around the edge of the bulk which prevents the ingress of air. The ducts are easily inserted and removed from the grain.

3.

The system can be dosed using either FRISIN^R (phosphine in compressed gaseous nitrogen) or ECO2FUME^R (phosphine in liquid carbon dioxide). A simple needle valve and flowmeter can be used but the gas can be used more economically using the CSL automated dosing system. It is important that the dosing gas supply does not run out and a suitable amount of manifolded cylinders will be required for the whole treatment unless they are changed manually during the treatment.

4.

It was not possible to fully meet the objective of maintaining a completely uniform concentration of phosphine within a bulk since the method does not rely on a total atmosphere replacement. However, the system can readily distribute and maintain concentrations within a relatively small range. It can produce a minimum concentration which is effective against all stages of both susceptible and resistant strains of common insect pest species at temperatures for which data exists. It is predicted that the dosing system can produce the required concentrations and exposure periods to control even the most resistant populations at low temperatures.

5.

The engineering objective to minimise leakage under a range of climatic conditions, apart from very strong winds, has been achieved.

6.

Adequate concentrations are not maintained during periods of high winds with this system but they are re-established within a short time once the winds have died down. An extension to the fumigation would be required in order to replace periods of low concentration.

7.

Re-circulation of phosphine within the grain bulk is required to produce adequate concentrations of phosphine in all parts of the bulk.. There is an optimum re-circulation rate. A minimum is required to produce the necessary pressures in the grain but too high a rate requires more dosing gas and is less economic.

8.

The project has provided an understanding of the leakage mechanisms:

a. The high rate of gas loss observed during high winds is caused by short term fluctuations in atmospheric pressure. During calm periods the pressure was seen to cycle through as much as 20 Pa (typically 8-12 Pa) within a period of 4-5 minutes. In windy periods the pressure could cycle through 60 Pa.

b. Gas density difference due to diurnal temperature changes causes gaseous exchange.

c. Normal barometric pressure fluctuations cause gaseous exchange.
d. Diffusion of gases is not important.

9.

The system design features for the effective system are:
a. The pressure at the centre of the bulk should be negative. This is provided by a fan(s) located so they do not influence the pressure at the periphery.
b. The pressure at the periphery of the bulk should be positive and a spacing of inlet ducts of about 5.25 mis indicated for this store. It will be different for other stores; more in larger stores and less in smaller ones.
c. Perforated ducts need to be sunk into the grain at the bulk centre and at the periphery.
d. The fan should be capable of producing a moderate flowrate through the grain of at least 3 cubic metres per minute in stores of the type tested.

10.

A good level of sealing as a pre-requisite for any phosphine fumigation system to be effective. The lining of storage walls and bulkheads before loading grain is a good method of achieving this and is recommended in the H-GCA's 1999 Grain Storage Guide. A covering sealing sheet should be pushed into the surface margins of the bulk and should enclose the re-circulation system.

11.

It is recommended that the fumigation parameters be determined from a knowledge of the resistance status of the pest population by a rapid test method capable of giving results in a working day and using doses for the control of all stages of resistant strains, if necessary.

12.

If phosphine is to continue to provide reliable control of insect pests in bulk grain there needs to be a wider appreciation in the trade of the long-term consequences of sub-standard treatments. Phosphine fumigation has been carried out in the past in difficult circumstances and accepting that control of mobile stages (larvae and adults) only will allow the grain to be traded. While this appears to be sound commercial practice, it does risk the development of resistance and future control problems. The topic of phosphine fumigation is considered to be a prime candidate for an H-GCA technology transfer exercise which should encourage uptake of the system resulting from this project.

13.

The current project has demonstrated that we can do much better when dosing phosphine though the solution provided by this system is technically more difficult than current practice. An informed customer, working with a fumigation contractor who is trained to use this technique, will be needed to implement the pre-sealing required to achieve the necessary standard of treatment.

14.

The re-circulation system will use less phosphine than the SIROFLO^{R} flow-through system to achieve the same concentration.

15.

A major implication from the project is that further development of the system is required for larger bulks.

3. INTRODUCTION.

3.1. Standards of phosphine fumigation of floor-stored grain.

Fumigation of floor-stored grain to a standard which achieves complete eradication of infestation is not easy and may be impossible by using the current widespread methods. The grain trade does achieve a high level of control and the remaining infestation is, often, difficult to detect unless a sufficient post-treatment inspection interval is allowed to enable surviving immature stages to be seen, mainly by the trapping of emerged adults. This is rarely carried out at present. Conventional dosing techniques use solid metal phosphide formulations which give off phosphine over a period of 2-4 days according to temperature and then leakage in a silo or floor store will allow the concentration level to reduce. When the standard of sealing is poor or under windy weather conditions the fall in concentration is often too great for an adequate exposure period to be obtained. In addition to the problem of the loss of concentration, there can be problems in distributing phosphine dosed as a phosphide formulation near to the grain surface, especially in deep grain.

Previous projects financed by the H-GCA have shown the considerable advantages of using a the use of cylinderised phosphine formulation, in this case phosphine in liquid carbon dioxide as a diluent, for continuous dosing to maintain concentrations (Bell, *et al.,* 1991; Wontner-Smith *et al.,* 1999).

With this scenario as a background, it is clearly necessary to increase the reliability of phosphine fumigation to produce a general increase in the standard of fumigation to minimise the risk of the development of resistance. This emerging problem requires the application of the best possible standards to prevent it and to contain it where it is known to occur.

3.2. Resistance to phosphine.

Where insects having resistance genes are present in a low standard fumigation, the resulting survival can lead to the selection of resistant insects (Mills, 1983) and this has far-reaching consequences for maintaining the standards of phosphine fumigation of grain beyond the immediate control failure.

In many countries strains resistant to phosphine have developed (Mills, 1983; Tyler *et al.,* 1983; Taylor, 1989; Pacheco *et al.,* 1990; Zettler, 1990). This has been mainly due to poor sealing standards and/or adverse weather conditions leading to low concentrations. The conditions for the development of resistance are worse in developing countries but even in developed countries standards of phosphine fumigation, particularly grain fumigation, are sometimes not adequate to ensure eradication of even normal susceptible strains. In the controlled fumigation system, SIROFLO^{R}, dosages have not provided a sufficient margin to prevent the development of resistance and require revision (P.J. Collins, pers. comm.). It is known that resistant strains are imported into the UK and other developed countries in consignments of animal food ingredients and infestation can readily reach farms and the grain trade via infested animal feed.

Methyl bromide, the only other major fumigant in general use, is being phased out under the terms of the Montreal Protocol On Substances Which Deplete the Ozone Layer. In the absence of methyl bromide, the use of phosphine is expected to increase and a consequent increase of the resistance problem can be expected. The absence of methyl bromide will preclude the previously useful, though unintentional, elimination of phosphine resistant insects. The use of organo-phosphorus insecticides for the disinfestation of and protection of bulk grain has significantly reduced due to health concerns and withdrawal from the market in some cases. These changes make the grain trade more dependent on phosphine than before and the trend is likely to continue.

Phosphine can still be used to control resistant strains if a sufficient gas concentration can be maintained over a long enough exposure period to control all stages. This can only be done where there is a good level of sealing and where there is a capability to re-dose, when necessary, by using a cylinderised-based formulation of phosphine, for example. However, the situation often arises where a generally adequate treatment of floor-stored grain suffers from small leaks which cause the dilution of phosphine by the ingress of air. This can lead to a wide range of concentrations, some of which can be selective. Of these, some will be selective in favour of heterozygous resistance which are very similar in tolerance to susceptible insects since the inheritance of the resistance is via an incompletely recessive major gene (Li and Li, 1994; Mills and Athie, 2000). This survival will increase the frequency of the resistance genes.

The very fact that resistance with an incompletely recessive major gene develops at all is indicative of either generally low standards or, at best, variable standards of phosphine fumigation. Once there is a significant proportion of heterozygous resistant individuals present, the selection process can continue so that the population becomes wholly resistant. This results from the mating of pairs of heterozygous resistants which produce homozygous resistant individuals advantaged by multiple exposures to higher selective doses of phosphine. It has been suggested by Zettler (1993) that phosphine is not used in sub-standard storages. However, phosphine is generally effective and the grain industry wishes to use it even if such storages could be readily identified. Variable concentrations in a generally well-sealed storage ought to be correctable but it requires a more sophisticated approach than that applied hitherto.

This project seeks a solution to the problem based on sound engineering principles and aims to develop a suitable robust dosing system which is usable by fumigation contractors.

3.3. Phosphine distribution in floor-stored grain.

As previously noted, good phosphine 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 upon to generate uniform distribution of phosphine 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 phosphine throughout the bulk. Pressure gradients of less than 1 Pa m^{-1} can be effective. Research has been carried out using re-circulation 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. Some UK fumigation contractors use re-circulation to overcome this problem but this practice is not common.

The problem of effective phosphine treatment of floor-stored grain has been tackled in Australia using the SIROFLO^R positive pressure system. This relies on mixing cylinderised phosphine with a fan-produced stream of air to a pre-set concentration and continually allowing this mixture to flow through the grain to give complete atmosphere replacement. The slight positive pressure produced prevents ingress of air. It is a total atmosphere replacement system and would be expected to require more phosphine than a system which relies on recirculation. The SIROFLO^R system works very well in grain bins and silos but it has proved unreliable in unsealed horizontal storages (Winks and Russell, 1994). They found that oscillating concentrations resulted from ‘chimney forces’ causing ingress of air down shed walls when the ambient air was cooler than the grain bulk during the night. While lower grain temperatures in the UK should lessen this problem, another approach is required which is more reliable and economical in the use of phosphine.

3.4 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 phosphine 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 Institution, 1972).

Floor stores are notoriously difficult to seal, particularly when fitted with a ventilation system. It is difficult to persuade 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. This is recommended in the H-GCA's Grain Storage Guide (Anon.,1999).

3.5 The use of cylinderised phosphine.

Two different kinds of cylinder-based phosphine is available commercially:

ECO2FUME which is a mixture of 2 % w/w or 2.6 % v/v phosphine in carbon dioxide available from Cytec Industries Inc. and used in SIROFLO[R].

FRISIN[R] which is a new formulation containing 2.1 % w/w or 1.7% v/v phosphine in nitrogen which has been developed by Service und Anwendungstechnik GmbH (Szemjonneck and Boeye, 1998).

An automated dosing system has been developed at the Central Science Laboratory (CSL) for the fumigation of bulk grain (Wontner-Smith *et al.,* 1999). The equipment is designed to maintain a pre-programmed concentration of phosphine from a cylinder-based supply for as long as necessary to achieve a successful fumigation.

Past studies at CSL (Wontner-Smith *et al.*, 1999) have shown that the effectiveness of cylinder-based phosphine can be increased by using circulation to improve distribution of gas throughout a bulk and so eliminating areas of low concentration.

A series of trials involving either the automated dosing system or dosing via a simple flowmeter, both formulations of cylinder-based phosphine and different systems of re-circulation were undertaken in bulks of grain of various shapes in the Storage Research Unit at CSL which resulted in a new technique for using re-circulation while minimising losses of phosphine due to leakage.

4. METHODS.

4.1 Modelling.

4.1.1 Computational Fluid Dynamics (CFD) model.

The purpose of computational modelling 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 co-ordinates 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 modelled by ascribing a porosity of 0.005 (c.f 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 0.2 mm.

4.1.2 Physical properties of the grain bulk.

The properties of the grain, in this case wheat at 13% m.c (wb) (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, nitrogen, carbon dioxide, oxygen and phosphine, 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}

4.1.3 Boundary conditions.

The plastic sealing sheet covering the grain was modelled 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.

4.2. Trials at Central Science Laboratory.

4.2.1. The store and bulk.

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 tight-fitting 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 μm polyethylene film, taking particular care in the corners and over the floor in the front and back of the bay for approximately 1m.

4.2.2. Monitoring of wind, temperature and concentration of phosphine.

In all the tests copper-constantan thermocouples and nylon-6 gas sampling line (2 mm ID) were placed at various representative positions in the grain. These were run to a mobile laboratory where the thermocouples were connected to a Yokogawa HR2300 hybrid chart recorder where temperature data was collected. The gas lines were connected to a Hewlett Packard 5890 gas chromatograph (GC) fitted with an automatic sampling loop, two 16 stream selection valves, a photo-ionisation detector and a 1 m x $^{1}/_{8}$ inch OD glass lined stainless steel column packed with Porapak QS. The concentration of phosphine was monitored throughout each trial by GC.

A weather station was positioned in the store to measure wind speed through the building. This was logged by the Yokogawa HR2300.

4.2.3. Monitoring of pressure in and around the bulk.

The pressure in and around the bulk was monitored continuously with the intention of confirming the leakage mechanism in relation to variations in climatic conditions (wind and temperature).

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 trial 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 minutes). The ambient pressure measurements were made using a static probe to minimise the dynamic effects of wind. The measurements were made at 10 second intervals and averaged over a 2 minute period. Recordings were made at 2 minute intervals. The barometric pressure was regularly recorded during the trials.

4.2.4. The Automated Dosing System.

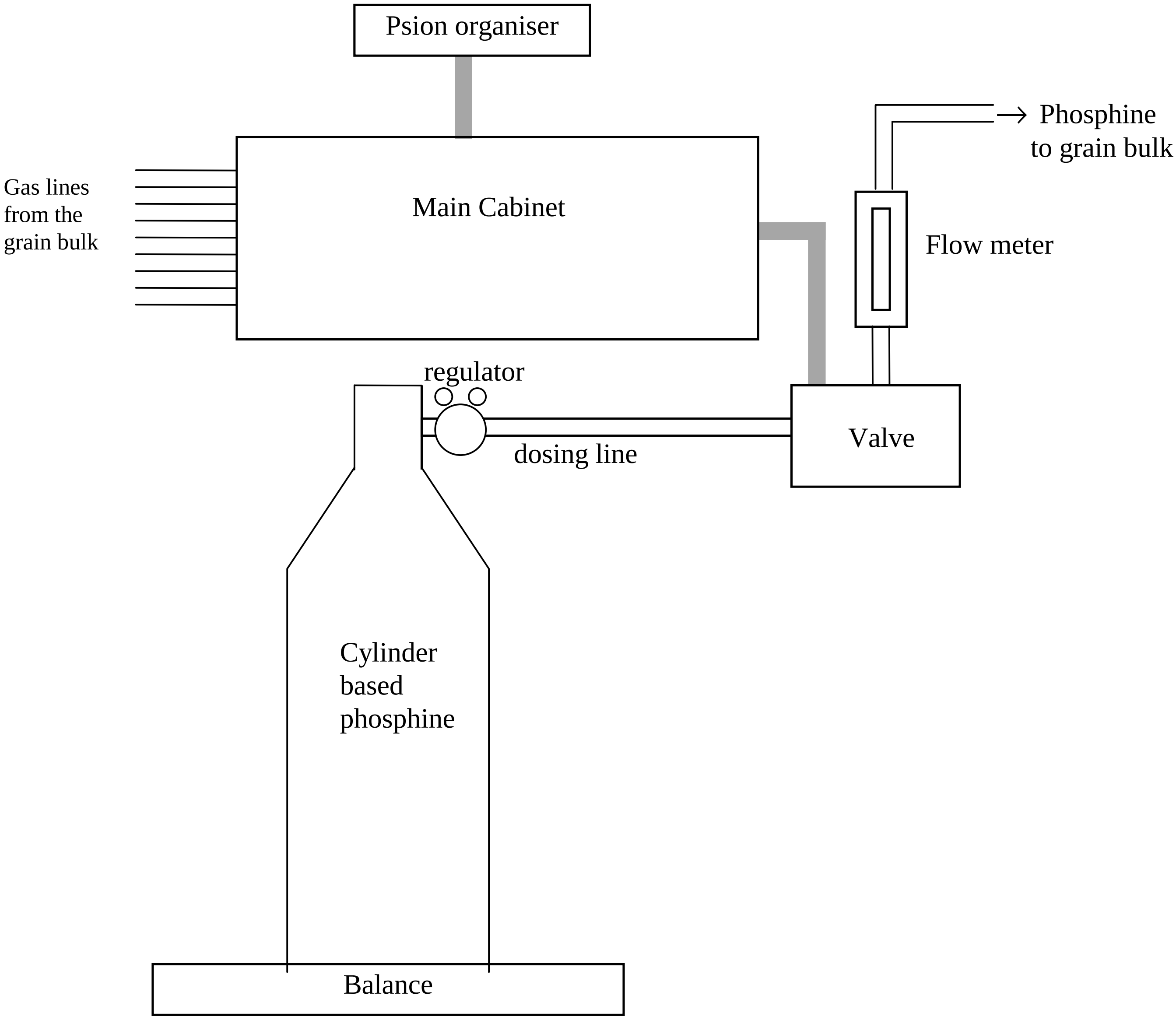
A microprocessor-controlled dosing system has been developed for use with cylinderised phosphine (Wontner-Smith *et al.*, 1999). This was used in the first four trials.

The dosing system (Figure 1) can serve up to sixteen separate areas. A sample of gas is drawn from each area in sequence via nylon 6 gas sampling lines (2 mm bore) to the main cabinet of the system where the concentration of phosphine is measured by an electro-chemical detector. The microprocessor compares the measured concentration level from every area with a pre-set threshold level. If a particular area is below the threshold level then it will receive phosphine for a programmed period (dose-time).

The phosphine is supplied via 9.5 mm nylon dosing lines which are opened and closed by a series of rack-mounted solenoid valves. The valves are controlled by the microprocessor in the main cabinet of the system to which they are connected via cables and interface with a gas manifold connected to a cylinder containing ECO2FUME[R] or FRISIN[R] gas. ECO2FUME[R] is delivered in 5 second bursts which occur every minute throughout the dose-time. The rate at which FRISIN[R] gas is dispensed from the cylinder is controlled using a regulator and a flow meter fitted with a needle valve.

When every area has been sampled and dosing has occurred, where necessary, the cycle is repeated. After a predetermined period the microprocessor terminates the sampling and dosing process. All variables are set using a Psion Organiser.

Figure 1. Microprocessor-controlled dosing system**.**



4.2.5. Preliminary trials.

A series of preliminary trials were carried out using a variety of re-circulation systems. The target minimum phosphine concentration for these trials was 0.1 g m^{-3} over the entire exposure periods.

The trials were undertaken using a low volume centrifugal fan. The autodosing system was used to dose ECO2FUME[R] into floor ventilation ducts in each trial.

(i) Air was sucked from a central floor duct and delivered into floor ducts near both ends of the bulk using a total airflow of 1.1 m^3 min^{-1}.

(ii) Air was sucked from a central floor duct and delivered to the four corners of the bulk from the top surface using total airflows of 2.0, 0.4 and 0.17 m^3 min^{-1}.

(iii) Suction from the centre top surface and delivery into the four corners of the bulk from the top surface at a total flow of 0.17 m^3 min^{-1}.

These systems, while a considerable improvement over existing practice, did not give the required level of mixing resulting in low concentrations at some positions.

Another trial was undertaken using a more powerful fan capable of delivering 44 m^3 min^{-1}. Once again, the autodosing system was used to dose ECO2FUME^{R} into the bulk. Four perforated ducts (1 m long and 0.15 m OD) were sunk into the grain using an industrial vacuum cleaner. Air was sucked from two ducts in the centre of the bulk and delivered to two ducts, one at either end of the bulk, using the fan which had been placed on the grain under the sheet. This system was suitable for bulks with and without a floor ventilation system.

Low concentrations were observed at 2 of the 16 sampling positions. However, the results were encouraging and showed that this re-circulation layout may be able to resist the effects of wind and diurnal temperature fluctuations if the positions of the delivery points were optimised.

4.2.6. Main trials.

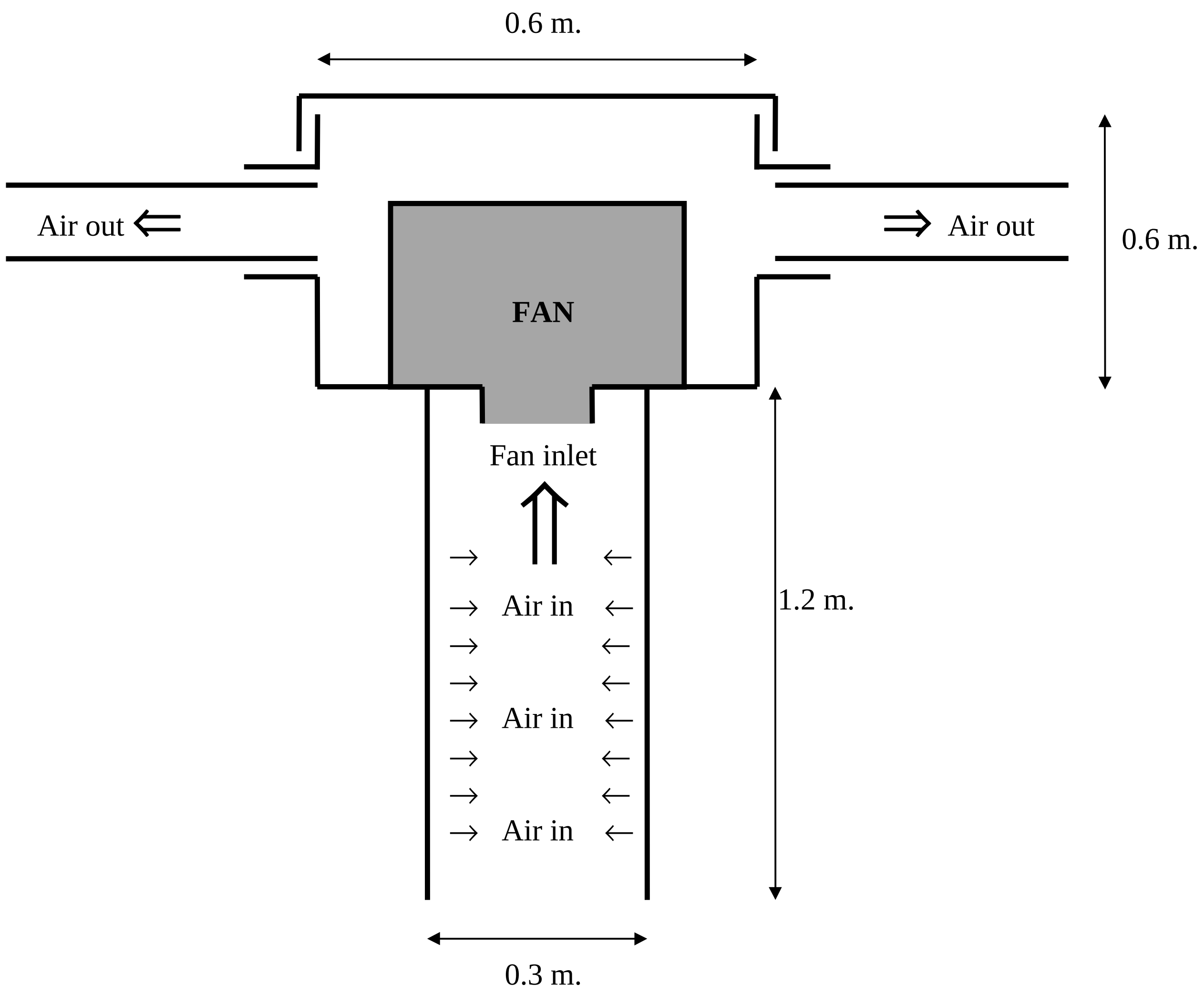
Four trials were undertaken using re-circulation systems designed to establish a 'positive pressure fence' around the bulk periphery. Three trials were needed to optimise the re-circulation rate, the phosphine dosing rate and the positioning of the peripheral output locations. A final trial was run under commercial conditions without experimental manipulations of variables.

4.2.6.1. The re-circulation system used in trials 1 and 2.

A new circulation system was designed for trials 1 and 2 (Figure 2) which consisted of a cylindrical polypropylene fan box (0.6 m ID) containing six outlets (0.11 m ID) spaced evenly around the side. The box rested on top of an inlet shaft (0.3 m ID) which was sunk into the grain down to the base of the box using a vacuum cleaner to remove grain.

A polypropylene spark-proof and corrosion-proof speed-controlled fume cupboard-type axial fan was inserted into the box in such a way that it drew air from the inlet shaft and delivered it into the fan box and out through the outlets. The speed of the fan could be controlled remotely using a manual controller.

Figure 2. Cross-section of the fan box and inlet shaft used in trials 1 and 2.

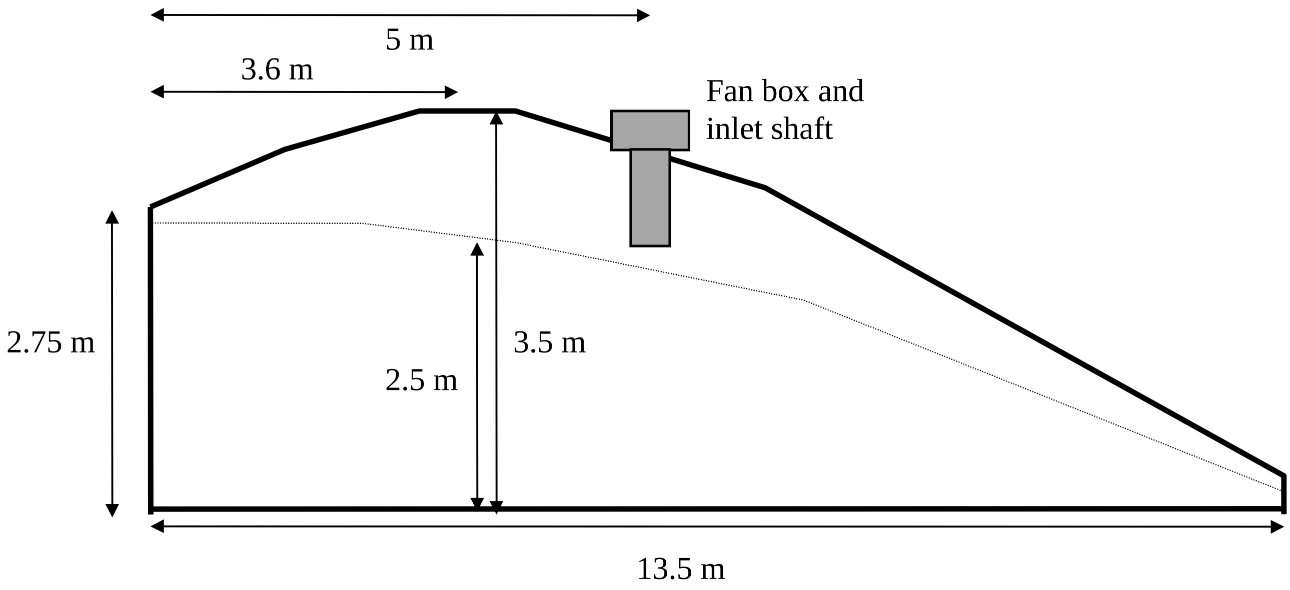


Up to six pipes could be connected to the six outlets of the fan box and unused outlets could be sealed with fumigation sheet.. The other ends of the pipes were connected to polypropylene outlet shafts (0.15 m ID) which were sunk into the grain to provide positive pressure around the edge of the bulk to prevent the ingress of air at the edge. The walls of the inlet and outlet shafts were perforated along their length by slits made using a circular saw to allow the movement of air. Part of the flow exited at the end of the shaft.

The fan was calibrated by measuring the total flow from the outlets with a vane anemometer at a range of fan speeds.

4.2.6.2. Trial 1.

The fan box and inlet shaft and four outlet shafts were positioned in the floor store containing 250 tonnes of grain (Figures 3 and 4). The grain was heaped with the peak towards the back grain wall which had been lined using 125 µm polythene.
Figure 3. Cross-section of the grain bulk used in trial 1.



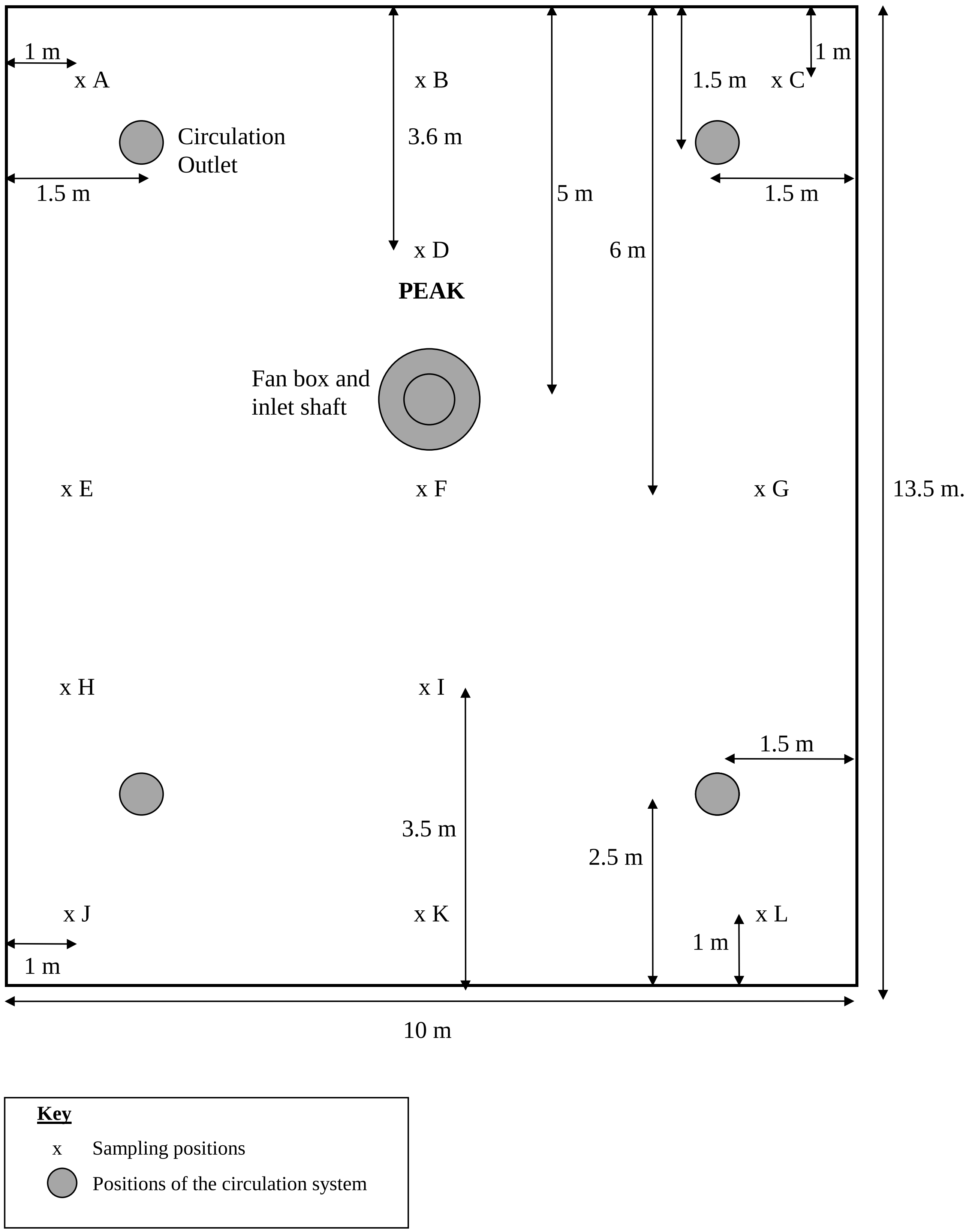
Key

Dotted line: Cross-section at the edges of the bulk.

Solid line: Cross-section through the centre of the bulk.

The dosing line for the dosing system was positioned in the inlet shaft so that the phosphine would pass through the fan and be delivered to the four outlet shafts. Gas sampling line was placed at various depths at the sampling positions given in Figure 4. Thermocouples were placed at the top and at the bottom of the bulk at position F.

Figure 4. Plan of the grain bulk used in trial 1 showing the re-circulation system and sampling positions.



The grain was sheeted using 125 μm polythene and the circulation system was switched on with the fan speed set at 6 m^3 min^{-1}. The dosing system was then switched on. The source of phosphine in this and all subsequent trials was FRISIN[R]. Trials 1 and 2 were dosed by the automated dosing system.

Table 2 gives the fan speeds used throughout the trial.

Table 2. Fan speeds used in trial 1.

Day	Time (hours)	Fan Speed (m^3 min^{-1})
1	0	6
3	47	3.5
5	94	4.6
7	141	3.5
8	170	4
9	192	3.5

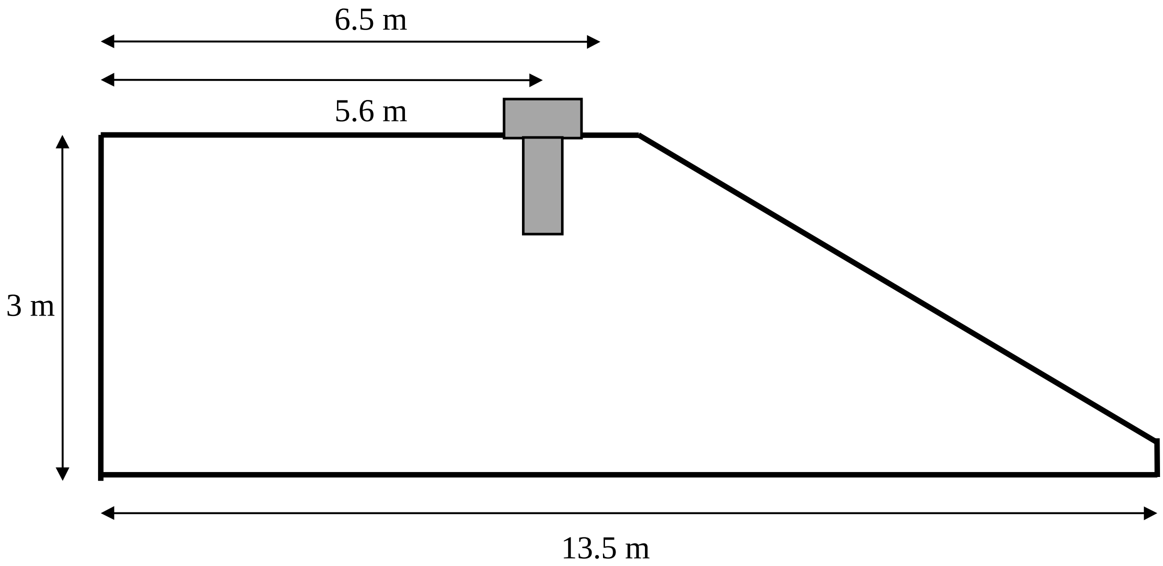
After nine days the dosing system was switched off and the concentration of phosphine in the bulk was allowed to decay.

Air pressures within the grain bulk were mapped with the fan running at full speed to discover the pattern of the re-circulation flows and to identify regions of the bulk which were at risk from inward leakage of 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 on a three-dimensional latice.

4.2.6.3. Trial 2.

The grain was un-sheeted and then re-shaped so that it was flat at the back with a slope at the front (Figure 5).

Figure 5. Cross-section of the grain bulk used in trial 2.



The thermocouples were replaced and gas lines were placed in the sampling positions given in Figure 6.

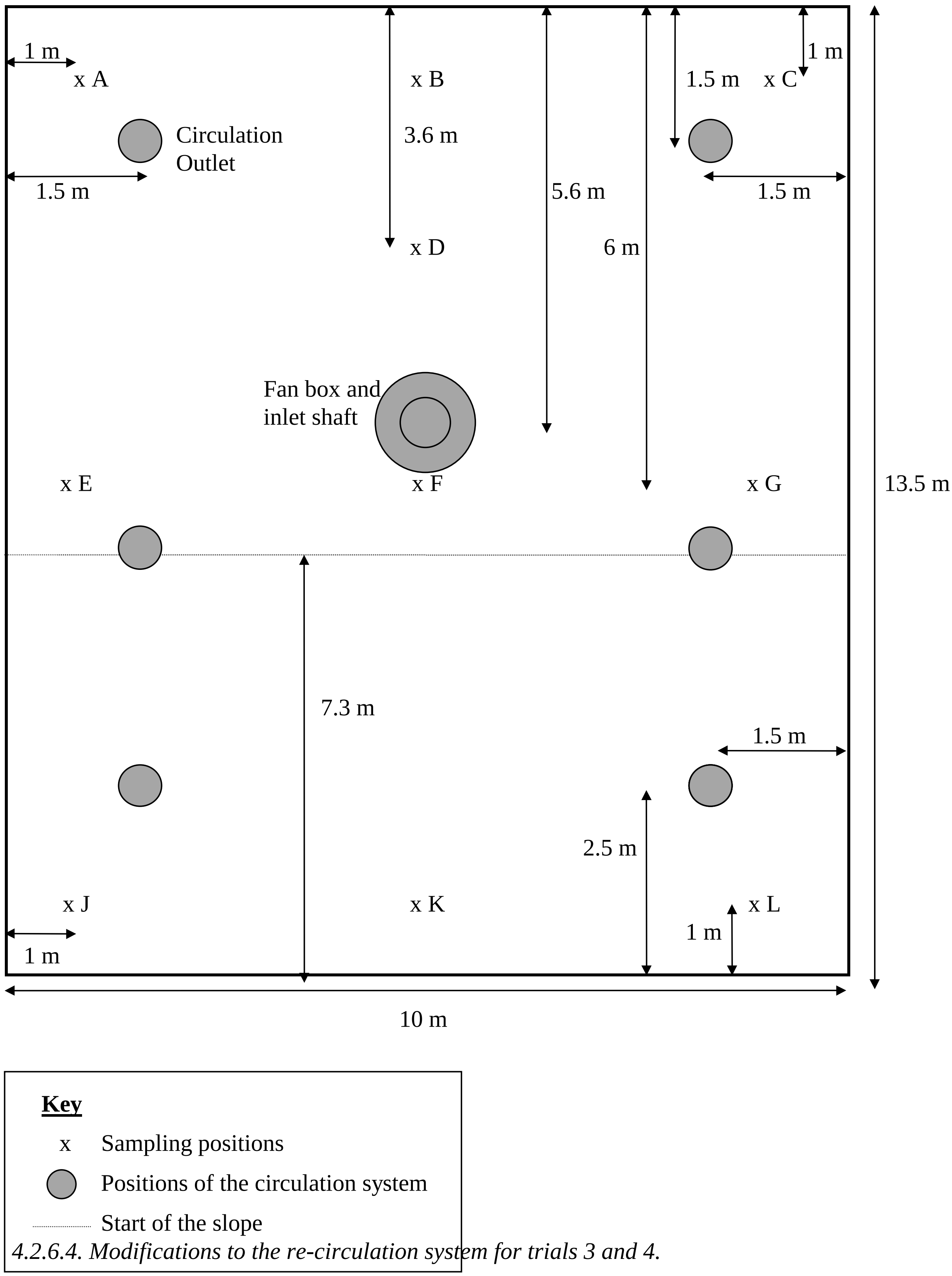
Two additional outlet shafts were added at the mid-point of the bulk sides to cover two points of negative pressure detected in trial 2 (Figure 6). The position of the fan box and inlet shaft was altered slightly so that it was more centrally located and the bulk was re-sheeted. The dosing system and the circulation system were then switched on with the circulation system fan set at 6 m^3 min^{-1}.

On the fifth day of the trial the fan speed was reduced to 4 m^3 min^{-1} and on the seventh day the fan speed was increased to 4.6 m^3 min^{-1}.

After nine days the dosing system was switched off and the concentration of phosphine in the bulk was allowed to decay.

Air pressures within the grain bulk were mapped with the fan running at full speed as before.

Figure 6. Plan of the grain bulk used in trial 2 showing the re-circulation system and sampling positions.



4.2.6.4. Modifications to the re-circulation system for trials 3 and 4.

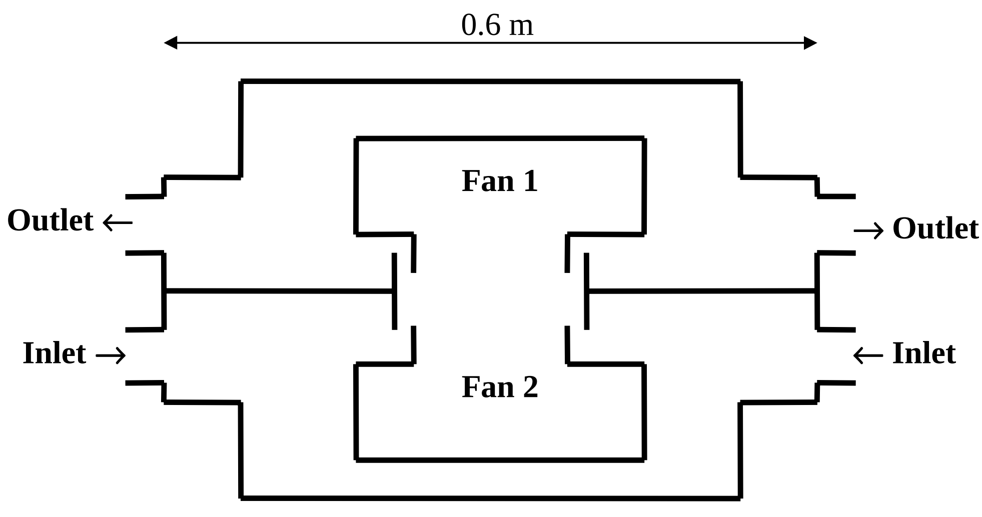
Results from trials 1 and 2 showed the need for eight outlets to the re-circulation system so that each side and each corner could be covered. Therefore a new system was designed (Figure 7). Eight inlets were also incorporated of a similar design to the outlets to replace the inlet shaft so that the fan box could be moved from one position to another with relative ease. The inlets and outlets were separated by a diaphragm to form inlet and outlet chambers.

A second identical fan was placed in the inlet chamber so that the effect of a reversal of the direction of flow could be examined. This was provided in order that the direction of flow could be changed, if necessary, in order to deliver phosphine to any 'dead spots' identified in the bulk which were not receiving sufficient gas due to being by-passed by circulation paths.

The inlets and outlets were connected to lengths of flexible polypropylene pipe (0.1 m ID). All 16 pipes were connected to 1.5 m long ducts which were inserted into the grain using a vacuum cleaner as before. The ducts were perforated along their entire length and open at the bottom end. They were of a smaller diameter (0.1 m ID) than the ones used in trials 1 and 2 so that they could be inserted and removed from the grain more easily.

The fans were calibrated as before.

Figure 7. Cross-section of the fan box used in trials 3 and 4.

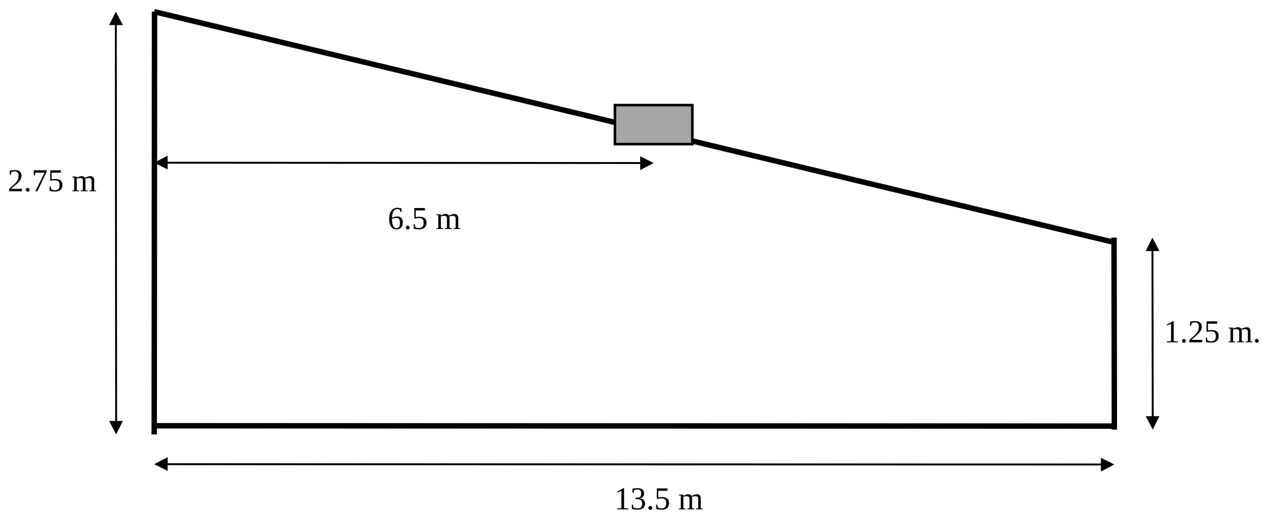


4.2.6.5. Trial 3.

The grain was re-shaped so that the bulk was as uniform as possible with a slight slope with the grain being 2.75 m deep at the back and 1.25 m deep at the front (Figure 8).

The re-circulation system was positioned so that the outlets of the fan box were linked to a ring of eight ducts at the periphery of the bulk and the inlets were connected to a ring of ducts near the centre of the bulk (Figure. 9). The perimeter was covered as uniformly as possible by having an outlet duct near to each corner and at the mid-point of each side.

Figure 8. Cross-section of the grain bulk used in trial 3.



The gas lines and thermocouples were replaced (Figure 9) and the bulk was re-sheeted using Bromotek sheeting.

The dosing gas was changed to FRISIN^R. The automated dosing system was not used in trials 3 and 4 since it was considered that for a single dosing point, continuous low flow dosing via a simple needle valve and flowmeter would be more appropriate and adequately economical. From the flowmeter a nylon pipe connected to a stainless steel probe that delivered the gas 1 m below the surface of the grain in the centre of the group of fan inlet ducts.

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 both the pressures and the phosphine concentrations within the bulk. The fan was switched on at an initial flow rate of 4.85 m^3 min^{-1} and the initial gas flow was set at 3 l min^{-1} (0.07 g phosphine min^{-1}). The phosphine concentration was monitored for a period of about 3 days for each of a range of fan speeds with the system blowing to or sucking from the periphery. The input rate for phosphine was also varied. The lapsed time from the start for each change is given in table 3.

Figure 9. Plan of the grain bulk used in trial 3 showing the re-circulation system and sampling positions.

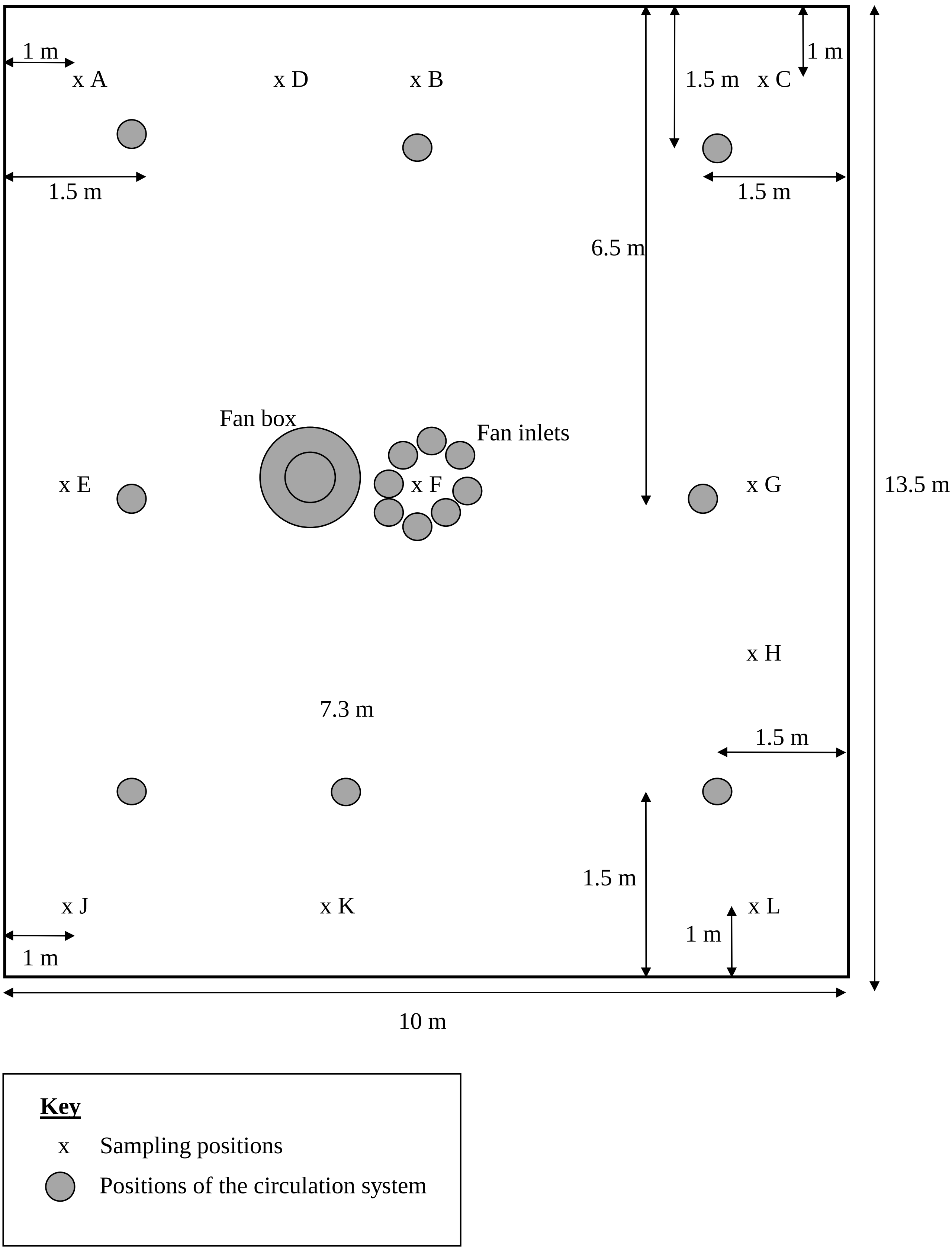


Table 3. Dosing and re-circulation parameter changes during the fumigation.

Lapsed time (hours)	**Phosphine input rate (g min^{-1})**	**Re-circulation rate (m^3 min^{-1}) + is blowing to perimeter. - is sucking from perimeter.**
0	0.072	+ 4.85
71	0.072	+ 3.59
148	0.042	+ 3.59
168	0.030	+ 3.59
219	0.030	+ 1.83
338	0.030	- 1.81
383	0.024	- 3.28
457	0.024	- 0.97
506	0.024	+ 0.82
574	0.024	0
623	0	0

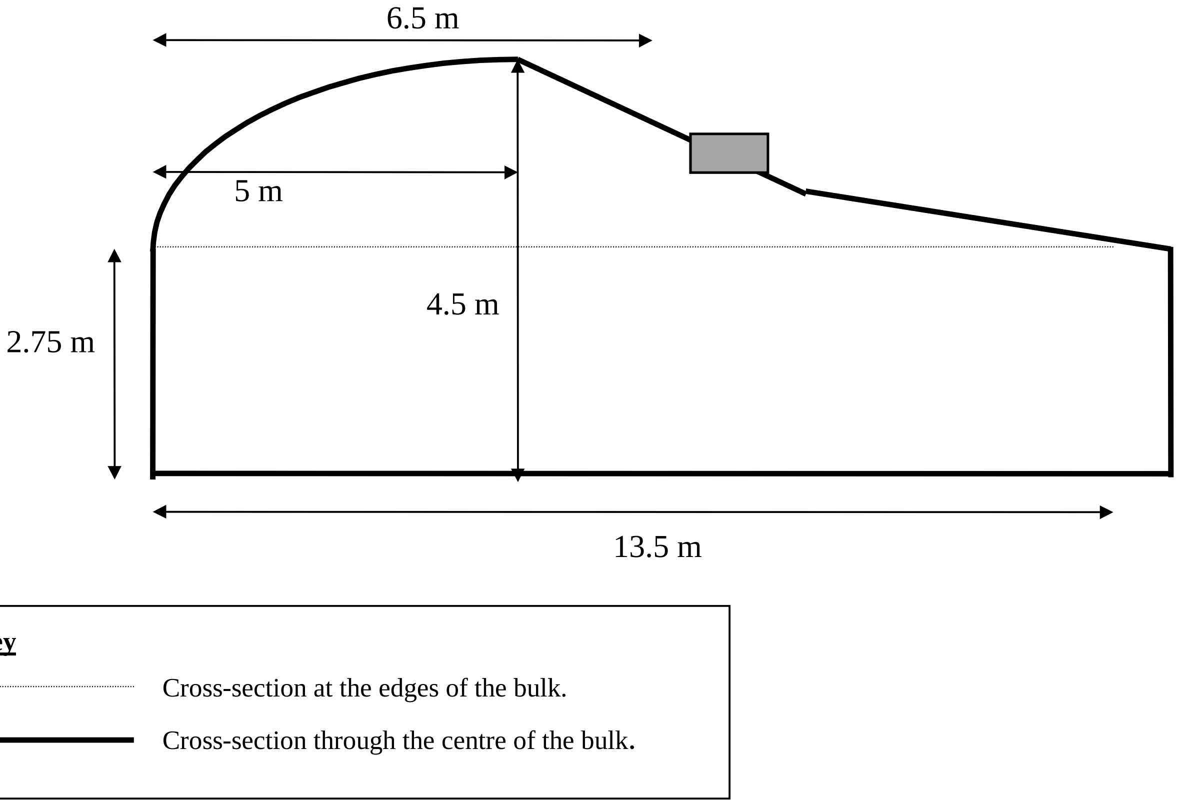
The re-circulation system was switched off after 574 hours (24 days) and the flow of phosphine was stopped after 623 hours (26 days). The decay in the phosphine concentration was then monitored.

Air pressures within the grain bulk were mapped with the fan running at full speed as in trials 1 and 2.

4.2.6.6. Trial 4.

A final trial was undertaken to use the system as it would be used in commercial practice without experimental manipulations. The amount of grain was increased to 370 tonnes so that the bulk approximated more to a commercial storage. Figure 10 gives the shape of the bulk used in this trial.

Figure 10. Cross-section of the grain bulk used in trial 4.

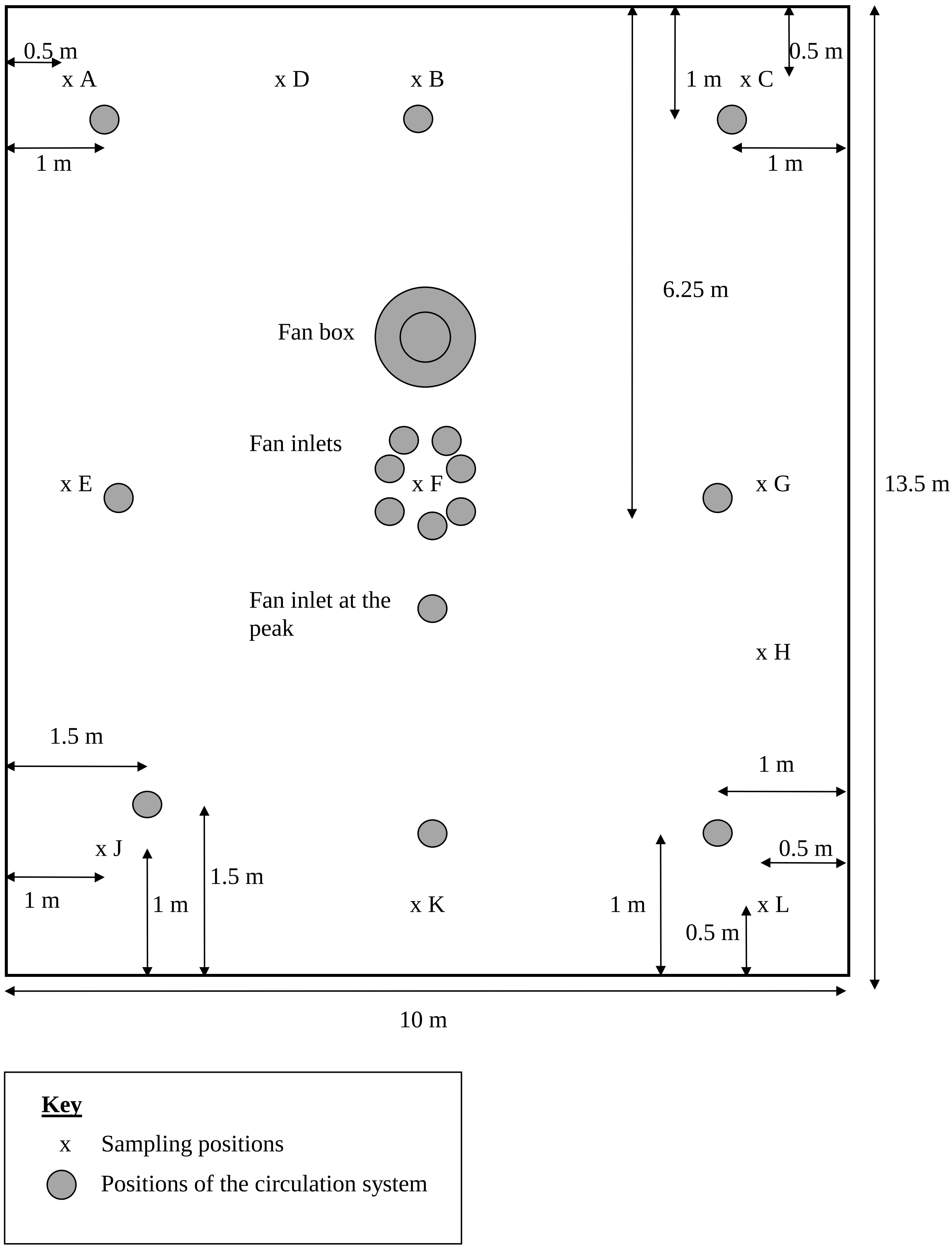


The re-circulation system was repositioned (Figure 11) with the outlet shafts around the perimeter of the bulk and seven of the inlet shafts in the centre. The remaining inlet shaft was placed at the top of the peak. The stainless steel dosing probe was placed in the middle of the group of seven inlet shafts.

The gas lines and thermocouples were replaced and the bulk was re-sheeted using Bromotek sheeting. The rate of dosing was set at 2.5 l min^{-1} of FRISIN^R gas (0.06 g phosphine min^{-1}) using the needle valve and flow meter and the flow of the re-circulation system was set at 2.9 m^3 min^{-1}.

Since the weather during the trial was exceptionally calm, after 12 days the flow was reduced to 0.5 l min^{-1} of FRISIN^R gas (0.01 g phosphine min^{-1}) overnight and then returned to 2.5 l min^{-1}. In this way the effect that a period of high wind might have on the concentration of phosphine in the bulk was mimicked and the rate of recovery of grain concentrations was observed.

Figure 11. Plan of the grain bulk used in trial 4 showing the re-circulation system and sampling positions.



A bioassay of older larvae and all stages of the pupa of a phosphine-susceptible strain of the commonly occurring and moderately naturally tolerant Rust-red grain beetle, *Cryptolestes ferrugineus* was included in the trial.

They had been acclimatised to the grain temperature of $10^{o}C$ before insertion into the grain. They were inserted into the grain at locations which previous trials had indicated would receive the lowest doses in order to present the 'worst case'. These were position G, mid-way along the right hand edge, and position H midway between the input duct at G and the duct at position L. Position H was considered to provide the most rigorous test since it was expected to receive the least pressure and phosphine, being half-way between ducts. The bioassay was placed in paired holders, each containing an escape-proof nylon mesh bag, at various depths at the bottom of the grain (3 m) and also at 2 m, 1 m and at the surface at positions G and H (Fig. 11).

The FRISIN[R] was switched off after 15 days and the decay in grain concentrations was observed. Two days later, the sheeting was removed and the bioassay samples were retrieved from the grain. The bioassay samples and controls were gradually returned to their optimum breeding temperature of $30^{o}C$ over a few days. They were then examined for emerging adults periodically for 3 weeks i.e. beyond the end of the control emergence.

Once again, air pressures within the grain bulk were mapped with the fan running at full speed.

At the end of the trial, after the grain had been aired, 6 grain samples, 3 from the surface and 3 from 2 m depth at various locations were taken for the determination of free phosphine residues. They were stored in sealed nylon bags in a freezer until they were chemically analysed using a GC-NPD method reported by Scudamore and Goodship (1986) and modified by Norman and Leonard (2000).

5. RESULTS AND DISCUSSION.

5.1. CFD modelling predictions.

The 250 tonne store with retaining walls on three sides and a sloping front face is shown schematically in Figure 12. The store is assumed to be symmetrical and one half only has been modelled. It shows a re-circulation system with a suction duct in the grain bulk centre and injection ducts 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 (purple lines).

Figure 12. Simulation with four re-circulation ducts, a re-circulation rate of 4.79 m^3 min^{-1} and leakage at all edges.

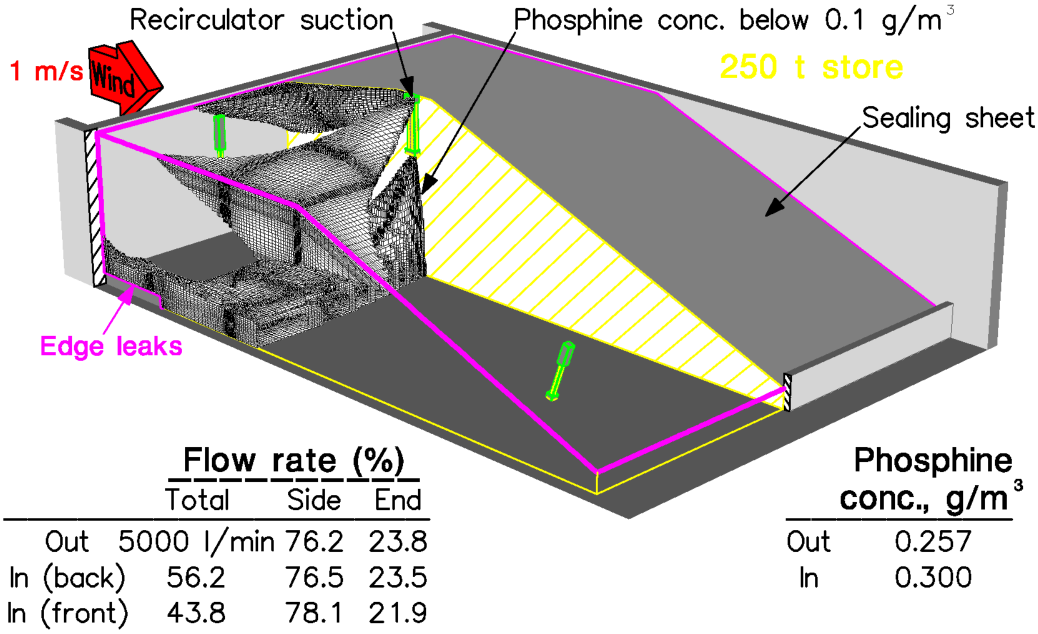
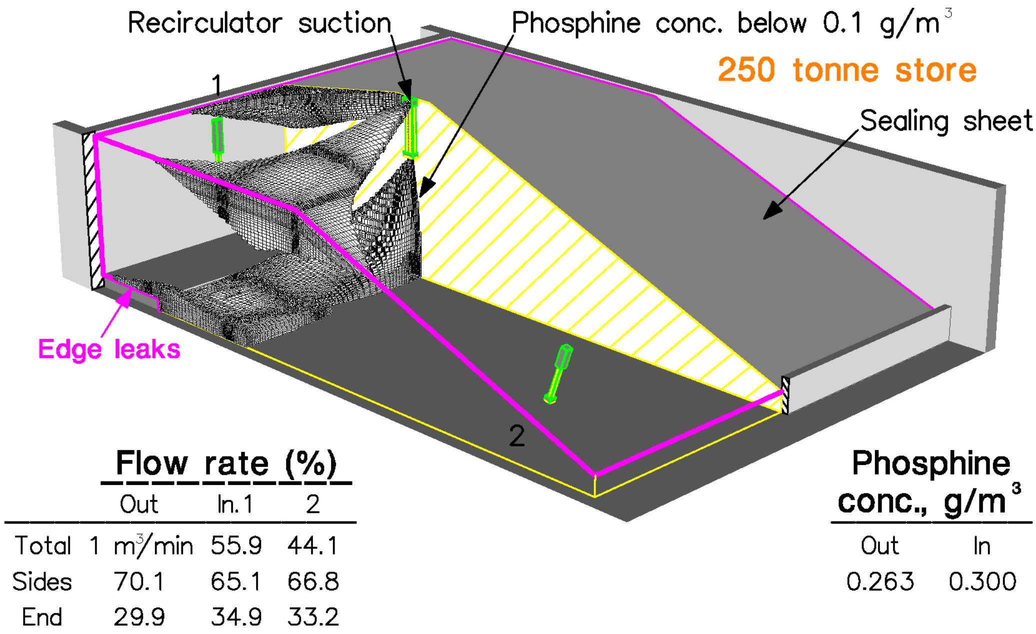


Figure 12 shows the results of a simulation of this layout after running re-circulation to a steady state aiming for a, normally excessive, concentration of 0.3 g m^{-3}. The re-circulation rate was 4.79 m^3 min^{-1} (into the whole store). The results show that the pressure distribution created by the re-circulation system itself leads to gas exchange between the store and its environment. It shows the volume of grain in which the phosphine concentration is less than 0.1 g m^{-3}, which amounts to 10.5% of the total volume. To maintain a phosphine concentration of 0.3 g m^{-3} in the gas injected into the grain, 0.206 g min^{-1} of phosphine must be added at the fan since the predicted concentration here is 0.263 g m^{-3}.

Figure 12 and the other simulations also give the percentage of the total flow from the peripheral inlet ducts together (back and front only in this case) together with the percentage of the flow passing through the side and end of each duct

Figures 13 shows the predicted volume of grain in which the phosphine concentration is less than 0.1 g m^{-3}, at a re-circulation rate of 1 m^3 min^{-1}. It is clear that the affected volume is similar to that shown in Figure 12, as is the leakage rate as a proportion of the recirculation rate. To maintain a phosphine concentration of 0.3 g m^{-3} in the injected gas, 0.037 g min^{-1} of phosphine 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 and this can be a considerable economy.

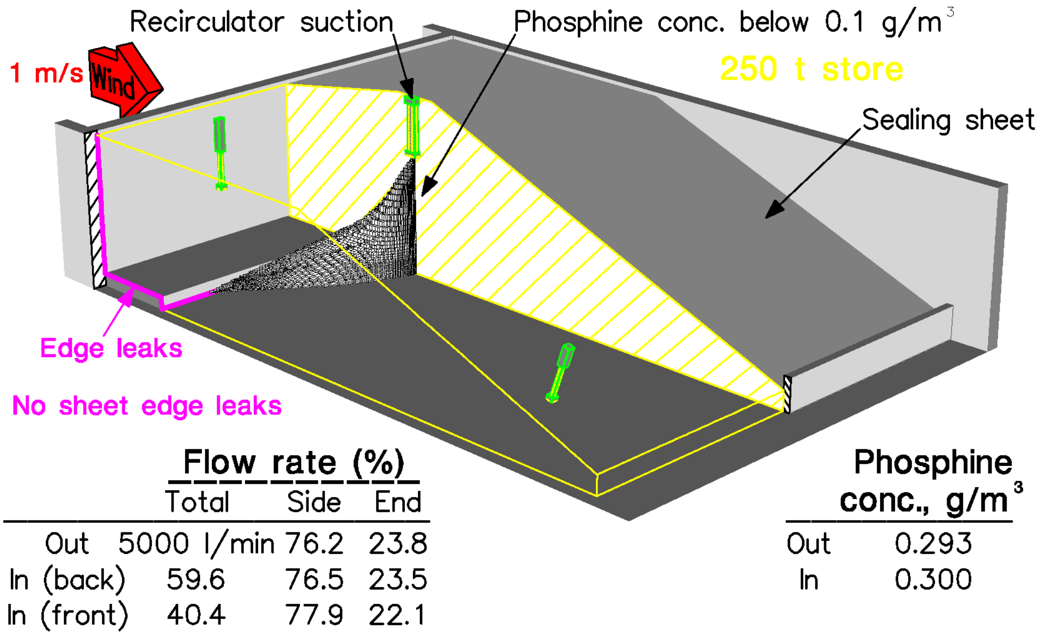
Figure 13. Simulation with four re-circulation ducts, a re-circulation rate of 1 m^3 min^{-1} and leakage at all edges.



There is evidence from the experimental results that the leakage shown in Figures 12 and 13 at the sheet side was present in the tests, due to the difficulty of sealing the sheet against a corrugated wall. However, tests with a sulphur hexafluoride (SF_6) based leak detector suggest that the edges of the sheet are generally well sealed. Also this test failed to find leakage near point G through the party wall into the next part of the store.

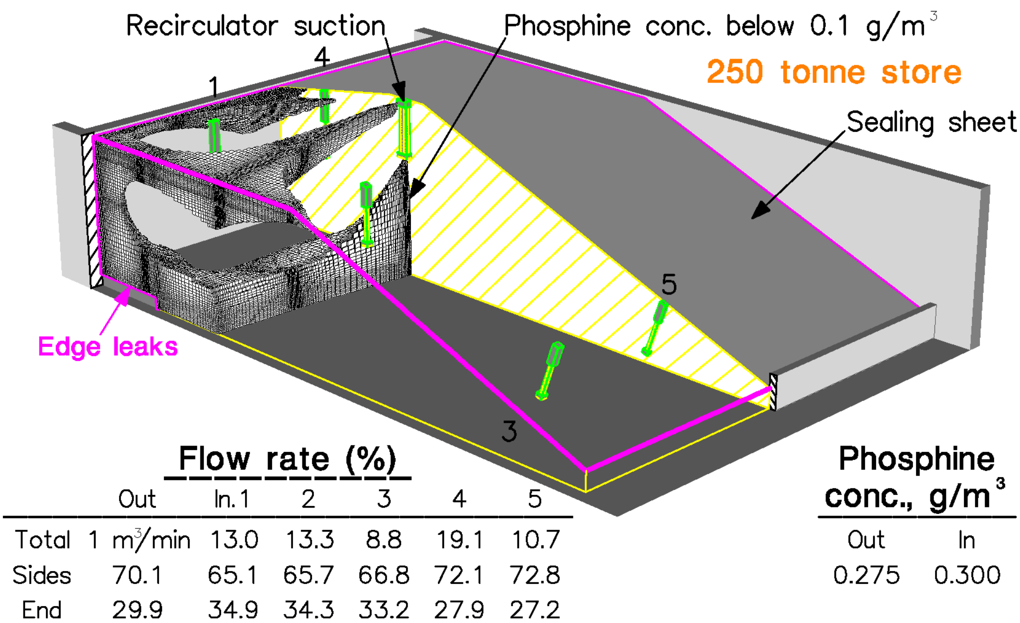
Figure 14 shows the results from another simulation with the same re-circulation rate as in Figure 12, 4.79 m^3 min^{-1} (into the whole store), but with leakage paths assumed to exist at the edges of the rear retaining wall only. The volume of grain in which the phosphine concentration is less than 0.1 g m^{-1} amounts to only 1.4% of the total volume, and the additional phosphine required is now only 0.034 g min^{-1}. The pressure distribution and hence the flow pattern near the floor, changed significantly.

Figure 14. Simulation with four re-circulation ducts, the re-circulation rate at 4.79 m^3 min^{-1} and with the leakage paths assumed to exist at the edges of the rear retaining wall only.



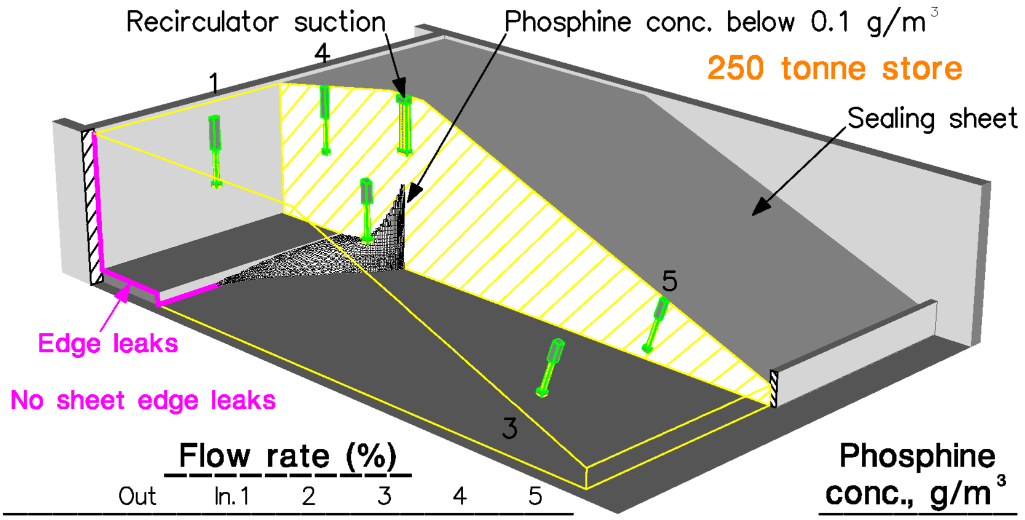
Figures 12 and 14 show that the effects of a 1 m s^{-1} wind blowing over the store have been included in the simulation. The pressures created by the wind were calculated in a separate model. The pressures at the leaks, relative to a downstream datum, were less than 0.5 Pa and the predicted effect of a modest wind on leakage rates when the system is running is negligible.

Figure 15. Simulation with eight re-circulation ducts, a re-circulation rate of 1 m^3 min^{-1} and leakage at all edges.



The predicted effect of using 8 injection pipes instead of four is shown in Figure 15. The re-circulation rate is 1 m^3 min^{-1} (into the whole store). The predicted percentage of the total gas flow through each of the 5 inlet ducts is given, ranging from 8.8% to 19.1%. Resistance to flow in grain is lowest in the horizontal plane and so, if there is the same pressure, the proportioning of the flow is related to the distance from the sucking ducts. There is still leakage as a result of the re-circulation system but the affected volume has been reduced from 10.5% to 8.4% of the total volume. The additional phosphine required is now 0.025 g min^{-1}. This trend is consistent with the trials results. Figure 16 shows a similar simulation but with the leakage paths assumed to exist at the edges of the rear retaining wall only. As expected, the smallest leakage occurs when the sheet edge leaks are eliminated.

Figure 16. Simulation with eight re-circulation ducts, the re-circulation rate at 1 m^3 min^{-1} and with the leaks paths at the edges of the rear retaining wall only.



Flow rate (%)

	Out	In.1	2	3	4	5
Total	1 m^3/min	13.8	13.5	7.8	20.2	9.6
Sides	70.1	65.1	65.7	66.7	72.1	72.6
End	29.9	34.9	34.3	33.3	27.9	27.4

Phosphine conc., g/m^3

Out	In
0.298	0.300

Table 4 summarises these results and compares the predicted phosphine supply rate with an actual result from Trial 3 (Table 3).

Table 4. Predicted and experimental phosphine usage.

Number of injection points	Assumed leak positions	Phosphine supply rate to maintain 0.3 g m^3 at 1 m^3 m^{-1} (g min^{-1})
4	Sheet and wall edges	0.037
8	Sheet and wall edges	0.025
8	Wall edges only	0.002
8	Unknown in trials	0.024 (measured)

Some of the sampling points used in the trials were located within the low phosphine zones highlighted in Figures 12, 13 and 15 which included sheet edge leaks. The predicted results are from steady-state analyses and therefore these sampling points would be expected to show consistently low concentrations. Since they did not show consistently low phosphine concentrations in the trials, it must be assumed that the sheet edge leaks were not generally significant. However, the predicted phosphine usage (0.002 g min^{-1}) with wall edge leaks only is far below the measured value (0.026 g min^{-1}), suggesting that the wall edge leaks are larger than the 0.2 mm assumed in the analyses. In future, it would be useful to see if floor leaks can be reduced by extending the injection pipes closer to the floor, perhaps about 1 m away.

The lack of ingress of air through the sheet edges also implies no ingress from the floor. In reality, this may not be perfectly sealed and it would be useful to see if floor leaks can be reduced by extending the injection pipes closer to the floor, to within about 1 m. The necessity for very low flows means that the diameter of the inlet pipes could be further reduced to 0.05 m and this would facilitate insertion into deeper grain.

The 'wind effect', which is evident in the experimental records as a decrease in phosphine 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 re-circulation system transit time is approximately 2 hours at a re-circulation rate of 4.79 m^3 min^{-1}, hence phosphine concentration recovers fairly quickly. This time would be longer in the most extended flow paths. Thus, the cessation of dosing during periods of high wind and a resumption with rapid re-circulation for a short period can be justified.

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. A subtle modification to provide the best layout of these would be an oval with the long axis in line with the longest side of the bulk, rather than a circle.

CFD modelling proved a very useful contribution to the project since it provided an understanding of gas flows within a bulk, aided the interpretation of the experimental results and provided ideas and tested improvements in the re-circulation system. It was hampered by a lack of detailed knowledge of exactly where leaks are located in a bulk but this will always be impossible in commercial bulks, even those sealed before the grain is loaded.

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

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

(iii) The quantity of phosphine required to replace losses as a result of re-circulation can be minimised by using a low re-circulation rate.

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

(v) After adverse weather, phosphine concentrations throughout the bulk will recover most quickly using a high re-circulation rate.

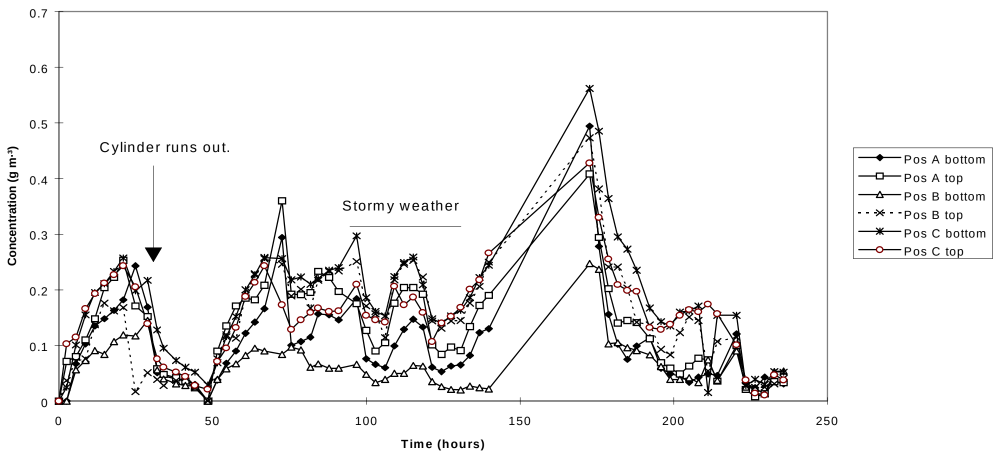
5.2. Experimental data for trials 1-4.

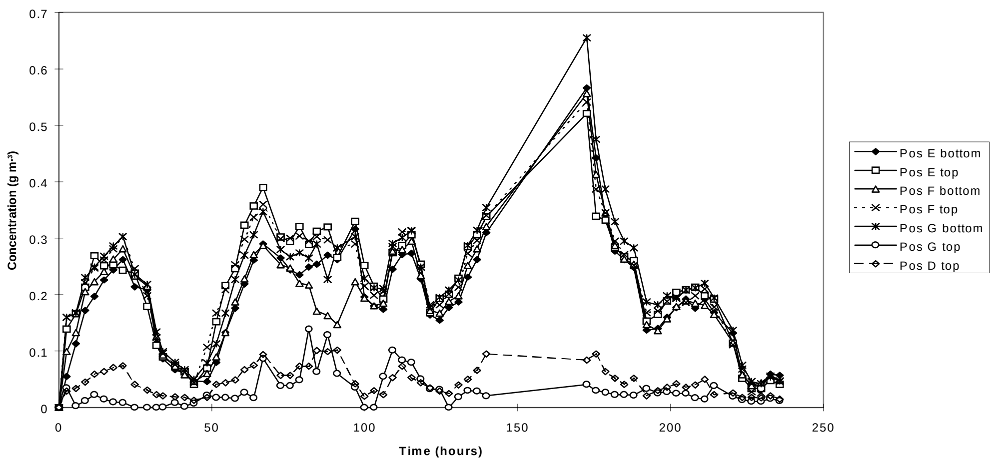
5.2.1. Trials 1 and 2.

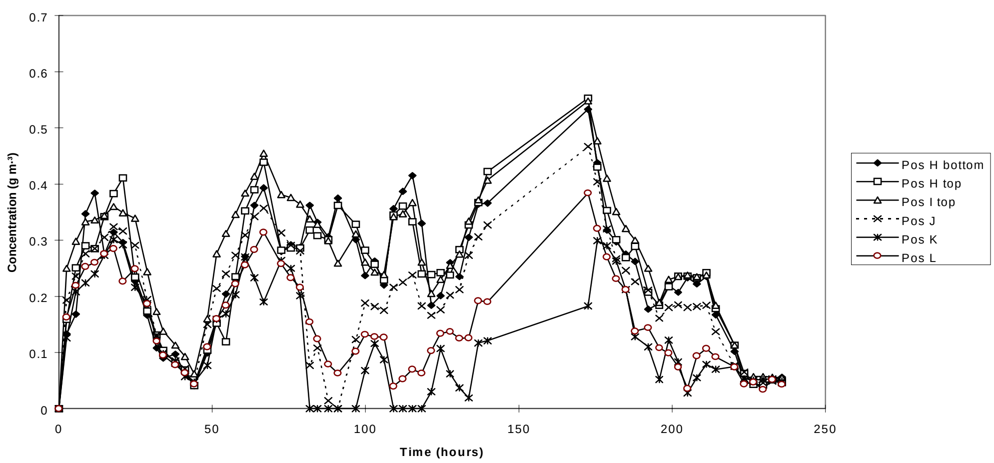
The dosing system was run over 9 days in both trials 1 and 2. The amount of FRISIN^R used was 42.6 kg in trial 1 (880 g of phosphine) and 35.2 kg in trial 2 (730 g of phosphine). The difference in the amount of phosphine used in the two trials was probably due to a small leak coming from the flow meter of the dosing system (Fig. 1) that was discovered towards the end of trial 1.

Figure 17 shows the concentration in the bulk against time during trial 1. It shows a reduction in concentration on day 2 (20 to 50 hours) due to the cylinder running out overnight. Stormy conditions were experienced on days 4 and 5 of the trial (80 to 120 hours). This caused low concentrations in several positions in the grain especially at the bottom of the slope (positions J, K and L), at the back (position B) and on the right side of the bulk (position G). When normal wind conditions had resumed the concentrations recovered within a day to give good concentrations everywhere except position G at the side of the bulk.

Figure 17. Concentrations of phosphine in the bulk during trial 1.







Even with the fan running at full speed an even distribution of gas was never achieved. Position G on the right hand side of the bulk at the surface always received low concentrations. Areas of negative pressure were observed near positions E and G in the pressure profile which could account for the low concentrations at position G. If a small leak was present somewhere near that position, air would be drawn in by the negative pressure causing low concentrations of phosphine.

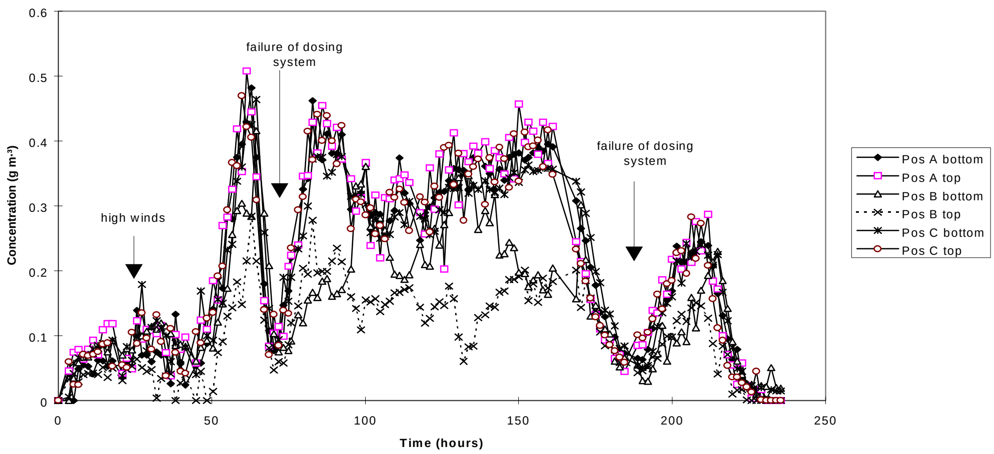
Figure 18 shows the concentration in the bulk against time during trial 2. In this trial two extra outlet shafts were placed in the mid-point of the sides of the bulk (Figure 6) to eliminate the areas of negative pressure identified. The first two days of the trial were carried out under windy conditions and low concentrations were seen throughout the bulk. When the wind speed decreased the concentrations rose quickly throughout the bulk.

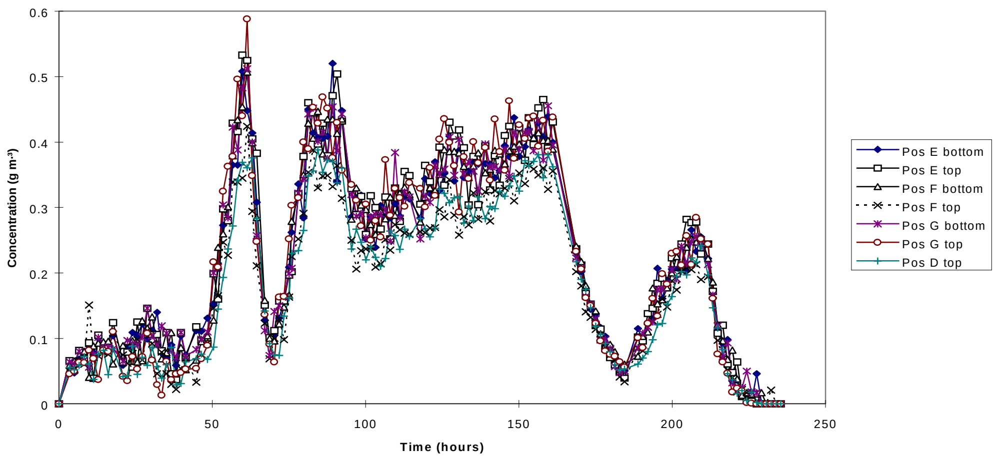
The low concentrations at 70 hours and at 190 hours were caused by the dosing system malfunctioning and switching off the cylinder supply. When the system was restarted the concentrations recovered very quickly. The malfunction appeared to be due to cold and damp affecting the Psion Organiser used to control the dosing system. This problem could easily be remedied in a commercial model which would not rely on an external controller.

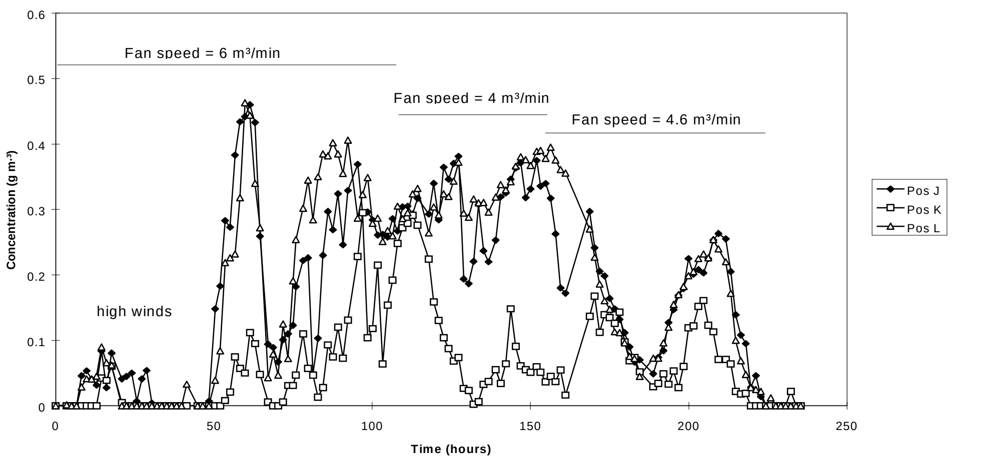
The distribution of phosphine was much more even than in the previous trial. However, low concentrations were seen at position K at the bottom of the slope in the middle especially when the fan speed was reduced to 4 m^3 min^{-1}. Areas of negative pressure were observed at position K and also position B at the back of the store where the concentration of phosphine was lower than elsewhere.

Areas of negative pressure in the middle of the back and front walls indicated a need for outlet shafts at these positions which was made possible by the redesign of the re-circulation system for use in trials 3 and 4.

Figure18. Concentrations of phosphine in the bulk during trial 2.







5.2.2. *Trial 3.*

Trial 3 used a total of eight inlet ducts and was planned to allow many experimental manipulations of the dosing system, including reversal of flow to give suction at the periphery. With eight inlet ducts, no areas of negative pressure could be detected around the edge of the store. Figure 19 shows the pressure profile along the back wall of the bulk. The highest pressures are associated with the injection tubes and this influence extends to the full depth of the bulk even though the tubes themselves were only 1.5 m long.

Figure 19. Over-ambient pressure profile along the back wall when using eight delivery ducts.

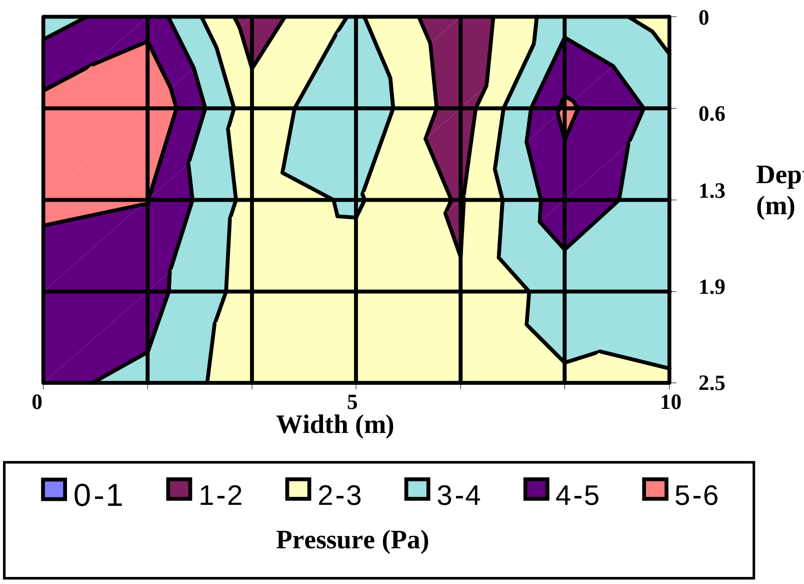


Figure 20 shows the concentrations in the bulk during trial 3.

During the first 120 hours the winds were 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 it was used to deliver gas to the periphery. This permitted a reduction in the circulation rate from 4.85 m^3 min^{-1} to 1.83 m^3 min^{-1} and a reduction in the dosing rate from 3 l min^{-1} to 1 l min^{-1} or 0.0774 to 0.0258 g of phosphine min^{-1} (Table 2)

With the exception of one position, concentrations substantially greater than 0.1 g m^{-3} were obtained everywhere except for a brief period where the flow of FRISIN[R] was interrupted after 220 hours.

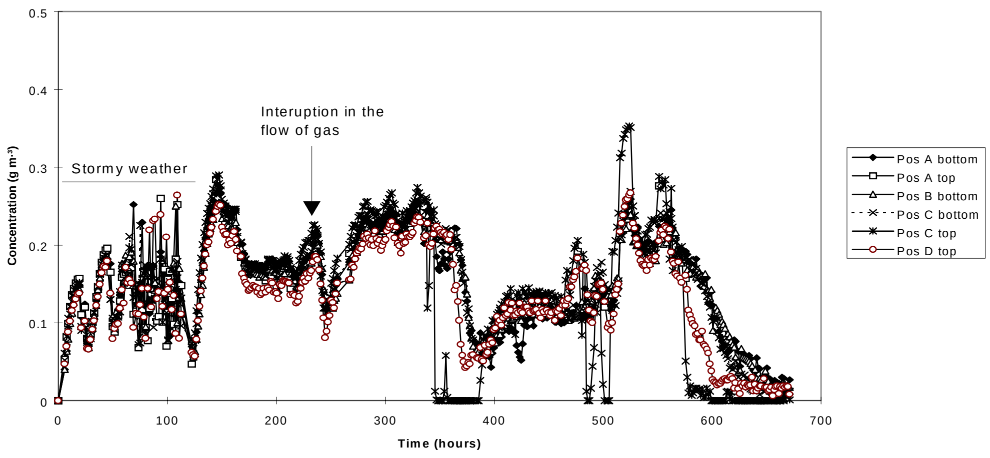
Between 220 hours and 340 hours the circulation system was set at 1.83 m^3 min^{-1} and concentrations in excess of 0.1 g m^{-3} where obtained everywhere including the weakest position. This appears to be the optimum flow rate for this bulk producing minimum leakage due to the circulation system while still providing an even distribution of phosphine. When the flow rate was reduced to 0.82 m^3 min^{-1} a less even distribution of phosphine was obtained.

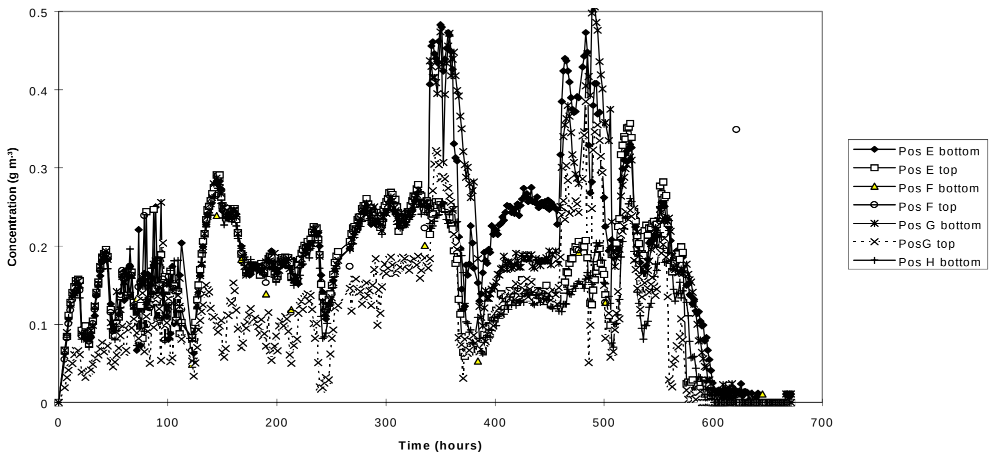
The reversal of the direction of flow of the re-circulation resulted in a less even distribution with some high and low concentrations. This was expected and was caused by air being sucked in from the edge of the fumigation enclosure. However, the flow reversal lasted for 7 days. It may be that a short (30-60 minutes) reversal of the flow direction per day would be beneficial in taking phosphine to areas by-passed by the normal circulation paths.

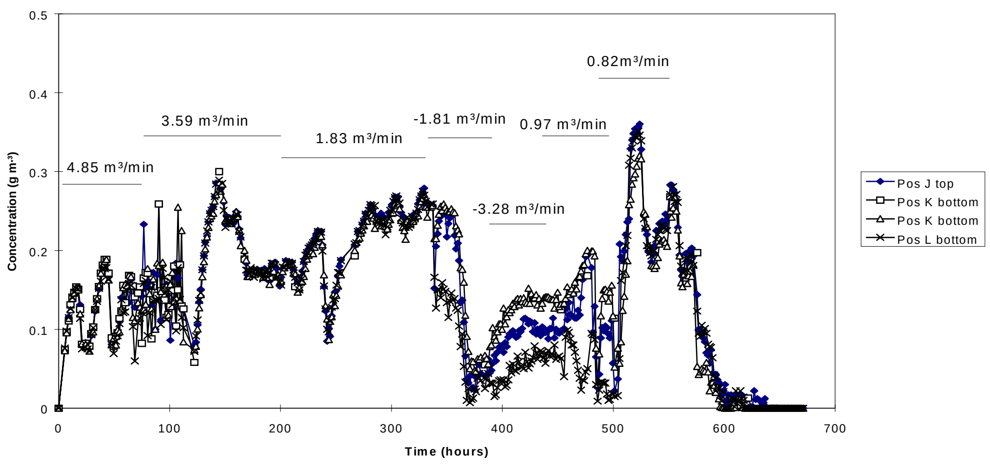
The trial was not primarily designed to achieve any particular exposure period or dose rate but rather to assess the effect of different re-circulation rates and dosing rates under stable wind conditions. However, a total of 50.85 kg of FRISIN[R] was used equivalent to 1.02 kg of phosphine or about 4.1 g $tonne^{-1}$. This in line with current dosage rates for solid phosphide formulations and was particularly economical for a trial which ran for 26 days.

The modelling and the working system was described, concentrating on the findings from trial 3, at a major international conference on the use of gases for control (Mills, *et al.,* in press).

Figure 20. Concentrations of phosphine in the bulk during trial 3.



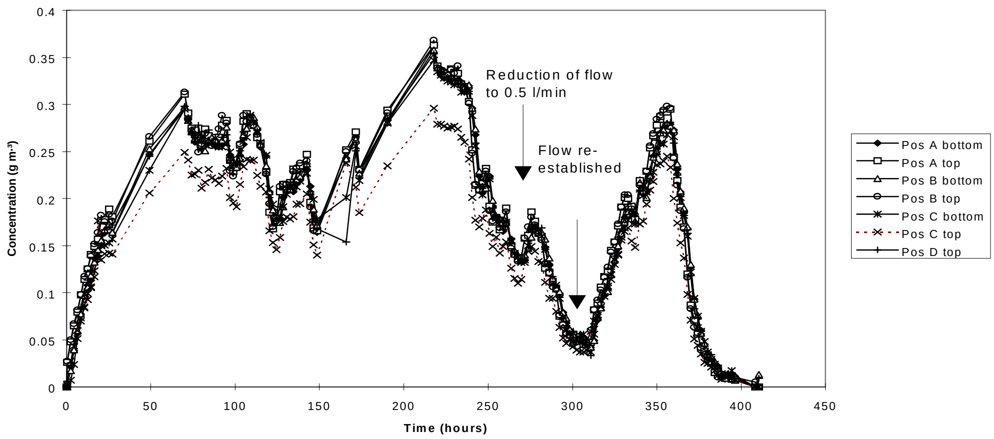


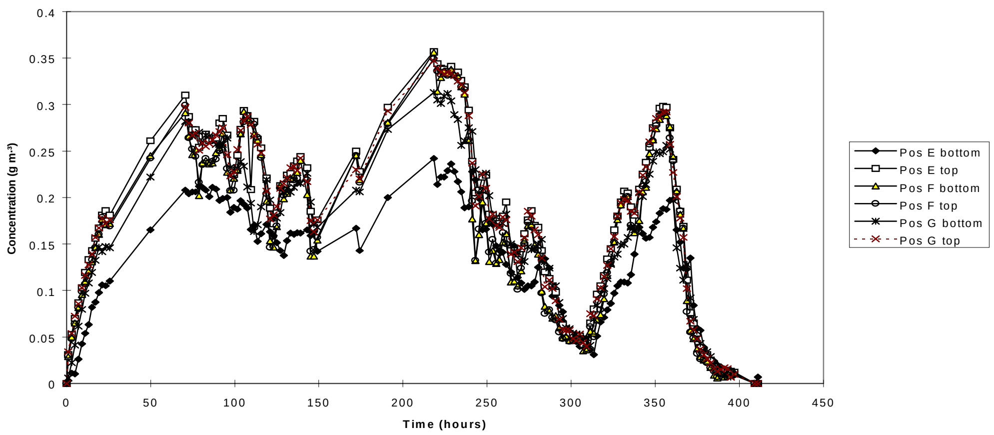


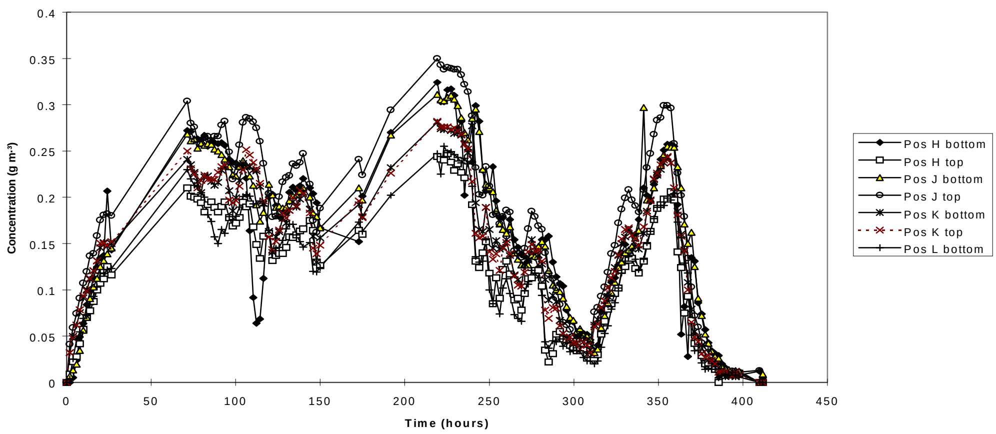
5.2.3. Trial 4.

Figure 21 shows the concentration of phosphine in the bulk during trial 4. Good concentrations were achieved everywhere except where the flow of FRISIN^R was reduced. After this reduction good concentrations were re-established within a few hours of the dosing rate being returned to 2.5 l m^{-1}.

Figure 21. Concentrations of phosphine in the bulk during trial 4.







A total of 37.3 kg of FRISIN^R gas was used (770 g of phosphine) which is equivalent to 2.1 g of phosphine tonne^{-1}.

It is worthwhile to compare the phosphine usage in conjunction with re-circulation with that necessary for the SIROFLO^R system for floor-stored bulks. Previous trials funded by H-GCA compared a SIROFLO^R and an early attempt at a re-circulation system, both over a seven day period (Wontner-Smith *et al.*, 1999). A 150 tonne bulk of feed wheat in the same store used in the current study was used. This re-circulation system employed two ducts blowing into the grain surface and sucking from a ventilation duct via perforated polyethylene lay flat tubing. Dosing was via four ventilation ducts under the control of the auto-dosing system. The amount of phosphine used was about 110 g per day and an average concentration of 0.249 g m^3 resulted. The SIROFLO^R trial used about 60 g per day, i.e. 55 % of that used in the re-circulation system, to produce an average concentration of 0.071 g m^3, i.e. 28 % of the average concentration obtained by re-circulation.

The usage in the current trial 4 was about 50 g per day and gave much higher concentrations with a minimum of 0.15 g m^3 when the system was dosing normally (Figure 21). The difference in phosphine economy will be larger when fumigating to control tolerant species or resistant strains. SIROFLO^R, used under Australian conditions where the grain is warmer than 20 ^oC, has a recommended concentration of 0.05 g m^3 to be maintained for 14 days to control tolerant pest species. This dosage schedule is likely to be increased to a concentration of 0.17, 0.3 or 1.0 g m^3 for 14, 10 or 7 days, respectively, to control highly resistant strains (Collins *et al*, in press). Still higher concentrations and longer exposure periods will be required for treatments under UK conditions below 20 ^oC. For example, for the control of highly resistant rust-red grain beetle, *Cryptolestes ferrugineus* at 15 ^oC, a concentration of 2.0 g m^3 must be achieved for 12 days (Price and Mills, 1988). These concentrations will require high daily dosage rates in the CSL-type store, particularly if SIROFLO^R is used.

5.2.3.1. Bioassay.

The mean emergence from the three controls was 119 adults (range 95-132) of which an estimated 50% were pupae at the time the trial started. A total of 16 samples were inserted into the grain and concentration time products (CTPs) at the top and bottom at position G at the surface and bottom were 64.0 and 64.6 g h m^{-3} respectively. CTPs at the same locations at position H were 38.4 and 57.4 g h m^{-3} respectively. An estimated 120 pupae were treated at each location and there were no survivors from a total of 960 pupae treated. The total exposure period was 17 days.

Laboratory toxicity data indicates that, at 5-10^oC, a 12-day exposure to 0.1 g m^{-3} (a CTP of 28.8 g h m^{-3}) would control pupae of this species (Clifton *et al.,* 1995). This dose would have been attained after the trial had run for 12 days. Control of the saw-toothed grain beetle, *Oryzaephilus surinamensis,* would have been attained in a 4-day exposure at this concentration. However, this trial would not have controlled the highly naturally tolerant granary weevil, *Sitophilus granarius,* which requires exposures at a concentration of 1.0 g m^{-3} of 18 days at 10^oC, more than 23 days at 7.5^oC and more than 28 days at 5^oC (Clifton *et al.*, 1995). However, this system would be capable of obtaining this concentration for whatever exposure period is needed. The precise exposure period required for control at the lower temperatures is not known since the exposures which allow survival were considered to be unobtainable from dosing by conventional formulations at normal leakage rates.

Information on the doses required for the control of resistant strains is scant, especially at low temperatures, again since there appeared little prospect of attaining them in practice. Data obtained at 15°C (Price and Mills, 1988), showed that a concentration of 2.0 g m^{-3} over a 12-day exposure period is required to control a highly resistant strain of *C. ferrugineus* and a 14-day exposure at this concentration failed to control a resistant strain of the rice weevil, *Sitophilus oryzae.* Control of a highly resistant strain of *O. surinamensis* is easier with almost complete control at 0.47 g m^3 over a 10-day exposure and control attained at 0.94 g m^{-3} over a 6-day exposure.

With this dosing system in place we have a means to attain these concentrations and exposure periods and can now design fumigations for the control of resistant strains. Some data exists on the dosage regimes to control resistant strains (Price and Mills, 1988) though further data is required, especially at low temperatures. The presence of resistance in a pest population in a grain bulk can be determined by collecting samples and subjecting adults to a same-day resistance test (Savvidou, *et al.,* 1994; Mills and Athie, 2000).

5.2.3.2 Residues.

Table 5 shows the free phosphine residue levels found in the grain after trial 4.

Table 5 . Free phosphine residues.

Sample number	**Location and depth**	**Residue level (ppm)**	**CTP g h m^{-3}**
1	Back right corner, C, surface	0.0069	-
2	Back right corner, C, 2m	0.0058	-
3	Bulk centre, F, surface	0.0084	70.0
4	Bulk centre , F, 2 m.	0.0037	-
5	Inter-injection duct location right side, H, surface	0.0013	38.4
6	Inter-injection duct location right side, H, 2m	0.0060	-

The CTPs obtained are given for the locations where the highest and lowest residue levels were obtained. A large proportion of the grain had been treated in the other trials and untreated grain added to the surface prior to trial 4. Free phosphine residues reduce quite rapidly with time by airing but it is likely that a small proportion of these residues originated from the other trials and therefore the values measured, especially at the back of the bulk, can be regarded as pessimistic for a single treatment. The highest residue, not surprisingly, was found at the centre surface location where the loss of phosphine after fumigation would be slow. The Codex Alimentarius maximum residue limit (MRL) for raw cereal grains is 0.1 ppm, 12 times higher than the highest residue observed. The residue would decay further upon airing. There is certainly no problem with residues originating by the use of cylinderised phosphine even if the concentration and exposure period have to be increased to deal with resistant insects.

The use of these formulations removes the residue problems associated with the use of solid phosphide formulations, particularly aluminium phosphide tablets, where an atypical sample can contain unspent phosphide and, hence, a residue beyond the MRL as well as an odour of phosphine on the grain.

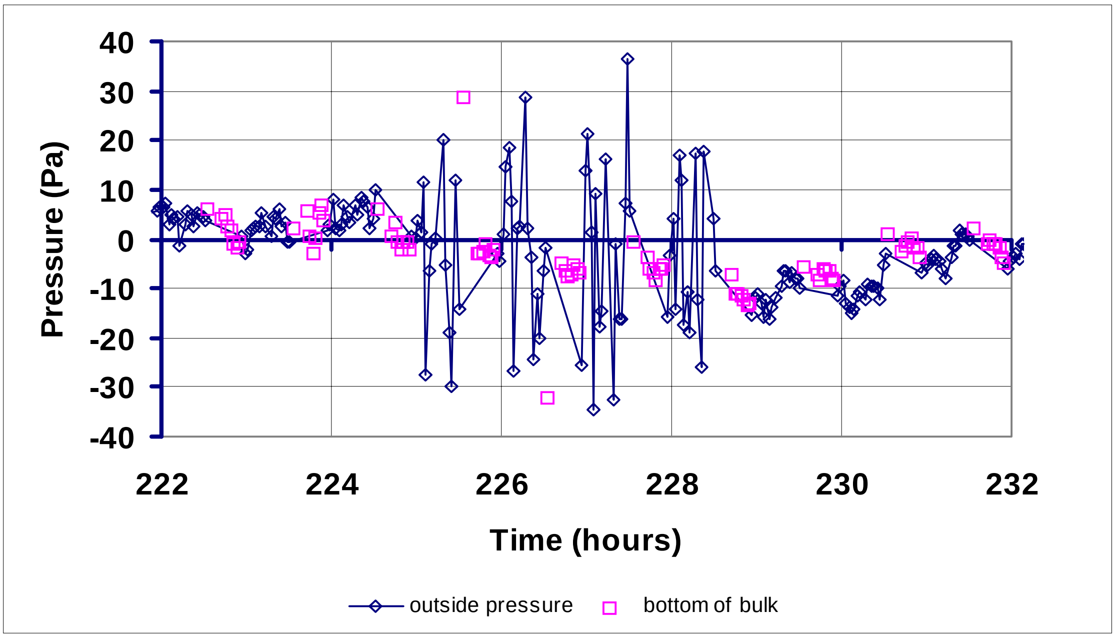
5.3. Understanding the leakage mechanism.

Pressure measurements in trials 1 and 2 showed some evidence that density differences between the air within the bulk and ambient was generating a pressure gradient that could cause vertical flow either upward or downward through the bulk but no simple link between climatic variations and the measured variation in phosphine concentration was observed. Extensive pressure measurements during these trials failed to show the existence of systematic pressure gradients from windward to leeward of the bulk. Dynamic pressures due to the wind did not appear to be generating pressure differences which would cause the levels of phosphine 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 pressure measurements in trial 3 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) within a period of 4-5 minutes.

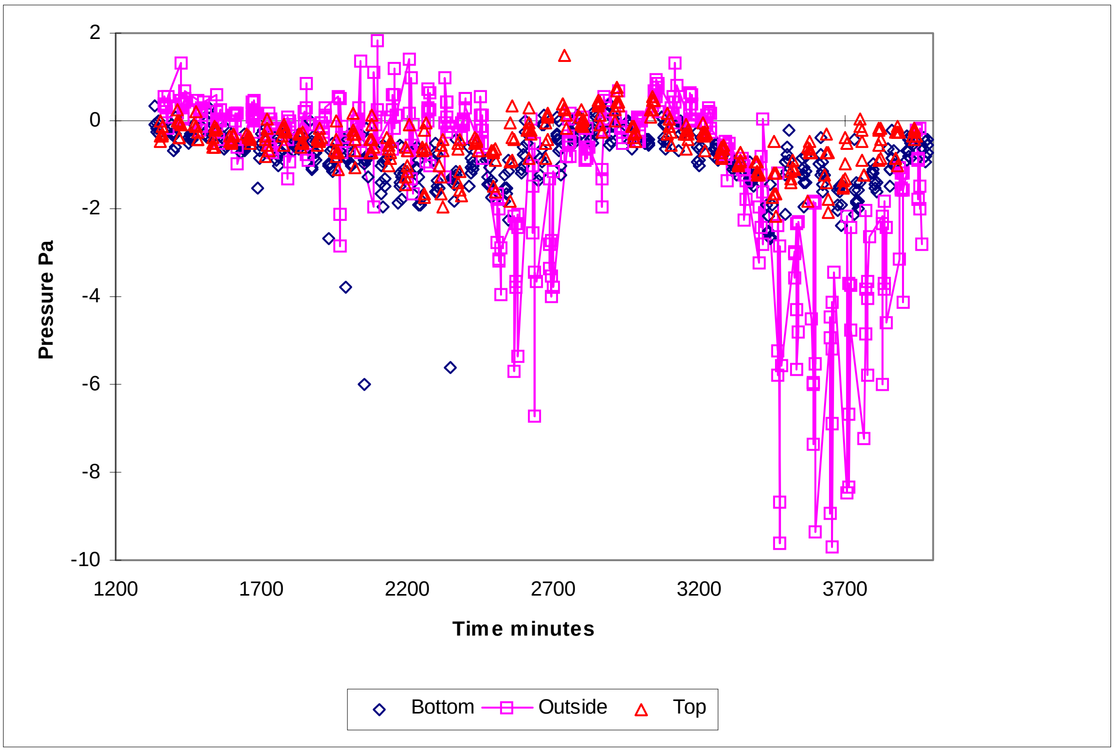
Figure 22 shows pressure measurements during a storm where pressure fluctuations of increasing amplitude were observed. Here the pressure cycled through as much as 60 Pa. Even during quiet periods before and after the storm there is continual fluctuation of ambient pressure. The amplitude of the pressure waves that were observed during the storm were substantially damped out in the bulk. The resistance to rapid pressure change through the sheeting and within the grain could account for this.

Figure 22. Ambient and bulk air pressure fluctuations during a storm.



Ambient pressure fluctuations of increased amplitude during another stormy period are shown in Figure 23. There is some evidence that the amplitude of the pressure waves is less damped at the top of the bulk compared with the bottom. Both are much less than outside the sheeting which illustrates the benefit given by the sheets during windy conditions. The five outlying low pressure readings at the bottom of the bulk in the early part of this segment were caused by the multiplexer cycle.

Figure 23. Ambient and bulk pressure fluctuations

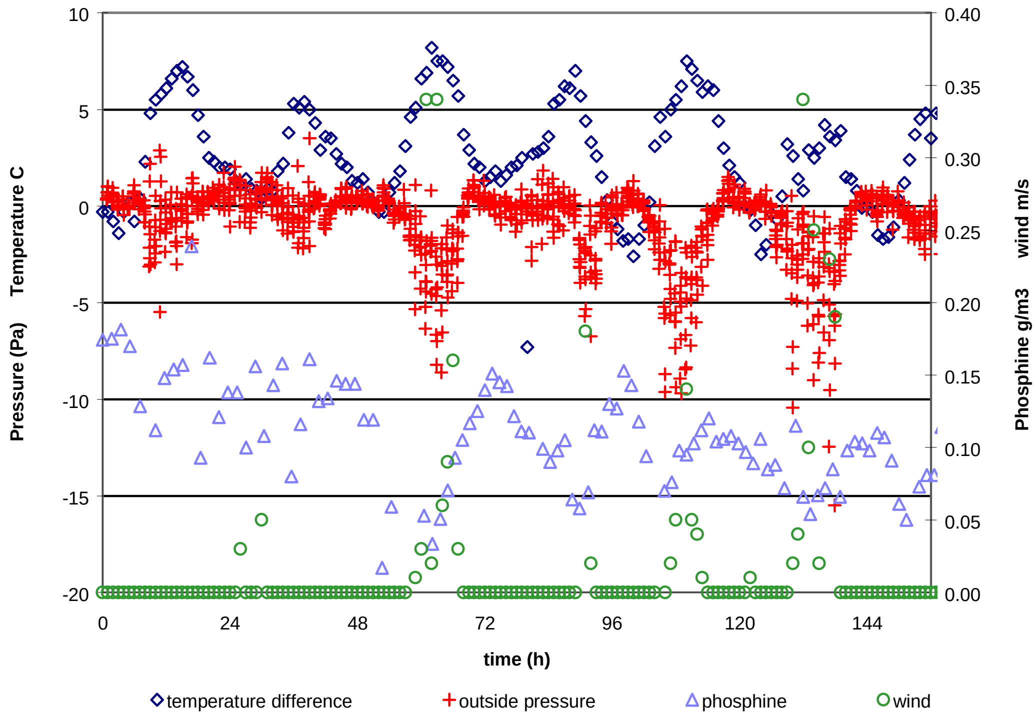


Exchange between air in the bulk and the surrounding atmosphere takes place as a result of small but repeated volume changes in the air. When pressure rises the air in the bulk is compressed and, if it is assumed that the boundary of the bulk is rigid, a small volume of outside air must move into the bulk diluting the phosphine. 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 phosphine with it. This process accounts for the leakage seen during windy periods.

Figure 24 shows pressure, wind and temperature variations over a period of varying wind conditions during trial 3. It shows the effect of wind and diurnal pressure and temperature variations on the phosphine concentrations at the worst position (top, G) where there appeared to be a leak in the building structure.

Leakage is a consequence of the sum of several forces acting on the bulk which can act together or modify each other's influence. The time taken for concentration changes to show are affected by the sampling interval and by the time taken for a 'change front' to move through the bulk. Figure 24 shows an association between changes in phosphine concentration and pressure fluctuations, temperature difference and wind. It is apparent that while pressure fluctuations are frequently linked to wind and temperature difference there are instances where these forces act independently to cause concentration change.

Figure 24. Pressure, wind and temperature variations over time and the resulting phosphine concentrations at the weakest sampling position.



There was evidence from the phosphine concentrations observed in trial 3 (Figure 20) that systematic increases in the circulation rate resulted in increased leakage of phosphine. 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 outflow at the sheet edge where the pressure is positive. Larger scale bulks may allow the cover sheet to avoid this 'tent' effect and to make a better seal at the grain surface, so minimising this re-circulation path.

6. RECOMMENDATIONS FOR FURTHER DEVELOPMENT OF THE SYSTEM.

The project tackled a complex problem and could not, within the budget, produce a set of optimum recommendations to cover different bulks of commercial grain. We have a clear idea of the way forward for future development.

1. The research took place solely in the store in the CSL Storage Research Unit, including a trial under commercial conditions. This trial was originally planned to take place in a larger commercially-owned bulk. However, this was not possible since the cylinderised formulations are not cleared as pesticides in the UK and the MAFF Pesticides Safety Directorate took the view that the active ingredient in these formulations and in the solid metal phosphide formulations were different. The only way forward was to seek administrative experimental approval, and so prevent the sale of the grain, or to seek an extrapolated approval. This latter course relied on an intent to subsequently register the formulation in the UK using data from the registration of FRISIN^R in Germany or ECO2FUME^R in Australia, for example. This also entailed the risk of not being able to trade the treated grain. The situation regarding an application for registration at the time of the trial was uncertain and remains so at present.

   While the re-circulation system has been trialed on different tonnages and bulk shapes at CSL, the project was limited by the size of the store and the maximum depth of grain which it can contain. Therefore, it remains necessary to test the system on a variety of commercial bulks in order to make more detailed recommendations and identify any problems in using it.

2. It is probable that there will be some economy in the dose of phosphine per tonne required in a larger store because of the benefit of smaller surface area to volume ratio. It is also likely that an increase in the spacing of the peripheral inlet ducts as a result of a greater distance from the central sucking ducts and the elimination of re-circulation paths above the grain will result in savings. This reduction in the number of inlet ducts will economise on effort and equipment costs in setting up the system.

3. The system clearly needs to be tested in deeper grain. Commercial bulks can be 10 m or more in depth and it not possible to extrapolate for grain this deep to determine the rate of re-circulation. It is possible that the system will benefit from sinking the ducts to nearer than 1 m of the floor in these and, indeed, in all bulks. An efficient system for sinking the smaller 5 cm diameter ducts, which are possible, into deep grain will be required.

4. The CFD model predicted areas of lower concentration as a result of the re-circulation system itself acting on leaks and sucking air into the bulk bottom. The significance of these is that, even at higher target concentrations, adjacent areas could show dilution of phosphine though they were not found in the trials carried out. They must be considered a potential problem requiring investigation. A solution may be a simple automation of the system so that the

direction of flow can be reversed for 30-60 min per day to bring phosphine into all areas.

5. The method needs to be tested using multiple re-circulation systems on bulks over larger areas before full recommendations can be made for the spacing of peripheral inlet ducts and re-circulation rates for different situations. It is not envisaged that there will be major problems to overcome for multiple systems.

6. The use of the CSL automated dosing system versus continuous dosing via flowmeters needs to be evaluated for multiple systems. It is necessary to determine the required dosing rate for these since there may be economies possible.

7. The problem of high winds of relatively short duration remains. The fumigator can obtain a local record of wind speeds and add periods of high wind to the planned duration of the fumigation. Trials are required with bioassays to confirm that this approach is valid. Confirmatory studies in the laboratory would back up the practical experience.

8. Experience needs to be gained on the effect of closing down the dosing gas during periods of high winds when the phosphine loss is greatest and, if it is beneficial, to automate it.

9. There is little data on the toxicity of the most resistant strains known, especially at 5-15^{o}C. Concentrations and exposure periods for control are required in order to run the system effectively against resistant populations.

10. The mechanisms which produce resistance; active phosphine exclusion and detoxification, are more efficient at higher temperatures. A study on the ease and rate at which insects develop resistance at lower temperatures would be desirable in order to be able to fully assess the risk posed by resistance to phosphine fumigation of bulk grain.

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