HGCA

PROJECT REPORT No. 41

NEW APPLICATION METHODS FOR THE USE OF PHOSPHINE TO DISINFEST BULK GRAIN

DECEMBER 1991

PRICE £6.00

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NEW APPLICATION METHODS FOR THE USE OF PHOSPHINE TO DISINFEST BULK GRAIN

by

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Final report of a two year project at the MAFF Central Science Laboratory, London Road, Slough, Berks., SL3 7HJ. The work commenced in February, 1989 and was supported by a grant of £65,884 from the Home-Grown Cereals Authority (Project No. 0006/2/88).

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ABSTRACT

1. With few compounds remaining cleared for use, fumigation as currently practised has limitations in dealing with infestation problems in floor-stored grain.

2. The fumigation of large bulks is costly and smaller stores are relatively more difficult to seal than larger ones of similar construction because of their greater surface area to volume ratio which permits a greater percentage loss of gas per unit time. The critical size of a storage facility for successful fumigation with phosphine varies widely with the type of construction but enclosures up to 1000 tonnes capacity are likely to give rise to problems, particularly under adverse wind conditions or at low temperatures.

3. Conventional phosphine formulations and the new Detia bag blanket have been tested using different dosing methods. Dosing both the grain surface and the ventilation ducts below the bulk improves gas distribution, particularly in large bulks.

4. Although formulations of aluminium phosphide release gas over a two or three day period, leakage of gas from smaller enclosures prevents an adequate amount of gas from remaining in the grain long enough to kill the more tolerant insect stages at low temperatures. At 5-10°C exposure periods need to be extended to at least 16 days.

5. Use of continuous gas flows from a cylinder-based mixture of 3% phosphine in carbon dioxide provides a means of sustaining sufficient levels of gas for a long enough period

to successfully treat smaller stores without increasing cost.

6. The cylinder-based mixture also offers a means of using phosphine to treat 'hot spots' in large bulks.

7. Some progress has been made in developing a means of determining phosphine dosages by simple chemical detectors.

OBJECTIVES

1. To establish new methods of presenting the fumigant phosphine to bulk grain to improve gas distribution and treatment efficacy, and to widen the scope for using the gas to control infestation in both small and large storage facilities.

2. To obtain data on gas distribution following current methods of applying phosphine to grain bulks, and to find the causes of the control failures often reported.

3. To develop appropriate analytical methods to monitor phosphine levels during treatment in the fumigation enclosure, and in the area surrounding the treatment zone at levels around the Occupational Exposure Limit (OEL).

INTRODUCTION

The use of phosphine to fumigate floor-stored grain under UK conditions has posed problems to the grain storage industry for some time because of the need for long exposures and the vulnerability of the treatment to windy weather. Since the increasing unpopularity and eventual withdrawal of liquid fumigants from fumigation practice there have been difficulties in obtaining satisfactory control of infestation on a regular basis with phosphine as the only recommended fumigant available. Sometimes, but not always, the reason for failure can be attributed to poor quality sheeting, too low temperatures or insufficient exposure time, or other instances where recommendations for treatment have not been followed adequately. However, some of the worst cases of failure have not been caused in these ways, and may have arisen simply because existing methods developed for phosphine usage do not extend to some of the current storage situations.

At the outset of the current project problems had been encountered both in the treatment of very large grain bulks of several thousand tonnes, and in treating smaller bulks in farm floor-stores. One monitoring exercise of a commercial treatment revealed that quite long periods were required for gas concentrations to build up in the deeper levels of a very large grain bulk, even though current recommendations of dosing appeared to have been followed. For large bulks there was also a lack of an effective method of fumigating a localised infestation, the only alternative being to fumigate the whole bulk with phosphine, a costly procedure.

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

The current project was launched to tackle some of these problems, and has concentrated on the testing and appraisal of new methods of treating bulk grain using phosphine, and on attending when possible at commercial treatments to monitor gas concentrations and identify problem areas. During the course of the programme some 9 separate fumigations have been carried out and analysed by the Slough team and two commercial operations have been monitored and evaluated.

MATERIALS and METHODS

TRIALS ON BULK GRAIN

Suitable sites within travelling distance of Slough were located by contacting farmers known to the Laboratory and asking them if they had grain in store and would be willing for an experimental treatment to be carried out. Sites were selected on the basis of size and included bulks of both wheat and barley, all at 14-15% moisture content. Contacts within the pest control industry who had expressed their willingness to help were invited to provide notification of commercial treatments so that monitoring of gas concentrations could be carried out.

Tests on existing phosphine formulations

(a) The first trial, conducted at a floor store near Great Missenden, Buckinghamshire, on a bulk of about 330 tonnes of wheat, provides a typical example of the procedures followed in the trials work described in this report. The grain, held in one of two bays measuring 9 x 28 metres, was reasonably level apart from a 1 metre deep trough across the bulk towards the back, and where it sloped to the floor at the front (Fig. 1). Generally the grain depth was about 3 metres.

Following a standard sampling procedure, a diagonal was traced across the bulk using string from the far back corner of the bay to the start of the slope near the central gangway. At each of these two positions, at the centre of the diagonal which coincided with the central trough, and at the start of the slope at the front centre, nylon gas sampling lines were inserted to the bottom of the bulk, to the midpoint between bottom and surface, and to just below the surface. Further lines were placed near the back of the store and down the slope at the front. All lines were run from the bulk to a mobile laboratory stationed nearby. Samples of grain were taken to check the grain moisture content and for use as controls for subsequent analysis of residues.

Over 40 cages containing 3-5 week old immature stages of a standard stock of *Sitophilus granarius* reared at 25°C, 60-70% r.h. in the laboratory were inserted in the grain alongside the gas sampling positions and elsewhere to supplement the information obtained on gas distribution and treatment efficacy. Cages were held in threaded cage holders linked to rod spacers which permitted insertion of cages at metre intervals to depths of up to 4 metres. Thermocouples were attached to the rods to obtain a representative profile of the temperatures within the bulk.

Efforts were then made to seal the bulk prior to dosing. The ventilation ducts beneath the bulk were sealed off as far as possible by glueing polythene sheets across the individual hatch plates along the main plenum duct, leaving a corner free for dosing, and also by sheeting the fan itself from inside and outside the duct. Light-weight laminated sheets of low permeability to phosphine were placed on the grain surface and pushed into the grain round the sides of the bulk to achieve a good seal. The sheets were then temporarily moved away from the centre for application of fumigant.

In this trial, the bulk was dosed at the rate of 5g phosphine per tonne by burying a new 6m length Detia bag blanket (which releases 1.1kg phosphine, equivalent to 100 Detia sachets) across the centre trough, and by inserting conventional Detia sachets into each aeration duct beneath the bulk to provide the remaining third of the dose. After these preparations were complete, the grain was sheeted over with the prepared laminated sheeting, glueing and taping or stapling all joins and taking special care to provide a good seal at the edges by weighting the sheet down with chain, and the sealing of the aeration duct hatches in the plenum chamber was completed.

Gas concentrations were monitored throughout the 16-day exposure period. The bulk was then unsheeted, taking all recommended precautions with regard to respiratory equipment, and allowed to air. Hand-held electronic detectors were tested in conjunction with Draeger and other detector tubes to investigate whether phosphine levels had fallen to below the OEL before moving on to the grain to remove lines and test insects and to take samples of grain from the top, middle and bottom of the bulk at selected positions, depending on the distribution of measured gas concentrations. These samples were analysed at the laboratory by the method of Scudamore and Goodship (1986) to check that phosphine residues did not approach the maximum residue limit (MRL) of 100µg/kg.

(b) Further trials conducted on the use of aluminium phosphide preparations included the treatment of a 700 tonne bulk of wheat in Suffolk with the conventional Detia sachets, again at 5g phosphine per tonne, dosing the aeration ducts as well as the grain surface (Fig. 2), a repeat trial at the Buckinghamshire site (Fig. 3), after lining the store before harvest with impermeable sheeting and testing the efficacy of bag blankets alone as a surface application method, and trials on a 900 tonne bulk of malting barley (cv Pipkin) in Norfolk (Fig. 4), and on a 500 tonne bulk of wheat in Cambridgeshire, again using the Detia bag blankets on the surface but allocating part of the dosage to the ducts in the form of sachets (Fig. 5). In all trials a similar gas sampling and bioassay plan was followed to that described above, extra sampling positions being employed when there was reason to believe that treatment efficacy in certain parts of the bulk could be affected by local factors.

<u>Tests on a novel cylinder-based supply of phosphine</u>

The remaining trials on bulk grain featured the use of a cylinder-based formulation of 3% v/v (2.6% w/w) phosphine in liquid carbon dioxide. Four different bulks were treated, one on the same 500 tonne bulk of wheat in Cambridgeshire that was used for the bag blanket trial, one on 330 tonnes of wheat in Berkshire (Fig. 6), one on 500 tonnes of wheat in Warwickshire (Fig. 7) and, lastly, on a 10,000 tonne bulk of barley in Worcestershire (Fig. 8).

For these trials, the ability to apply gas continuously permitted the testing of new dosing strategies. In the first trial, nearly a third of the total dosage of fumigant was applied at a relatively high flow rate over the first day (about 0.7m^3 per hour of the mixture or 35g per hour phosphine, about 1.6g phosphine per tonne of grain) and thereafter at about one quarter the initial rate. For the trial in Berkshire the aim was to maintain a steady flow throughout the fumigation but the overall dosage was increased from about 5 to 10g phosphine per tonne. In the third trial in Warwickshire, efforts were again made to maintain a low flow rate from the start and the overall dosage was reduced to 5g per tonne. The fourth trial explored the potential for using phosphine as a spot treatment method and compared the effect of multiple and single point continuous flow systems (Figs. 9 and 10), dosing two separate parts of the 10,000 tonne bulk, at a rate of 5g phosphine per tonne for the treatment zone and its surrounding area, amounting to a total of 100 tonnes of grain.

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

At the Cambridgeshire site, two cylinders were linked together to a common manifold and reservoir to provide a means of running four dosing lines to the 500 tonne bulk from a central supply source. The trial in Berkshire featured dosing from four separate cylinders without the use of a reservoir while the Warwickshire trial featured the use of separate reservoirs for each cylinder. In the "spot treatment" test on the 10,000 tonne barley bulk in Worcestershire, a manifold was used to supply the four dosing lines for the multiple dosing point treatment, while the single point dosing line was run from the cylinder via its own reservoir.

Monitoring of commercial treatments

During the programme, two commercial treatments were attended, one at Bottesford, Leicestershire, and the other at Little Staughton, Cambridgeshire, both involving treatment of intervention wheat. The Bottesford treatment was of a 9,500 tonne bulk of feed wheat. The grain bulk measured 36 x 70m with peaks rising to 7.5m above floor level. An unusual feature was that the grain walls had been lined internally with 250µ polythene sheeting. The grain had been aerated via six on-floor ventilation ducts which protruded from the grain at the front of the slope.

The bulk contained a heavy infestation of flat grain beetle *Cryptolestes ferrugineus*, mainly confined to along the back wall where melting snow had given rise to some dampening earlier in the winter. Fumigation of the whole bulk was recommended. The contractor agreed to treat the rear third of the bulk at 6g phosphine per tonne and the remainder of the bulk at 3g per tonne. A tablet formulation Detia gas Ex-T was used in the treatment. As the department's mobile laboratory was in use elsewhere, monitoring of gas concentrations was restricted to three locations (Fig. 11). A total of seven sampling lines were inserted prior to dosing. During the time under gas, Draeger detection tubes were used to provide a rough measure of the gas level. On days 3, 10, 15 and 20, and on day 21 when the fumigation ended, duplicate samples of gas were taken into partially evacuated glass flasks for analysis at the laboratory.

The monitoring exercise at Little Staughton was of a partial treatment, at the grain merchant's request, of a 15,000 tonne bulk with a localised infestation, again of *C. ferrugineus*, near a roof leak half way down one side of the shed. The fumigation contractor decided to treat an equivalent of 1000 tonnes of grain at a rate of 10g per tonne. This was achieved by the use of "Fumisleeves" which were made of fine mesh woven nylon with a laid flat width of 11cm and over 2m in length. These were slid over sections of UVPC 50mm diameter piping which were pushed 2m into the grain. As the plastic tube was withdrawn, 300 Phostoxin tablets were dropped into the sleeve by means of a funnel and were held in position as the sleeve progressively collapsed.

Thirteen Fumisleeves were inserted immediately around the hotspot and a further 21 at 5m intervals on either side and parallel to the side wall. The area was covered with a 6 x 40m polyethylene sheet of thickness 30μ which in turn was covered by another sheet twice the size. The sheeting layout, together with the Slough team's gas sampling positions, are shown in Fig. 12. On this occasion the mobile laboratory was available to permit continuous monitoring of gas concentrations from 24 positions.

GAS ANALYSIS AND DOSAGE DETERMINATION

Analysis of phosphine

Most analyses of gas levels were performed with a Hewlett Packard 5880 gas chromatograph fitted with a modified stream selection valve permitting sequential sampling of up to 32 lines. For analysis of phosphine a flame photometric detector was used with an oven temperature of 200°C. Using a 1 metre Porapak Q column, the retention time was about 12 seconds. The gas chromatograph was programmed to monitor gas levels from all sampling positions during each fumigation on a four hourly cycle. The effect of the presence of carbon dioxide in the trials on the cylinder-based mixture on the analysis of phosphine was investigated. Additional readings of gas levels in the treatment area were taken using portable instruments and kits being evaluated for measurement of concentrations near the OEL during the large-scale experimental trials.

At the end of each fumigation the total dosage obtained at each sampling point was calculated as a concentration x time product (Ct) using a computer programme to estimate the area under the curve of a plot of exposure time against concentration.

Development of a passive dosimeter

To find a means of evaluating fumigation efficacy without the need for sophisticated equipment, laboratory tests were run to develop a passive means of estimating fumigation dosages. Detector tubes produced commercially by Draeger, Gastec and Kitagawa have been tested under closely controlled experimental conditions to assess the prospects for conversion from rapid measurements of ambient concentration levels to a longer term assessment of total achieved dosage. The test method involved opening tubes to the atmosphere and placing them in visible compartments of a fumigation chamber in which a known phosphine concentration had been set up and measured by gas chromatography. For some experiments tubes were joined together to increase the length of the reagent column. At the end of each of a range of predetermined exposure periods, tubes were removed from the chamber compartment and the length of the reaction stain inside was measured to the nearest 0.5mm. This value was then compared to the measured Ct product for the treatment exposure. The procedure was repeated with a different concentration but similar Ct products to check for consistency of response.

RESULTS

TRIALS ON BULK GRAIN

Tests with conventional formulations

The first trial at the site in Buckinghamshire highlighted the difficulty of retaining gas in a small store for an adequate period to achieve control. In fact windy conditions prevailed throughout the trial and little gas remained after the first week (Table 1), necessitating an additional application of fumigant (another bag blanket placed centrally on the 330 tonne bulk of wheat). In spite of this measure, some immature *S. granarius* still survived at several positions and Ct products were low at many points in the bulk (Table 1). Grain temperatures ranged from 7 to 12°C.

In the trial conducted in Suffolk on 700 tonnes of wheat, where currently registered phosphine formulations were used and applied both to the surface and to the ventilation ducts, a very much better result was obtained. Gas distributed well, and of the test insects inserted into the grain there was only a single survivor from those removed on the day the bulk was unsheeted after a 15-day exposure and none at all from a duplicate set of samples removed 6 days later. Concentrations remained above 0.05 mg/l at all points, giving rise to high Ct products (Table 2). Grain temperatures (5-9°C) were lower than in Buckinghamshire but ambient temperatures during the trial, which was conducted in

April, were higher.

The store in Buckinghamshire was retested in the Autumn of 1989 after the loading of 500 tonnes of wheat into the polythene-lined bay, dosing with bag blankets as before but this time using two because of the extra grain. Although gas distributed more slowly than previously, a somewhat better result was obtained, with gas remaining at most points for the duration of the exposure (Table 3). However, there was still some survival of immature *S. granarius* even though grain temperatures ranging from 10-19°C were higher than the 7-12°C recorded the previous March.

The trial on the 900 tonnes of barley in Norfolk featured both surface dosing with bag blankets and dosing of the ventilation ducts with sachets, taking care not to allow maximum concentration levels in the ducts to approach the flammability threshold. Initially gas distributed well but unfortunately the trial coincided with the late January storms and gas concentrations fell to zero at several points, resulting in survival of test insects after termination of the trial in February (Table 4).

Results at the Cambridgeshire site were again adversely affected by windy conditions and by the end of the first week gas levels at some positions had fallen below 0.01 mg/l (Fig. 13). Here two bag blankets had been applied along the centre of the store with supplementary dosing of bags into alternate ventilation ducts, resulting in a total dosage rate of 7g per tonne, a higher level than the 5g per tonne employed in earlier trials. Grain temperatures ranged from 7 to 16°C and low levels of survival of the *S. granarius* bioassay samples occurred at several sampling positions (Table 5).

The phosphine residue levels in this and the previous trials did not approach the MRL of 100µg/kg at any position (Table 6).

Trials with phosphine from cylinders

After the trial with bag blankets at the Cambridgeshire site, the same bulk treated with phosphine applied as a gas in carbon dioxide from cylinders gave a better overall result. Some frosting of cylinder regulators occurred during the initial purge of the bulk, causing a slight delay in the initial dosing. However, as soon as the purge was completed, gas levels rapidly dropped at all points necessitating the establishment of a maintenance gas flow from day 4 (Fig. 14). During this topping-up phase, problems were encountered in maintaining stable, low gas flows of 400-500 ml per minute at each of the 4 outlets from the gas reservoir, and flow meters required constant adjustment. The ability to introduce gas continously did nevertheless ensure that except in areas of excessive leakage, a sufficiently long enough exposure could be arranged to achieve control. The total Ct products obtained in the two trials on this grain bulk are compared for all sampling positions in Table 7. The very much higher Ct products obtained in the phosphine/carbon dioxide fumigation resulted in a far greater level of control than in the bag blanket trial (Tables 5 and 8) while fumigant residues remained low.

The Berkshire trial featured the use of 4 independent dosing lines, each run direct from a cylinder via a flow meter. Flow meters were each set to a flow rate of 300-400ml per minute to run for 16 days and provide a total phosphine dosage of 5g per tonne of grain. This level was increased to 700ml per minute when it was discovered that gas levels at many points failed to rise above 0.1mg phosphine per litre (Fig. 15), and a further two days were added after gassing before unsheeting. This poor gas distribution was subsequently partly explained by a collapsed ventilation duct. Again constant adjustments of needle valves and flow meters were necessary to maintain a steady flow and avoid stoppages. In spite of the rather low Ct products obtained at several of the 21 points sampled and generally low grain temperatures of 5-9°C, survivals of the *S. granarius* bioassay stages were recorded from only 6 out of 28 positions (4 out of 21 in Table 9), possibly because of the extended exposure period of 22 days).

For the Warwickshire trial, the provision of a separate reservoir for each outlet resulted in an improvement for the maintenance of gas flows but nevertheless there was still a tendency for a gradual decline in the amount of gas passing through each of the 4 flow meters and a marked diurnal cycle of output was evident which resulted in gas levels throughout the 500 tonne bulk reaching a peak each afternoon and falling at night (Fig. 16). In general, the control achieved by the 16-day exposure period at grain temperatures between 6 and 10°C was very good, with survivals occurring at only two out of 18 positions (Table 10).

The trial in Worcester concentrated on the use of the mixture as a potential means of treating a localised area of a large bulk. Grain temperatures were low, ranging from 2 to 6°C, and in both experimental spot treatments gas tended to sink into the grain and leave the surface zone with low concentrations (Figs. 17 and 18). The treatment with four dosing probes (Fig. 17), a central probe with a triangle of three others, each 1m from the centre, was also beset by difficulties in maintaining the required level of output from each dosing line. The flow rate from the single probe, which was intended to equal the sum of the outputs of the four probes, was comparatively stable and gas concentrations (Fig. 18) and the levels of kills obtained after the 15-day fumigations were in general comparable with those for the treatment using four probes (Table 11), and were actually higher for the upper layer of grain within the 1m treatment zone.

Because of the problem of maintaining low flow rates of the mixture, cylinders were provided with metering valves to control gas flow rate and flow meters were fully opened and used only to measure rather than regulate flows. Using this arrangement it was possible to maintain more even gas flows than with any other system formerly tested (Table 12).

Monitoring of commercial treatments

The whole bulk treatment of 9,500 tonnes of wheat in a polythene-lined store at Bottesford proved to be a successful fumigation but gas concentrations in grain at 4 to 7°C took 10 days to peak at 2.5m depth or below, and even longer at the sides (Fig. 19). In fact the Ct products of about 85 to 130mg hours per litre obtained at the side sampling positions (only surface shown in Fig. 19, others were lower) would not have controlled *S. granarius* had these been present in the grain instead of *C. ferrugineus*.

The treatment of 1000 tonnes within a 15,000 tonne bulk of wheat at Little Staughton was again successful in controlling the localised *C. ferrugineus* infestation, but Ct products decreased markedly as the side wall was approached (Table 13) and would have permitted survival of immature stages. Gas concentrations built up very slowly in the treatment zone and it subsequently transpired that many of the tablets in the "Fumisleeves" used for dosing had not fully broken down at the end of the 12-day fumigation.

GAS ANALYSIS AND DOSAGE DETERMINATION

Analysis of phosphine in carbon dioxide was possible with little difficulty in separating peaks for phosphine from background interference. The gas chromatographic method permitted estimation of phosphine concentrations within the treatment zone and was also capable of measuring trace levels below the OEL.

In monitoring the working environment in the vicinity of a treatment area, attempts to measure concentrations near the OEL with two instruments based on an electrochemical cell proved unsuccessful and detector tubes remain as the only viable means for such measurements in practice.

Trials using detector tubes as a means of monitoring fumigation dosages have demonstrated that Draeger tubes, working on the principle of conversion of a gold salt to colloidal gold (colour change yellow to brownish black) give consistent results, but only up to modest Ct products of 20-25 mg hours per litre. On the other hand the Kitagawa tubes, which had a narrower bore and worked with mercuric chloride as a reagent (colour change white to yellow) continued to respond to Ct products up to 100 mg hours per litre but displayed an inherently greater degree of variation, the colour change having the disadvantage of fading after a few days.

Gastec detector tubes, again featuring a mercury-based reagent but with a different indicator, gave similar results to the Draeger tubes with the colour change reaching the far end of the tube after exposures to Ct products of only 40 to 50 mg hours per litre.

Experiments were then performed with two tubes joined end to end for both Draeger and Gastec detectors. This extended the range of dosages which could be monitored but the stain length was dependent on concentration to a greater extent than Ct product and at lower concentrations tended to level off regardless of the exposure period for both makes of tube (Figs. 20 and 21). Gastec tubes appeared to provide the more consistent results for concentrations between 0.1 and 1.0 mg per litre and Ct products of up to about 150 mg hours per litre, but there is a need for much further development to produce a satisfactory total dosage monitor.

DISCUSSION

Phosphine is a fumigant with many advantages and has come into world-wide use for the treatment of bulk commodities. However, attempts to extend its use into new situations arising because of changes in storage practice or loss of previously used control agents are fraught with difficulties. Some pests are tolerant of exposure to phosphine at particular stages of development (Bell, 1976) and their control requires lengthy exposure periods, especially at low temperatures. A dosage schedule prepared at this Laboratory for the European Plant Protection Organisation (Anon, 1984) is given in Table 14.

The picture emerging from the field trials conducted in this project is that conventional methods of treating smaller bulks of grain with phosphine are unlikely to be reliable in achieving an adequate degree of control, especially at lower temperatures. The store tested with and without a polythene lining in Buckinghamshire was of modern construction and appeared in every way typical of many facilities in the UK used to store grain on the floor. Although the trials at this site were conducted in typical weather conditions in the spring and autumn, and every effort was made to achieve a good seal of the bulk, especially in the second trial with the lining of the store prior to harvest, in neither case did it prove possible to retain gas throughout the period of exposure recommended for temperatures down to 10°C or below.

Leakage is largely dependent on the surface area of the enclosure when measures have been taken to achieve a good seal. As the size of the enclosure increases, the surface area to volume ratio reduces progressively. Hence, if the volume is increased eightfold (a doubling of linear dimensions), the surface area is only increased fourfold and leakage of the enclosed gas volume will proceed at only half the percentage loss rate. This effect may be the critical factor for bulks of 500 tonnes or less when exposures have to be extended beyond two weeks. The success of the trial in Suffolk on a 700 tonne bulk was probably due to a shorter exposure period being required as a result of higher minimum grain temperatures rather than the slightly greater size.

The benefit of utilising aeration ducts for dosing bulks was evident from the trials at the Buckinghamshire site and also from comparisons with the results of previous trials. With phosphine moving through grain at the rate of up to 3m per day (Friemel, 1984), dosing at the surface and in the ducts below offers the prospect of all parts of a 6m deep bulk being permeated by gas within 48 hours, allowing a day for sufficient gas to be released from tablets or sachets.

The dosing of ventilation ducts needs to be conducted with some degree of caution. Although gas is evolved from sachets or pellets of formulated aluminium phosphide relatively slowly there is a possibility of high concentrations of gas building up in the confined space within a duct. The amount of formulation placed within a duct is therefore restricted so that freespace concentrations of phosphine do not exceed the flammability threshold of 1.8% by volume.

The critical size of a grain bulk for successful use of phosphine as a fumigant has not yet been determined, but in typical shed stores 500 tonnes appears too small at low temperature, and windy conditions apparently rendered a 900 tonne bulk vulnerable to excessive gas loss. Although gas distribution can be improved by dosing at the surface and underneath the bulk, the problem of gas retention is less easy to overcome.

Thus, with the strategy of dosing both the grain surface and the ventilation ducts, a solution to some of the problems encountered with treatment of large bulks may be to hand, but an alternative approach is needed for the smaller store. One such approach is the development of a means of continuously introducing fumigant throughout the exposure period to replace gas leaking out. The current tests on a cylinder-based supply of 3% (2.6% w/w) phosphine in carbon dioxide have shown that simple methods exist to enable this to be done. The "Siroflow" system already in use in Australia incorporates a cylinder-based 2.6% mixture of phosphine in CO_2 which is introduced into grain stores via a fan driven airstream (Winks, 1990) but the present tests show that introduction of gas directly from cylinders can be equally successful.

Some problems in the use of the phosphine in CO_2 mixture have been encountered and resolved. The first trial demonstrated that there was no advantage in an initial high application rate to "flush" the store, the gas applied leaking away rapidly, presumably because of the high concentration gradients present. It proved possible to remain within the existing recommended dosage level of 5-6g per tonne even for smaller stores by setting the appropriate steady gas flow to run continuously throughout a 16-day exposure. At this rate of introduction of gas there was never any problem of frosting up of cylinders even in the coldest weather. However, controlling gas flows through separate needle or ball valves or flow meters was not completely satisfactory, as there was a continual tendency for flows to fall off necessitating frequent adjustments. The provision of a gas reservoir in the dosing line only partly resolved the problem. The best result was obtained, especially for the lowest flow rates, by using a metering valve and leaving flow meters fully open. An account of the first trials with the mixture was presented at the Fifth International Working Conference on Stored Product Protection at Bordeaux in September 1990 (Chakrabarti *et al.*, 1991)

Before the continuous flow system developed in this study can come into use in the UK, the cylinder-based formulation of phosphine in CO_2 needs to be registered for use under the Food and Environmental Protection Act and although approval for the mixture should not be a problem, there are delays. As yet no company has taken the initiative to seek approval. Without the mixture, however, the best use of commercially available formulations still leaves problems for the treatment of smaller bulks or for the treatment of localised infestations in very large bulks along the lines of the formerly widely practiced 'spot' fumigation using liquid fumigants.

ACKNOWLEDGEMENTS

This research programme was funded jointly by the Pesticides Safety Division of the Ministry of Agriculture, Fisheries and Food and the Home-Grown Cereals Authority. The authors wish to express their gratitude to Detia Export GmbH for providing free samples of their current aluminium phosphide formulations and to BOC Ltd, Special Gases Division, for supplying cylinders of the phosphine carbon dioxide mixture. Thanks are also due to those farmers and storekeepers who provided their grain and facilities for the experimental programme. The authors would also like to acknowledge the help and input provided by many individuals at the Central Science Laboratory and in particular to the technical support in the operation of the trials and presentation of results provided by Mr T J Wontner-Smith and Mr S K Cardwell.

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Table 1

Results of the trial in Buckinghamshire on 330 tonnes of wheat, dosing aeration ducts with Detia Gas Ex-B sachets and the surface with a bag blanket, and redosing with a second bag blanket after 7 days, a total dosage rate of 8.5g phosphine per tonne.

Position	Depth in grain (m)	Gas concentration level (mg/l) after no. of days indicated				Total Ct product after 16 days (mg.h/l)
		2	5	9	12	
A, top of slope at front near gangway	Surface	0.26	0	0.07	0.02	13*
	1.4	0.34	0	0.08	0.01	15
	2.8(b)	0.69	0.13	0.17	0.03	59
B, centre of bulk	Surface	11.4	3.1	0.26	0.05	1080
	1.0	12.4	3.5	0.35	0.02	1160
	2.0(b)	0.79	0.57	0.11	0.01	239
C, far corner at rear of store	Surface	0.02	0	0.01	0	6
	1.4	0.02	0	0.01	0	2*
	2.8(b)	0.02	0.01	0.01	0	3*
D, centre, at rear of store	Surface	0.24	0.02	0.30	0.06	72
	2.8(b)	0.04	0.02	0.02	0	10
E, centre, at start of slope	Surface	0	0	0.01	0.29	34
	2.8(b)	0.40	0.05	0.10	0.02	33
	In duct	0.04	0.33	0.13	0.01	83

b = bottom. * Survivals of test insects near these positions.

Table 2

Results of the Suffolk trial on 700 tonnes of wheat, dosing with sachets on the grain surface and in aeration ducts at the rate of 5g phosphine per tonne.

Position	Depth in grain (m)	7 day Ct product (mg.h/l)	14 day Ct product (mg.h/l)	Total Ct product (mg.h/l)
A, front corner	0.5	118	224	282
on slope	1.5 (bottom)	122	244	256
B, on diagonal	0.5	327	391	395
between A	1.5	319	418	426
and C	3.0 (bottom)	293	406	415
C, centre	Surface	455	499	500
	0.5	654	720	720
	2.5	272	319	321
	5.0	830	960	965
D, on diagonal	Surface	255	260	260
between C	0.5	187	206	206
and E	1.5	252	295	296
	3.5 (bottom)	251	343	347
E, back corner	0.5	315	415	418
	1.5 (bottom)	413	526	529
F, back centre	0.5	182	200	200
	1.5	257	293	294
	3.5 (bottom)	258	337	340
G, front centre	Surface	380	388	389
near	0.5	746	855	865
bulkhead	1.5	145	165	166
	3.5 (bottom)	289	374	379
	Under sheet over bulkhead	295	302	303
Duct 1	Near end	859	1097	1102
Duct 2	Near end	959	1111	1119
	Far end	984	1129	1137
Duct 3	Middle	1449	1591	1594
	Near end	1100	1248	1250

Table 3

Results of the second trial in Buckinghamshire, on 500 tonnes of wheat after lining the store before harvest, dosing the surface with two Detia bag blankets (4.4g phosphine per tonne).

Position	Depth in grain (m)	Gas concentration (mg/l) after given no. of days				Total Ct product after 16 days
		2	5	9	12	(mg.h/l)
A, far corner at rear of store	Surface	0.13	0.15	0.03	0	18*
	1.5	0.05	0.17	0.01	trace	16*
	3.0 (bottom)	0.03	0.16	0.07	0.01	12
B, centre of bulk	Surface	1.49	1.55	0.31	0.09	264
	1.0	2.32	1.49	0.30	0.09	287
	2.0 (bottom)	3.42	1.40	0.30	0.09	322
C, top of slope, at side	Surface	0.59	0.21	0.03	0.01	72
	1.4	0.76	0.07	0.08	0.03	65*
	2.4 (bottom)	0.40	0.09	0.08	0.03	55*
D, centre at side	Surface	3.69	0.99	0.10	0.02	277
	2.8 (bottom)	0.92	0.56	0.10	0.02	97
E, back centre	1.5	0.02	0.06	0.01	0	9*
	3.0 (bottom)	0.03	0.07	0.01	0	11*
F, centre top of slope	Surface	0.17	0.01	0	0	8*
	In duct below	0.01	0	0	0	1*

* Survivals of test insects recorded near these positions

Table 4

Efficacy assessment of a trial on 900 tonnes of barley in Norfolk, dosing with bag blankets on the surface and sachets in the ducts at 5g phosphine per tonne. Stormy conditions prevailed during trial in January, 1990.

Position	Depth in grain (m)	Grain temperature (°C)	Corrected % mortality of *S. granarius*	Ct product (mg.h/l)
A, top of slope, at front corner of bulk	Surface	6.1	99	154
	1.0		100	200
	2.0 (bottom)	7.0	100	88
B, centre of bulk	Surface	7.7	100	367
	2.0	12.7	100	416
	4.0 (bottom)	13.0	100	477
C, back of bulk, in corner	Surface	5.6	11	Trace only
	1.0		18	Trace only
	2.5 (bottom)	8.1	0	Trace only
D, on diagonal between A and B	Surface	5.4	100	317
	2.0	8.2	100	318
	4.0 (bottom)		100	314
E, back of bulk near rear door	Surface		76	82
	3.5 (bottom)		0	Trace only
F, centre at side of bulk	Surface		98	21
	3.0 (bottom)		98	21
G, centre part way down front slope	Surface			312
	1.0	7.9	100	
	1.5 (bottom)			71

Table 5

Efficacy assessment of a treatment at 7g phosphine per tonne with bag blankets and sachets of aluminium phosphide of a 500 tonne bulk of wheat in Cambridgeshire.

Position	Depth (m)	Mean grain temp. (°C)	No. *S. granarius* emerging from 2 cages	% kill	Ct product (mg.h/l)
A, rear corner	Surface	7	0	100	128
	1.0	13	0	100	130
	Bottom (2.5)		0	100	122
B, centre	Surface	7	2	96.4	143
	1.0	14	0	100	110
	2.0		0	100	88
C, front corner	Surface	7	3	94.6	47
	1.0	12	0	100	23
	Bottom (2.0)		5	91.1	30
E, highest point of bulk	Surface	8	1	98.2	136
	1.0	16	0	100	141
	1.5		1	98.2	
	2.5		1	98.2	153
	Bottom (3.5)		0	100	211
Site controls		7	56		
Laboratory controls		25	194		

Table 6

Residues of phosphine in trials involving the use of the new Detia bag blanket in fumigating cereal bulks (prefumigation samples zero in all cases).

Site	Cereal	Position of sample (see Figs)	Ct product (mg.h/l)	Residue (ppb)
Bucks, 1st trial	Wheat	A, surface	13	4.0
		A, bottom	59	1.0
		B, surface	1080	18.0
		B, bottom	239	9.0
		C, surface	6	0.4
		C, bottom	3	0
		D, surface	72	1.7
		D, bottom	10	0
		E, surface	34	1.3
		E, bottom	33	0.9
Bucks, 2nd trial	Wheat	A, surface	18	1.0
		A, bottom	12	1.0
		B, surface	264	9.0
		B, bottom	322	8.0
		C, surface	72	4.0
		C, bottom	55	2.0
		F, surface	8	1.0
		F, bottom	1	0
Norfolk	Barley	A, surface	154	1.0
		A, bottom	88	0.6
		B, surface	367	2.0
		B, bottom	477	2.0
		F, surface	21	0.6
		F, bottom	21	0.6
		G, surface	312	2.0
		G, bottom	71	0.7
Cambridgeshire	Wheat	A, surface	128	0
		A, bottom	122	2.0
		B, surface	143	2.0
		B, bottom	72	2.0
		C, surface	47	4.0
		C, bottom	30	2.0
		D, middle	160	3.0
		E, middle	153	2.0
		G, middle	84	0

Table 7

A comparison of Ct products and residues of phosphine obtained in the two trials on a 500 tonne bulk of wheat in Cambridgeshire.

Position	Depth (m)	Bag blanket Ct product (mg.h/l)	Bag blanket Residue (ppb)	PH_3/CO_2 Ct product (mg.h/l)	PH_3/CO_2 Residue (ppb)
A, rear corner	Surface	128	0	318	5.0
	1.0	130		264	
	2.5 (bottom)	122	2.0	297	4.0
B, centre	Surface	143	2.0	169	2.0
	1.0	110		152	
	2.0	88		93	
	2.5 (bottom)	72	2.0	50	0
C, front corner	Surface	47	4.0	215	3.0
	1.0	23		121	
	2.0 (bottom)	30	2.0	56	5.0
D, back centre	Surface	154		214	
	1.0	160	3.0	188	0
	2.0 (bottom)	277		114	
E, highest point of bulk	Surface	136		412	
	1.0	141		453	
	2.0	153	2.0	484	2.0
	3.5 (bottom)	211		739	
F, front centre	Surface	12		31	
	1.0	5.5		25	
	2.0	66		70	
G, catwalk side (centre)	Surface	42		61	
	1.0	84	0	104	0
	2.0 (bottom)	99		100	

Table 8

Efficacy assessment of a treatment with 3% phosphine in carbon dioxide fed from cylinders into the same 500 tonne bulk of wheat in Cambridgeshire tested previously with conventional phosphine formulations and at the reduced dosage rate of 5g phosphine per tonne.

Position	Depth (m)	Mean grain temp. (°C)	No. *S. granarius* emerging from 2 cages	% kill	Ct product (mg.h/l)
A, rear corner	Surface	6	0	100	318
	1.0	11	0	100	264
	Bottom (2.5)		0	100	297
B, centre	Surface	6	0	100	169
	1.0	15	0	100	152
	2.0		0	100	93
C, front corner	Surface	6	0	100	215
	1.0	10	0	100	121
	Bottom (2.0)		2	97.3	56
E, highest point of bulk	Surface	7	0	100	412
	1.0	17	0	100	453
	1.5		0	100	
	2.5		0	100	484
	Bottom (3.5)		0	100	739
Site controls		6	73		
Laboratory controls		25	432		

Table 9

Efficacy assessment of the trial on 330 tonnes of wheat in Berkshire, dosed at the rate of 9.7g phosphine per tonne using a 3% mixture of phosphine in carbon dioxide.

Position	Depth (m)	Mean grain temp. (°C)	Mortality (%) of immature *S. granarius*	Ct product (mg.h/l)	Phosphine residue (ppb)
A, rear corner	Surface		100	36	
	1.0	8.1	97.9	33	2
	2.0		97.9	62	
	2.8(bottom)			33	3
B, centre	Surface		100	47	
	1.0		100	41	3
	2.0	6.9	100	76	
	3.0(bottom)			357	7
C, front corner	Surface		100	74	5
	1.0	8.1	100	109	4
	2.0		100	120	4
	3.0(bottom)			128	4
D, back centre	Surface		100		
	1.0		100	47	
	2.0	6.2	100	73	
E, front centre	Surface		100		
	1.0	8.4	99.3	90	
	2.0		100	120	
F, front corner	Surface		100		
	1.0		100		
	2.0	6.0	100	70	
G, peak	Surface		100	36	2
	1.0	8.5	88.8	38	
	2.0		100		
In duct 2, near D				1040	
3, near E				650	
Site controls in other grain in shed		8.4	143 emerge (2 cages)		

Table 10

Efficacy assessment of the trial in Warwickshire on 500 tonnes of wheat at 6-10°C, dosed at the rate of 5g phosphine per tonne using a 3% mixture of phosphine in carbon dioxide.

Position	Depth (m)	Corrected % mortality of immature *S. granarius*	Ct product (mg.h/l)	Phosphine residue (ppb)
A, far corner	Surface	100	150	12.0
	1.0	100	175	3.0
	1.7 (bottom)	100	576	24.0
B, centre	Surface	100	201	6.0
	1.0	100		
	1.5		326	12.0
	2.0	100		
	3.0 (bottom)	100	898	24.0
C, top of slope, near side wall	Surface	96.1	146	1.0
	1.0	100	196	2.0
	2.0 (bottom)	100	203	2.0
D, back centre	Surface		155	5.0
	1.0		443	19.0
	2.5		1187	15.0
E, front centre	Surface	100	239	9.0
	1.0	100		
	2.0 (bottom)	100	537	5.0
F, front, at edge of grain slope		97.4*	445	12.0
G, centre at side	Surface	100	186	15.0
	1.0	100		
	2.0 (bottom)	100	473	17.0
H, at side, half way down grain slope	Surface		185	3.0
	1.0 (bottom)	100	226	5.0
I, half way down grain slope in centre	Surface		277	17.0
	1.0		551	5.0
Site controls held at 5-7°C:		76 emerge, 18.9% of 25°C controls		

* Insect samples were about 0.7m from gas sampling point

Table 11

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

Area and sampling position	Depth (m)	Mean grain temp. (0C)	Corrected % mortality of immature *S. granarius*	Ct product (mg.h/l)	Phosphine residue (ppb)
Area 1, <u>4 dosing points</u>					
A, at central dosing point	Surface		20	4.1*	0
	1.0		61		
	3.0		100	57	2
	5.0		100	262	7
B, 0.5m from A	Surface	7.6	21	0.3	0
	1.0		50		
	3.0	2.3	100	45	0
	5.0		100	273	2
C, 1.0m from B	Surface		14	0.4*	
	1.0	6.0	41		
	3.0		96	18	
	5.0	2.2	100	155	7
D, 2.0m from B	Surface			0.2	
	3.0			2.1	
E (1.5m from	2.0		95	3.5	2
F (centre	2.0		89	3.2	2
Area 2, <u>single dosing point</u>					
G, 0.5m from centre, near side	Surface	6.3	98	42	1
	3.0		96	27	2
	5.0		100	434	11
H, 1.0m from G	0.5		98	31	
	3.0		97	42	
I, 1.0m from H	0.5			53	
	3.0			44	
J, 0.5m from centre, opposite G	Surface		82	6.5	
	3.0		100	252	
	5.0		100	1,368	
K, 1.0m from J	Surface		2	1.3*	
	1.0	5.5	46		
	3.0		93	9.3	
	5.0	2.0	100		
L, 1.0m from K	Surface			1.7	
	3.0			0.7	
Between sheets at centre				2.3	

* Ct product at 0.5m depth

Table 12

Fall off of flow rates of 3% phosphine in carbon dioxide from a small gas reservoir following a single adjustment of a Flowstat metering valve or of a Whitey needle-type valve.

Time (h) from adjustment	Flowstat (ml/min)	Whitey needle (ml/min)	Pressure at cylinder manifold (psi)
0	105	920	92
0.5	95	900	92
1.0	90	300	92
1.5	90	275	92
2.0	87	200	92
2.5	82	150	93
3.0	78	100	93
3.5	76	<100*	95
4.5	74	<100*	95
5.5	71	low*	95
6.0	70	nil	95
23.0	60		95
25.5	55		95
27.5	50		95
94.0	45		95

* As read from a 100 - 1000 ml/min flow meter

Table 13

Ct products and temperatures recorded during the commercial treatment of part of a 15,000 tonne bulk of wheat at Little Staughton, Cambridgeshire.

Position	Depth of grain (m)	Grain temp. (°C)	Ct product (mg.h/l)
A, 1.5m from side, centre of the infested spot	Surface	23	35
	0.5	22	33
	1.5	22	31
	2.5	20	24
	3.5 (bottom)		25
B, 1m towards the side wall from A	Surface		19
	0.5		9
	1.5		9
C, 1m from A along diagonal	0.5		21
	2.0		23
	3.7 (bottom)		17
D, 2m from C	2.0		35
	4.0 (bottom)		54
E, 3m from D	2.5		94
	5.0 (bottom)		46
F, 2m from A,	Surface	18	58
	1.5	20	51
	3.0		31
G, near edge of 2nd sheet, 20m forward of A	0.5		28
	1.5		16
	4.0 (bottom)		4

Table 14

Minimum exposure periods (days) required for control of all stages of the stored product pests listed, based on a phosphine concentration of 1.0g/m³. (EPPO Fumigation Standard 18)

Species	Common names	Temperature 10-20°C	Temperature 20-30°C*
Oryzaephilus surinamensis	Saw-toothed grain beetle	3	3
Cryptolestes pusillus	Flat grain beetle	5	4
Oryzaephilus mercator	Merchant grain beetle		
Tribolium castaneum	Rust-red flour beetle		
Lasioderma serricorne	Cigarette beetle	5	5
Acanthoscelides obtectus	Dried bean beetle	8	5
Corcyra cephalonica	Rice moth		
Cryptolestes ferrugineus	Rust-red grain beetle		
Plodia interpunctella	Indian-meal moth		
Ptinus tectus	Australian spider beetle		
Rhyzopertha dominica	Lessor grain borer		
Sitotroga cerealella	Angoumois grain moth		
Tribolium confusum	Confused flour beetle		
Ephestia cautella	Tropical warehouse moth	10	5
Ephestia elutella	Warehouse moth		
Ephestia kuehniella	Mediterranean flour moth		
Caryedon serratus	Groundnut borer	10	8
Trogoderma granarium	Khapra beetle	16	8
Sitophilus granarius	Grain/granary weevil	16	12
Sitophilus oryzae	Rice weevil		
Sitophilus zeamais	Maize weevil		

* All species listed succumb to a 4-day exposure at this dosage level at 30°C or above.

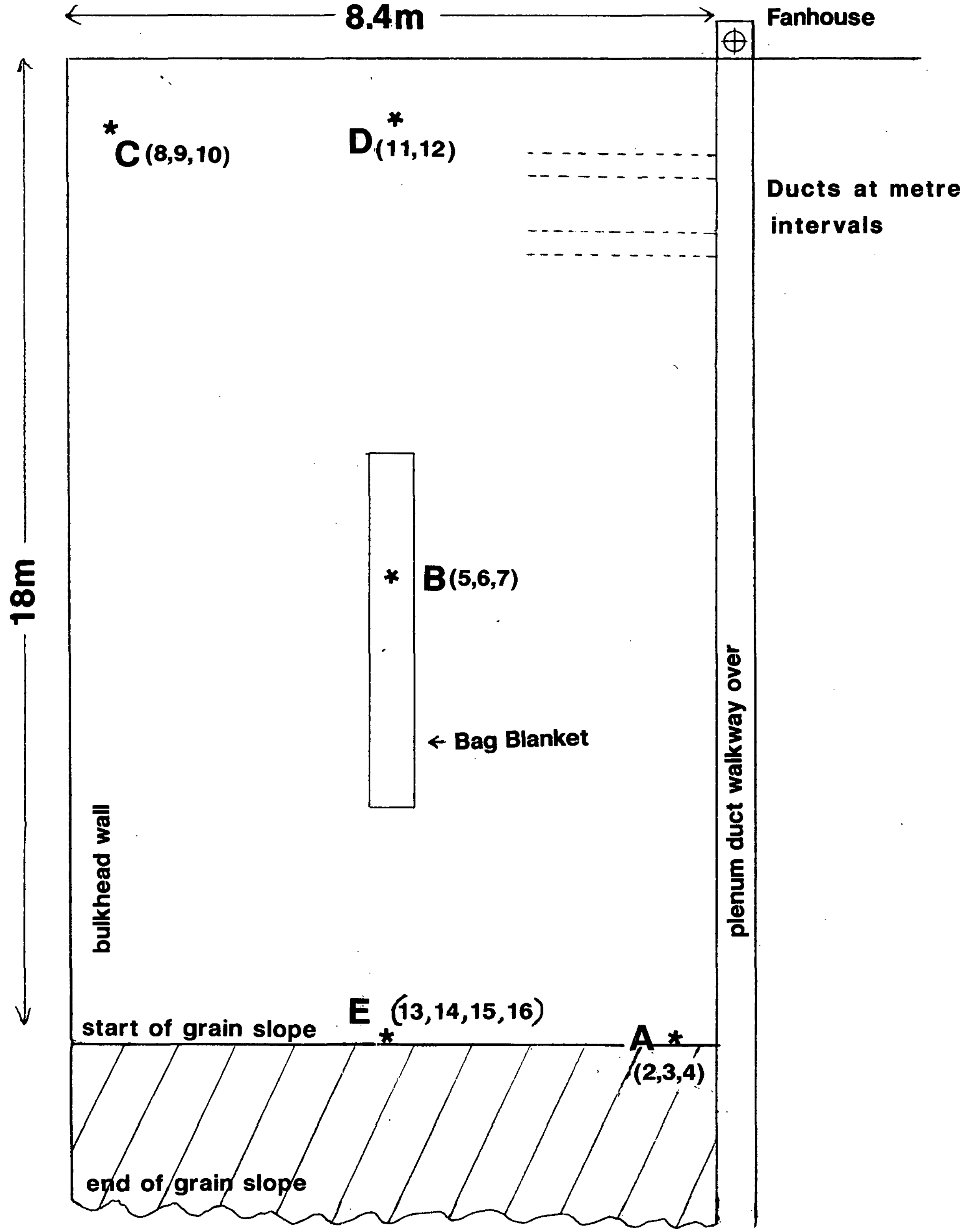


Fig. 1 Plan of the Buckinghamshire Grain Store Showing Gas Sampling Positions and Line Numbers

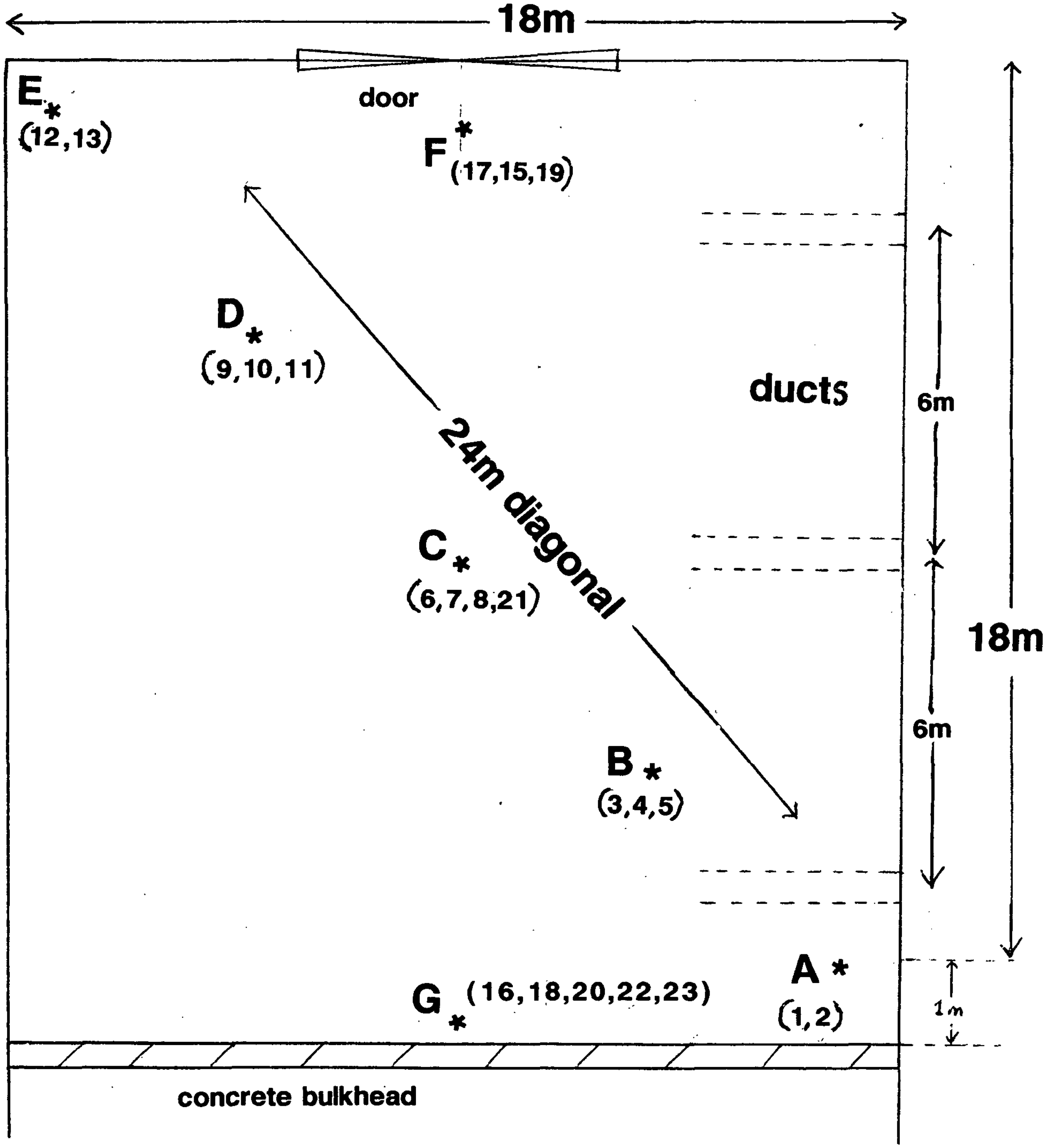


Fig. 2 Plan of the Suffolk Grain Store Showing Gas Sampling Positions and Line Numbers

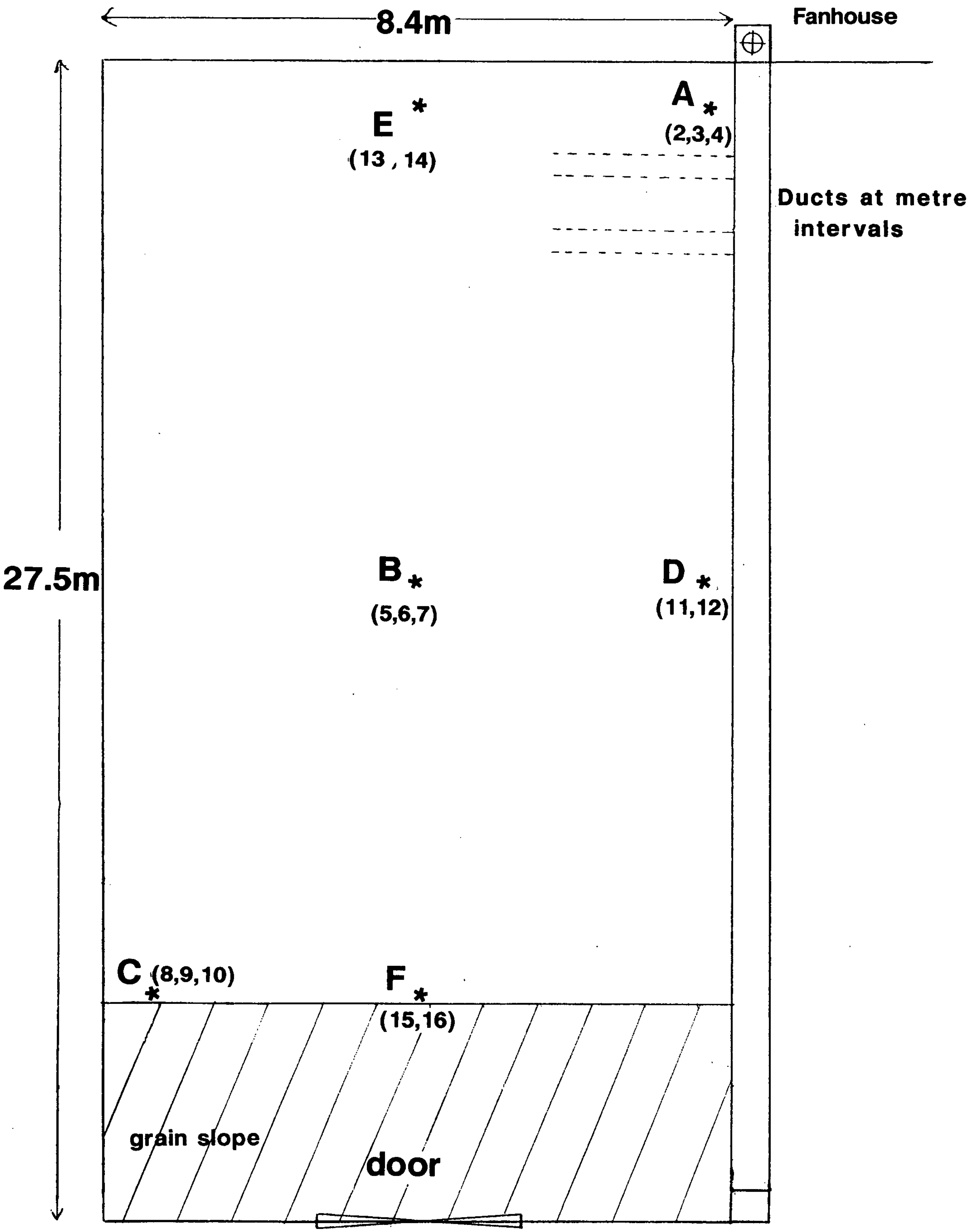


Fig. 3 Plan of the Buckinghamshire Site Showing Gas Sampling Positions and Line Numbers for the Trial after Lining the Store before Harvest

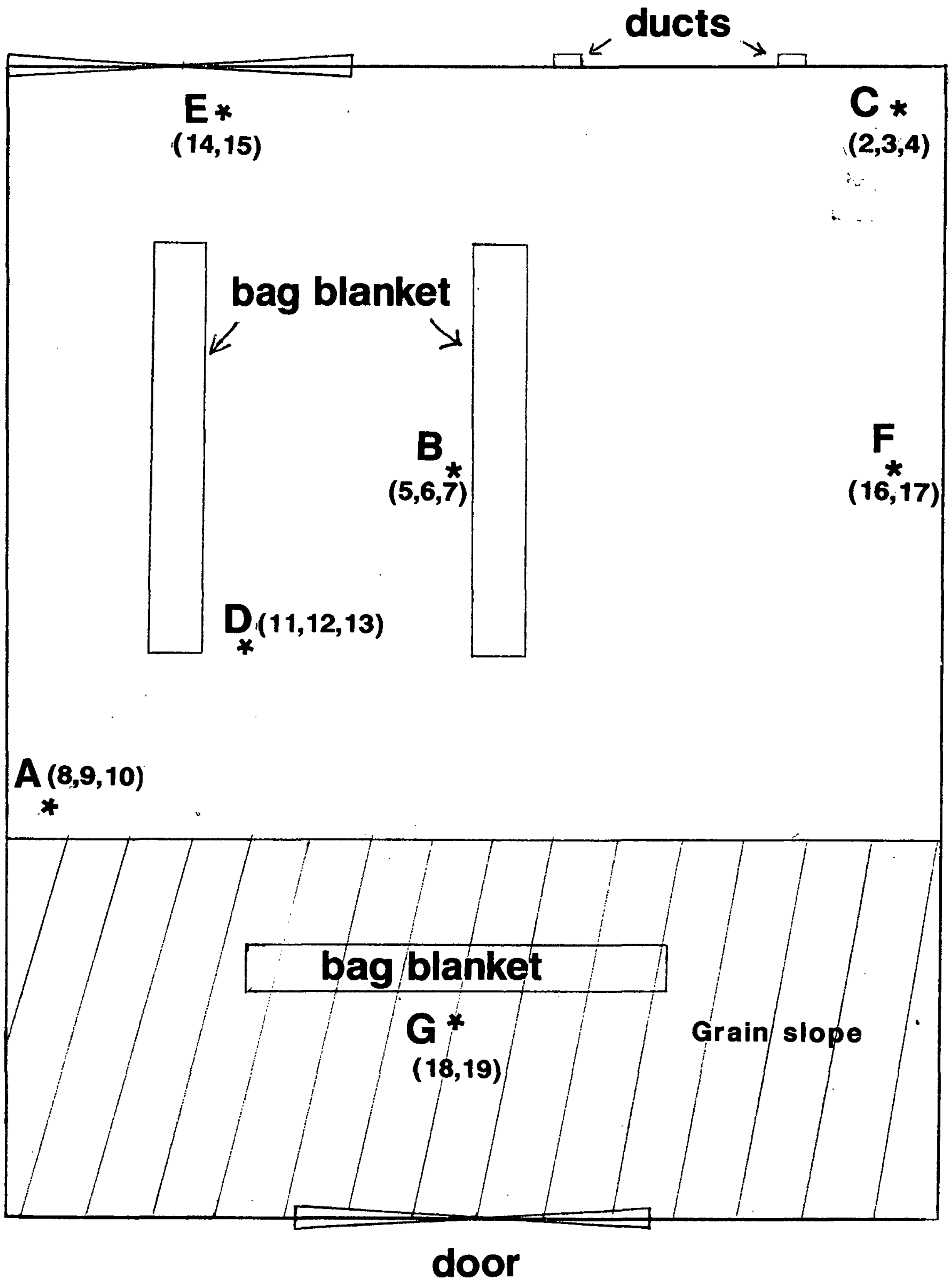


Fig. 4 Plan of the Norfolk grain Grain Store Showing Gas Sampling Positions and Line Numbers

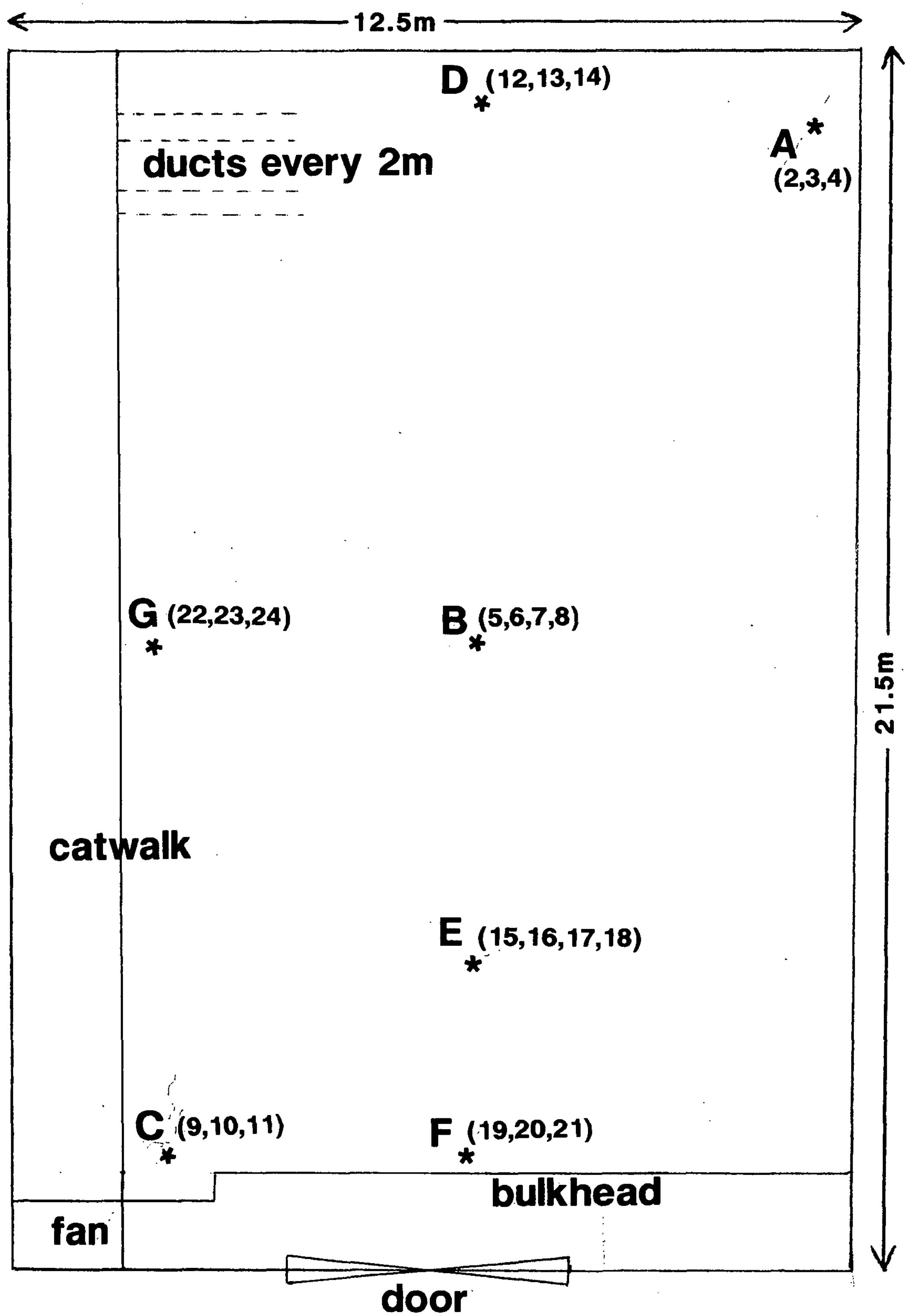
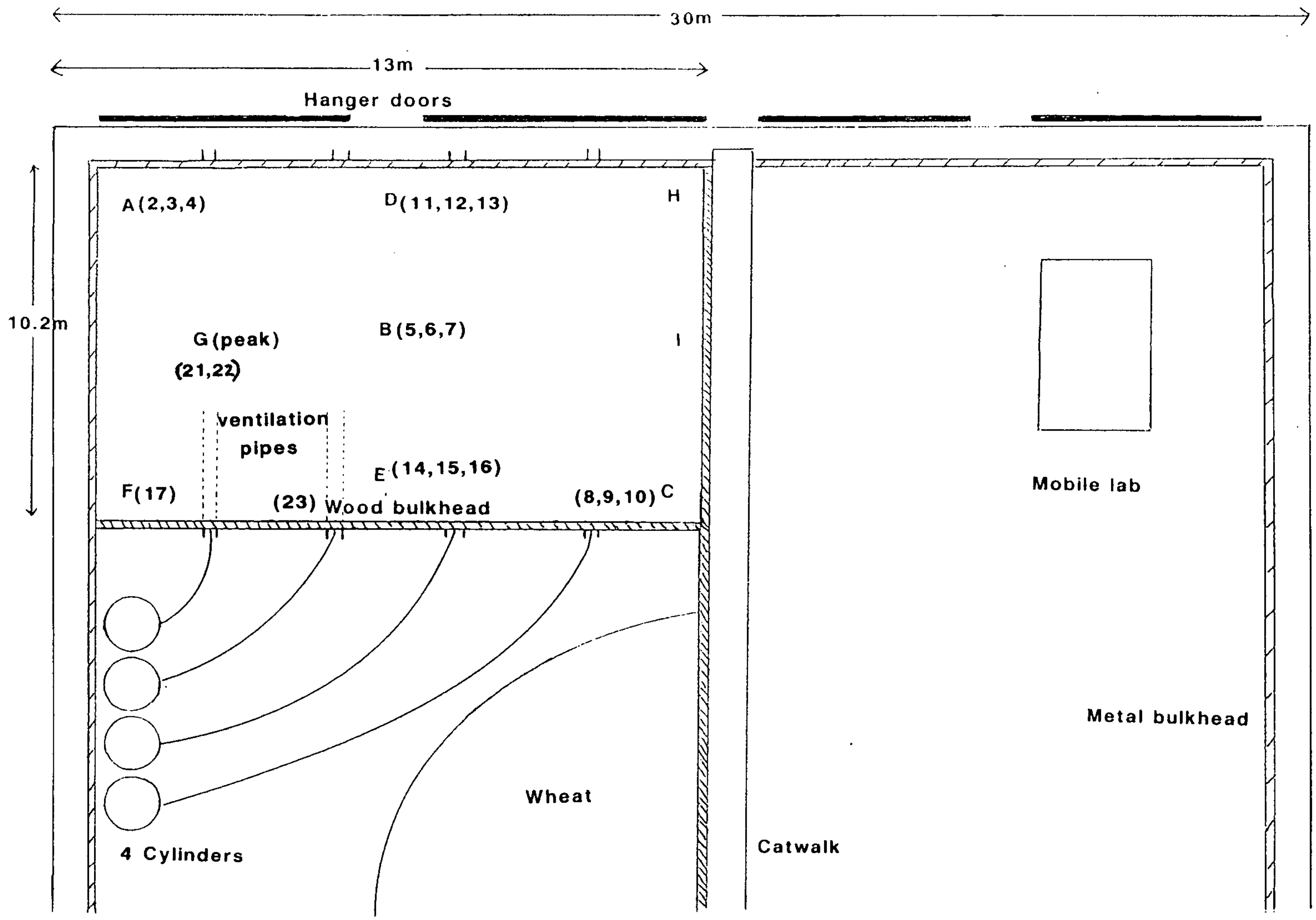


Fig. 5 Plan of the Cambridgeshire Site Showing Sampling Line Numbers at each of the Sampling Positions

Fig. 6 Plan of the Berkshire Grain Store Showing Bioassay and Gas Sampling Positions and Line Numbers



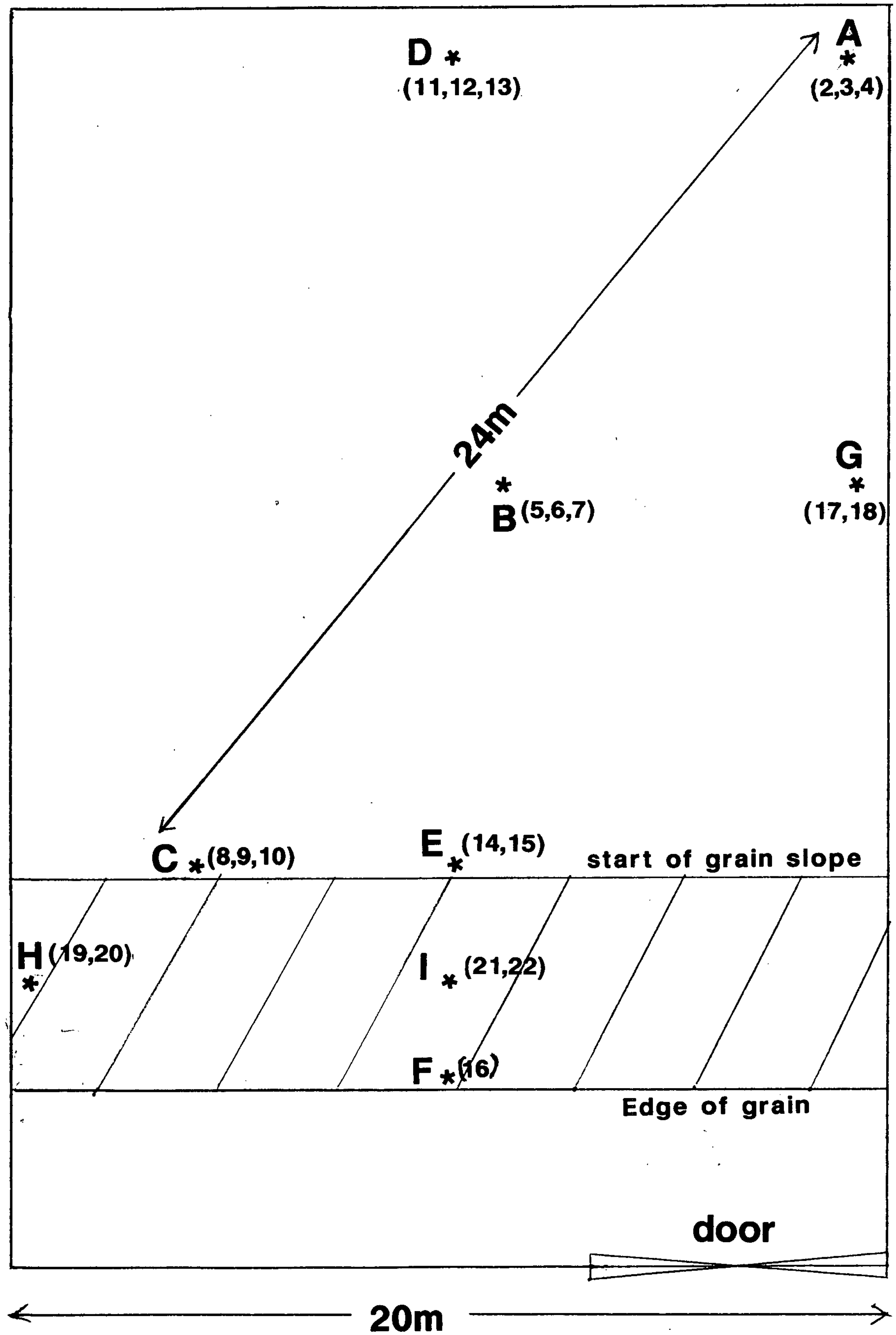


Fig. 7 Plan of the Warwickshire Site Showing Gas Sampling Positions and Line Numbers

Fig. 8 Plan of the Worcestershire Grain Store Store Used in the Spot Fumigation Trials with the PH3/CO2 Cylinder-Based Mixture

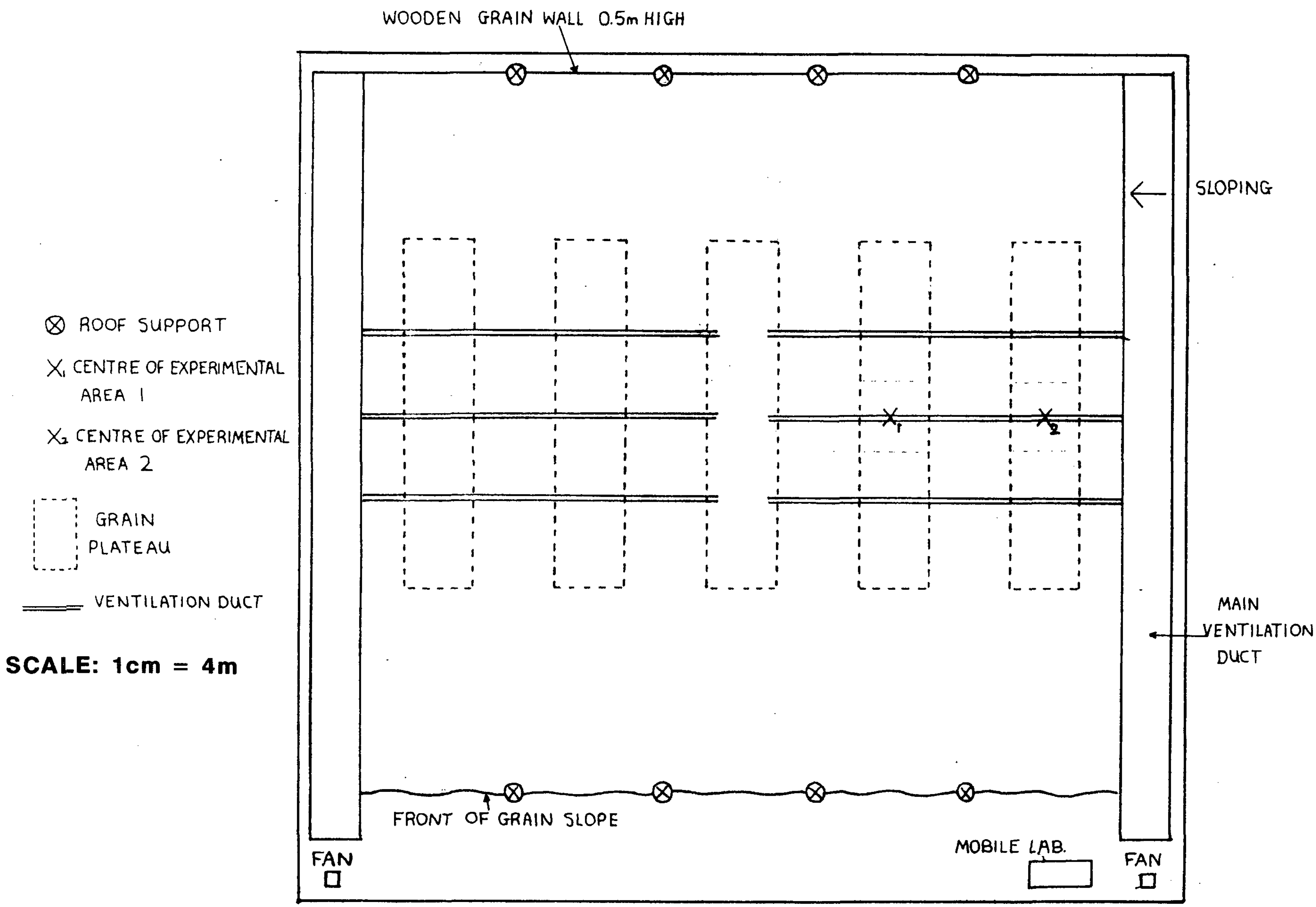


Fig. 9 Gas Sampling Positions at the Worcestershire Store for Experimental Area 1 Where PH_3/CO_2 Mixture was Applied from 4 Dosing Points from the Manifold

A - 2 - Bottom 5.25m
3 - 3m from the surface
4 - 0.5m " " "
B - 5 - 5.25m " " "
6 - 3m " " "
7 - surface
C - 8 - 5.25m " " "
9 - 3m " " "
10 - 0.5m " " "
D - 11 - 5.25m " " "
12 - 3m " " "
13 - surface
E - 14 - 2m " " "
F - 15 - 2m " " "

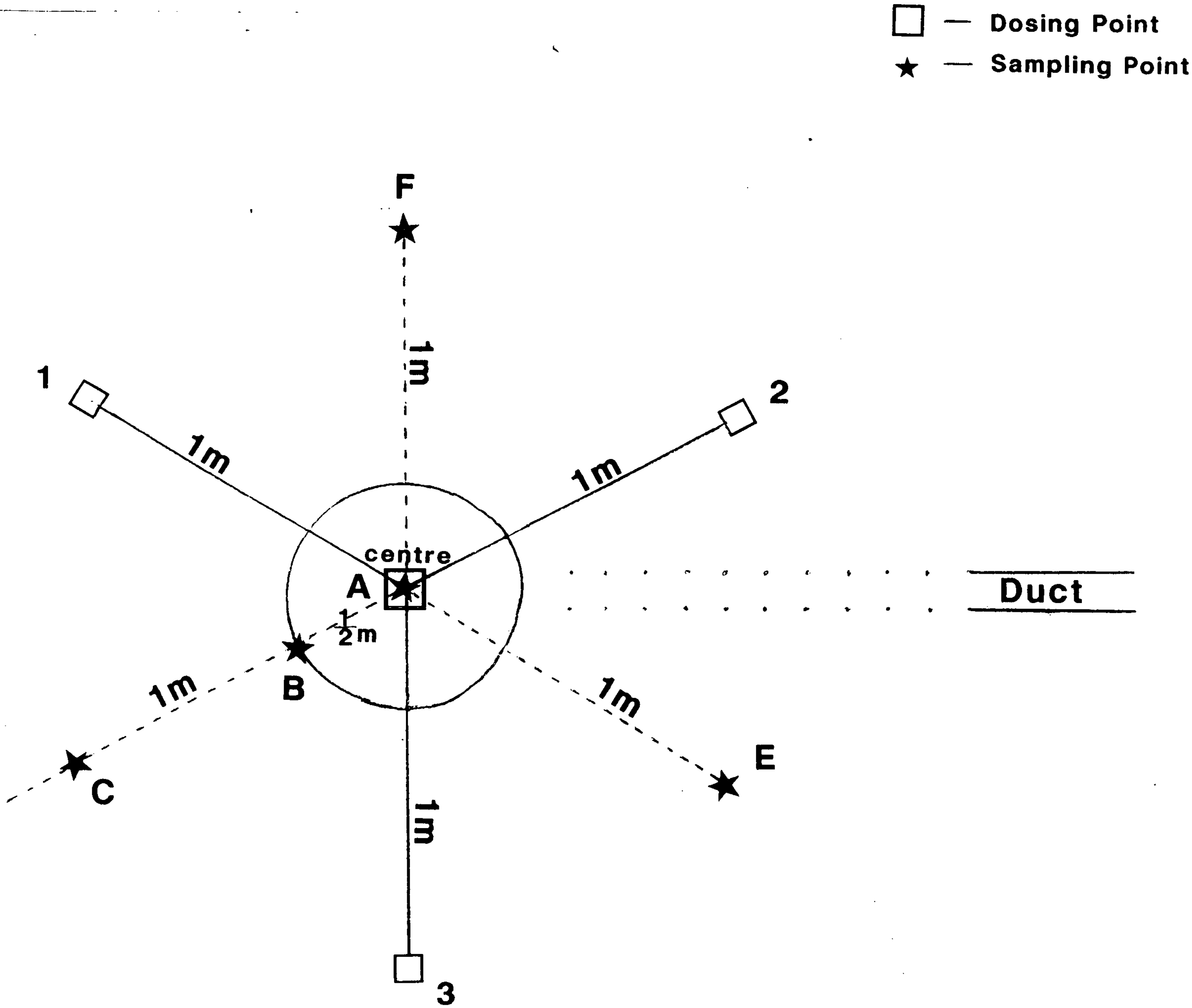


Fig. 10 Gas Sampling Positions at the Worcestershire Store for Experimental Area 2 Where PH3/CO2 Mixture was Applied to the Centre Alone

G - 16 - 5m from the surface,bottom
17 - 3m " " "
18 - surface
H - 19 - 3m " " "
20 - 0.5m " " "
I - 21 - 3m " " "
22 - 0.5m " " "
J - 23 - 5m " " "
24 - 3m " " "
25 - surface
K - 26 - 3m " " "
27 - 0.5m " " "
L - 28 - 3m " " "
29 - surface
30 - Between sheets at the centre

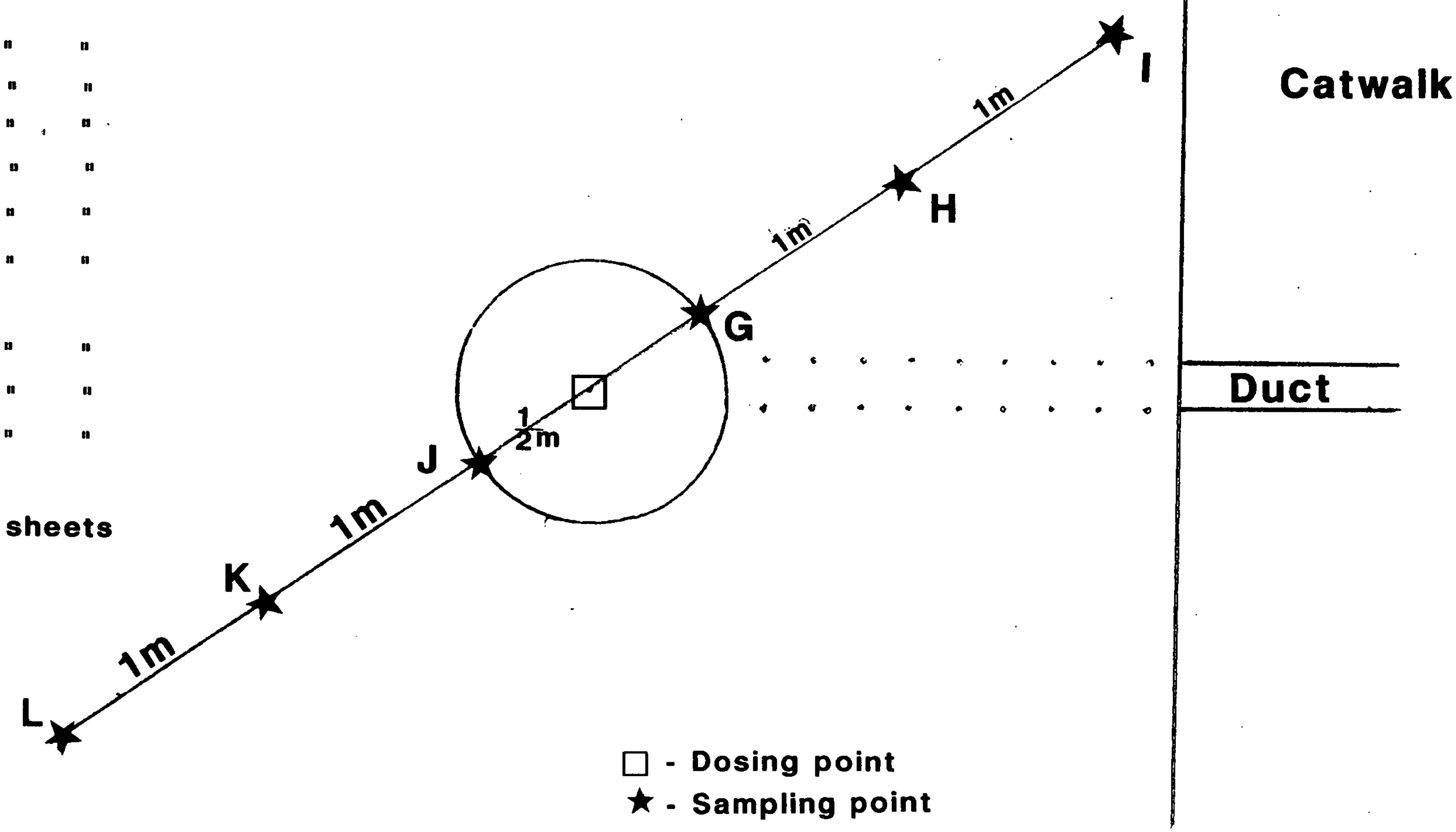


Fig. 11 Plan of the Bottesford Grain Store
Prior to Fumigation with Detia Tablets

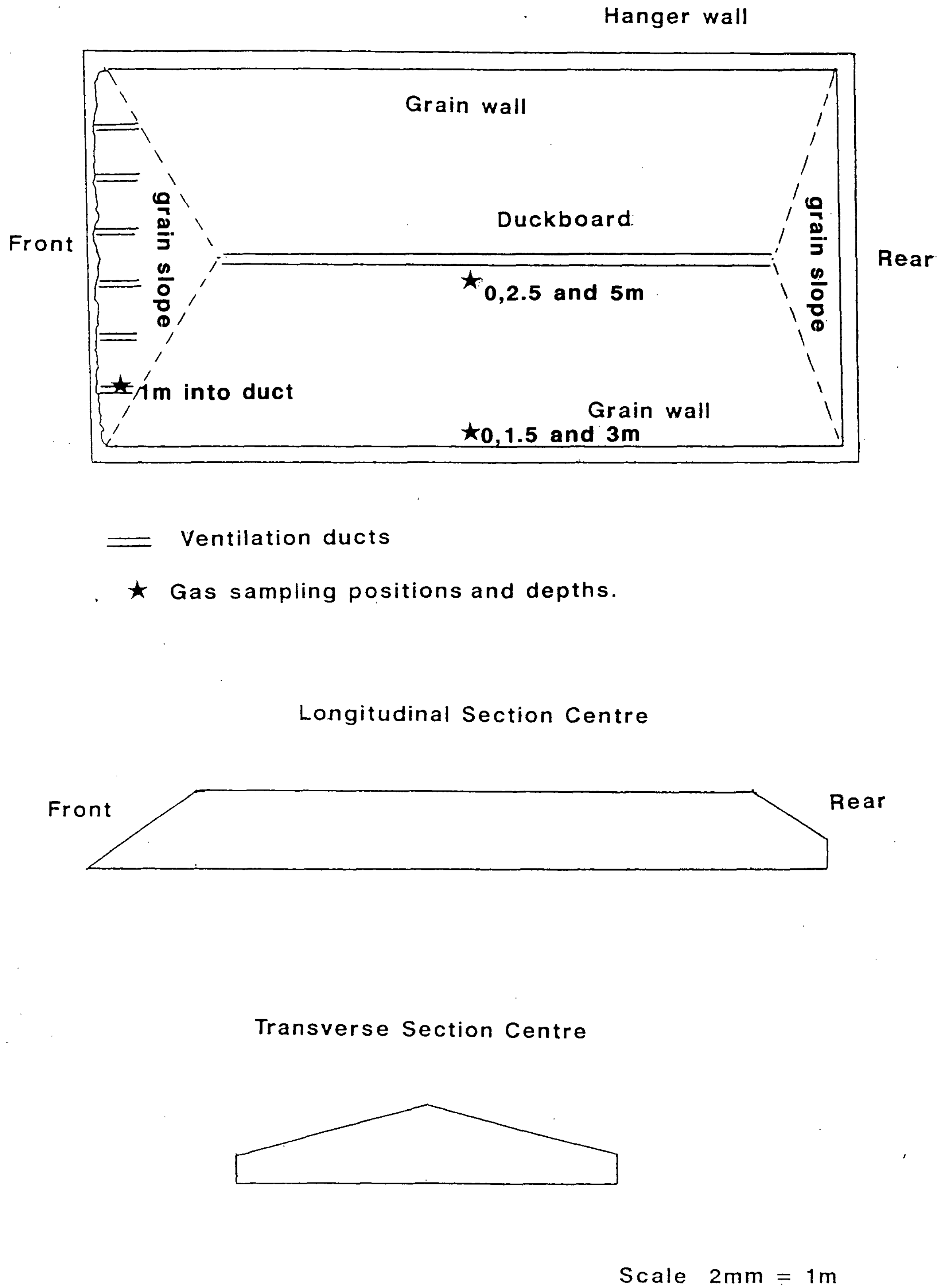


Fig. 12 The Dosing,Sheeting and Sampling Positions at the Little Staughton Grain Store Treated with Fumisleeves Each Containing 30 Tablets (30g PH3)

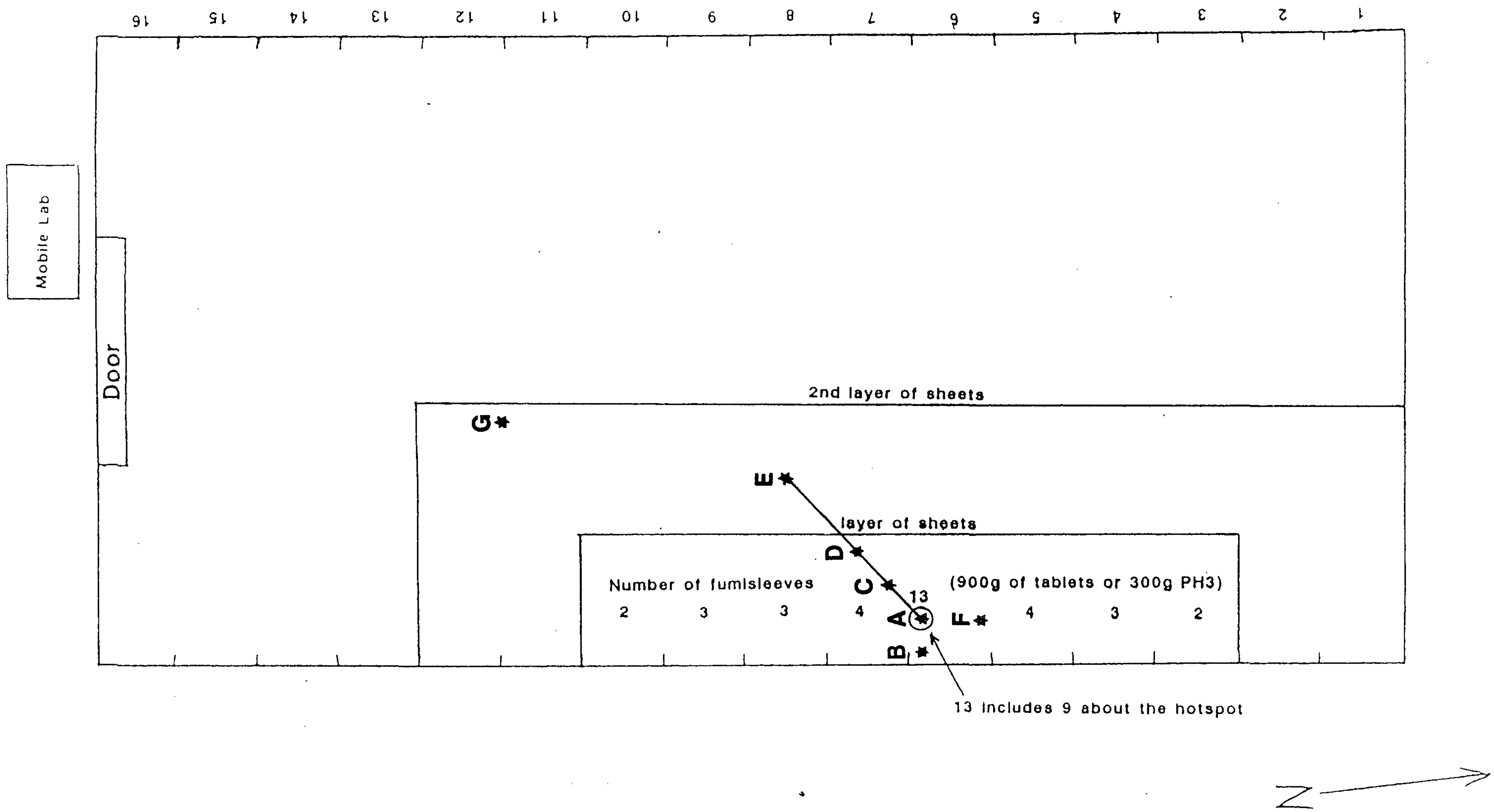


Fig. 13 Gas Concentration Profiles at the Cambridgeshire Site Using Detia Bags

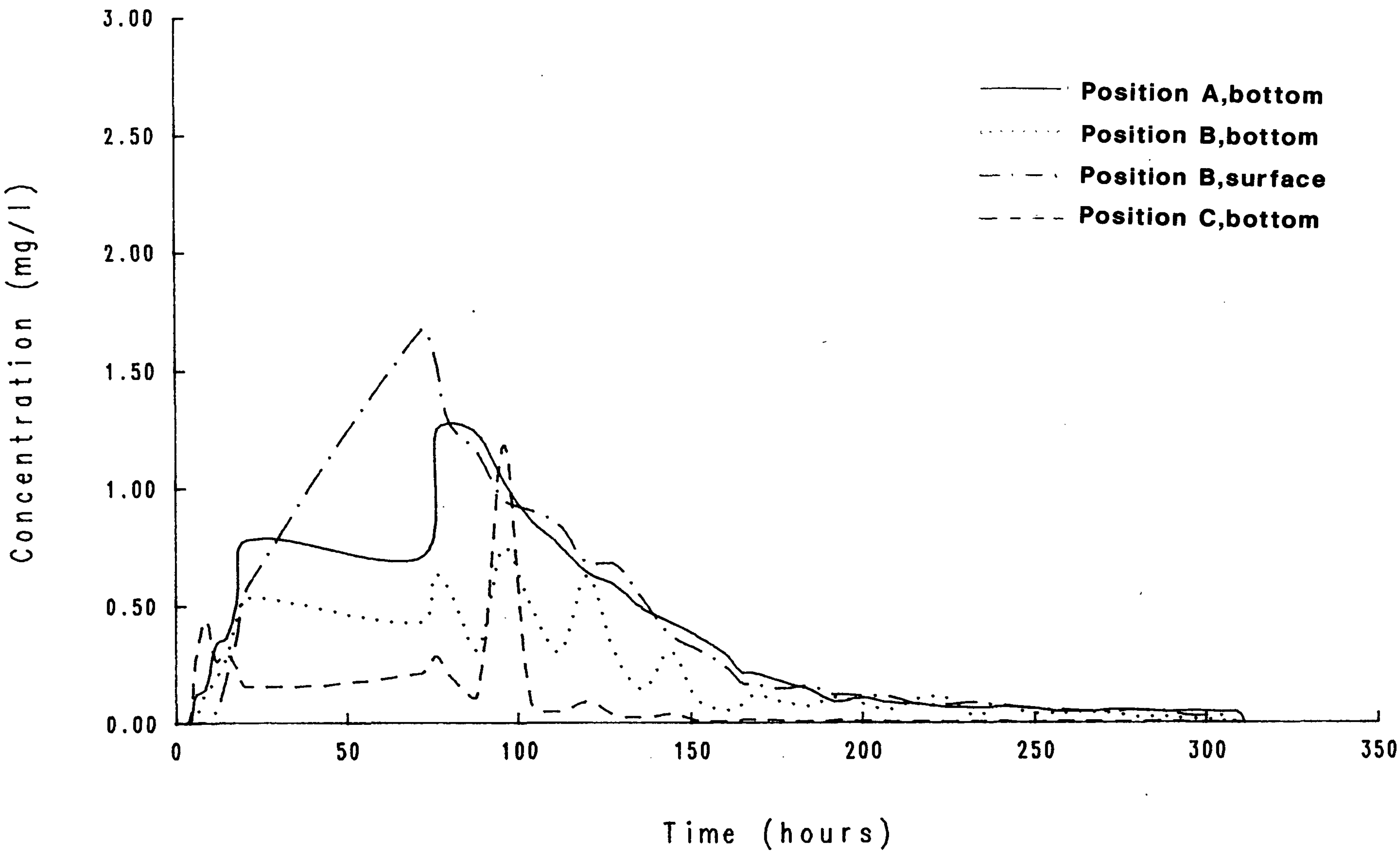


Fig. 14 Gas Concentration Profiles at the Cambridgeshire Site Using the Phosphine/Carbon Dioxide Mixture

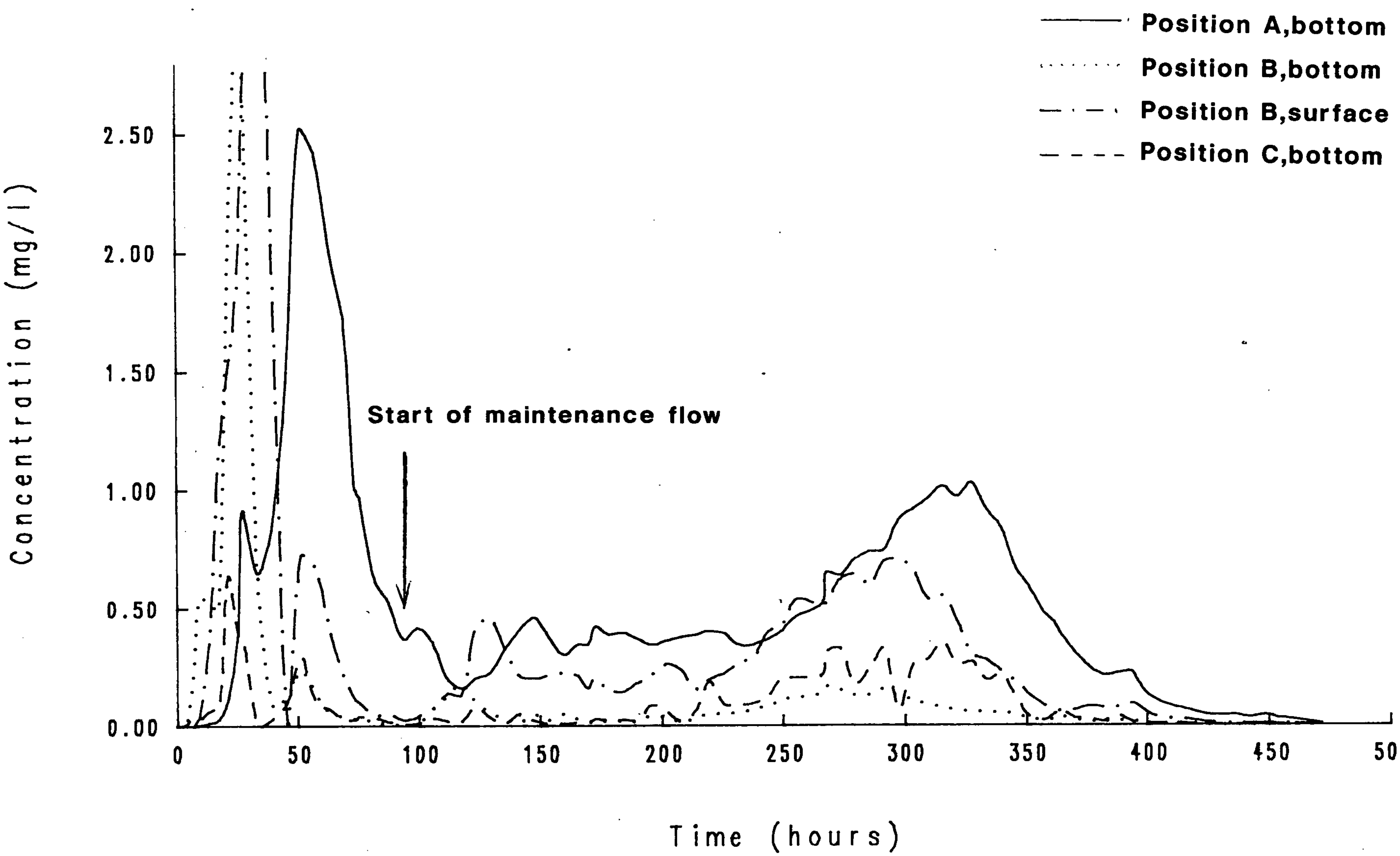


Fig. 15 Gas Concentration Profiles at the Berkshire Site Using the Phosphine/Carbon Dioxide Mixture

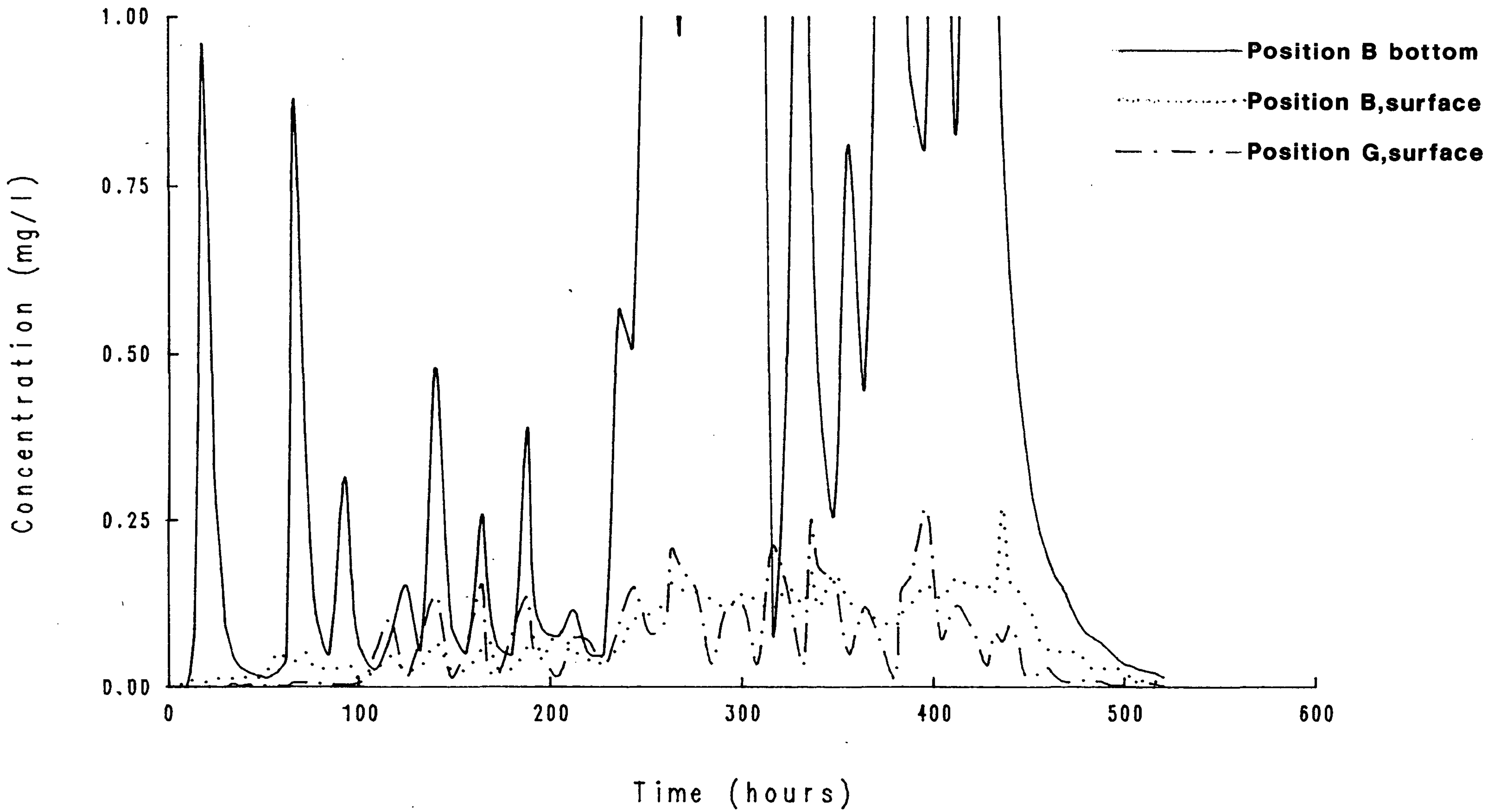


Fig. 16 Gas Concentration Profiles at the Warwickshire Site
Using the Phosphine/Carbon Dioxide Mixture

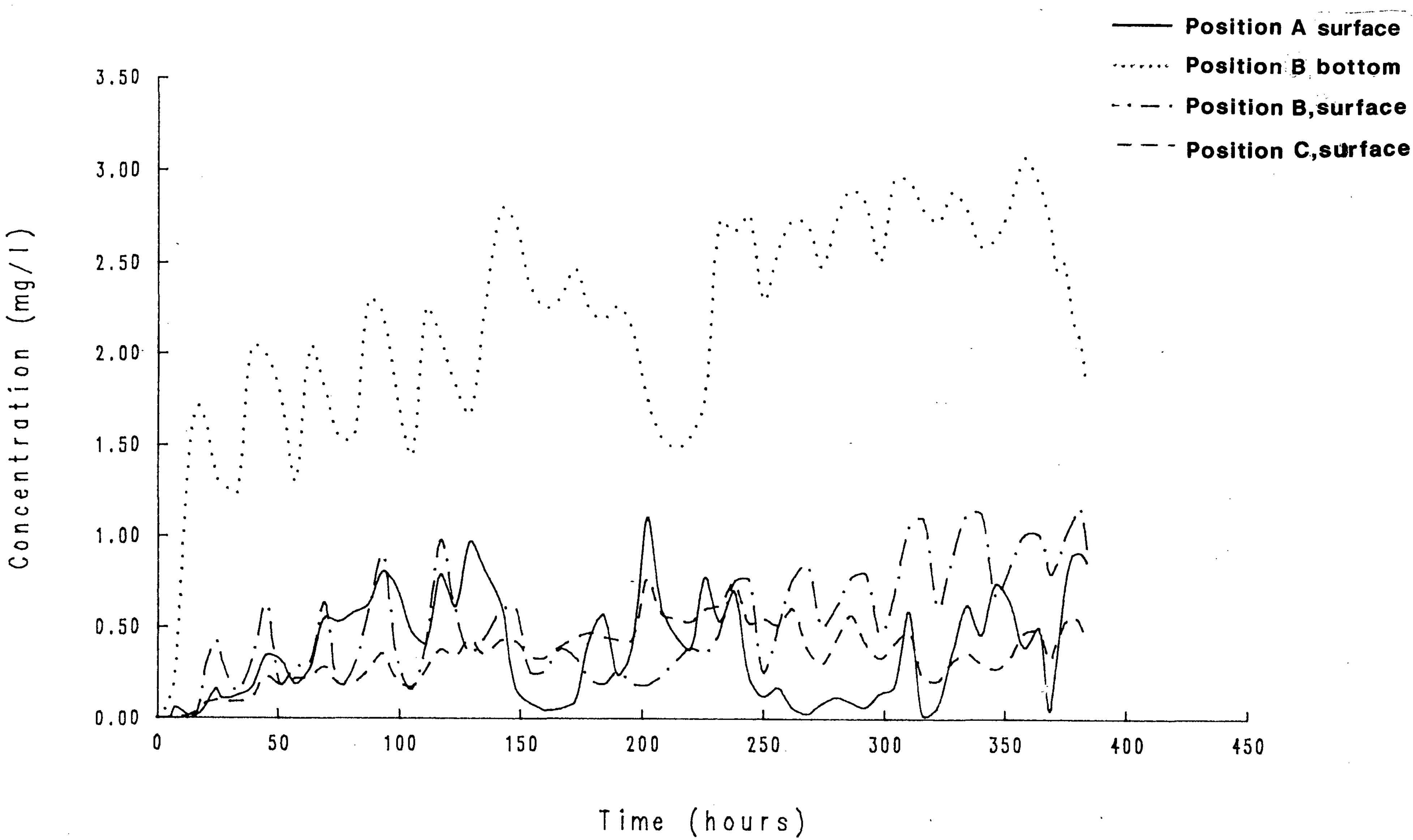


Fig. 17 Gas Concentration Profiles at the Worcestershire Site with Four Probes to Dose a Localised Region of the Bulk with the Phosphine/Carbon Dioxide Mixture

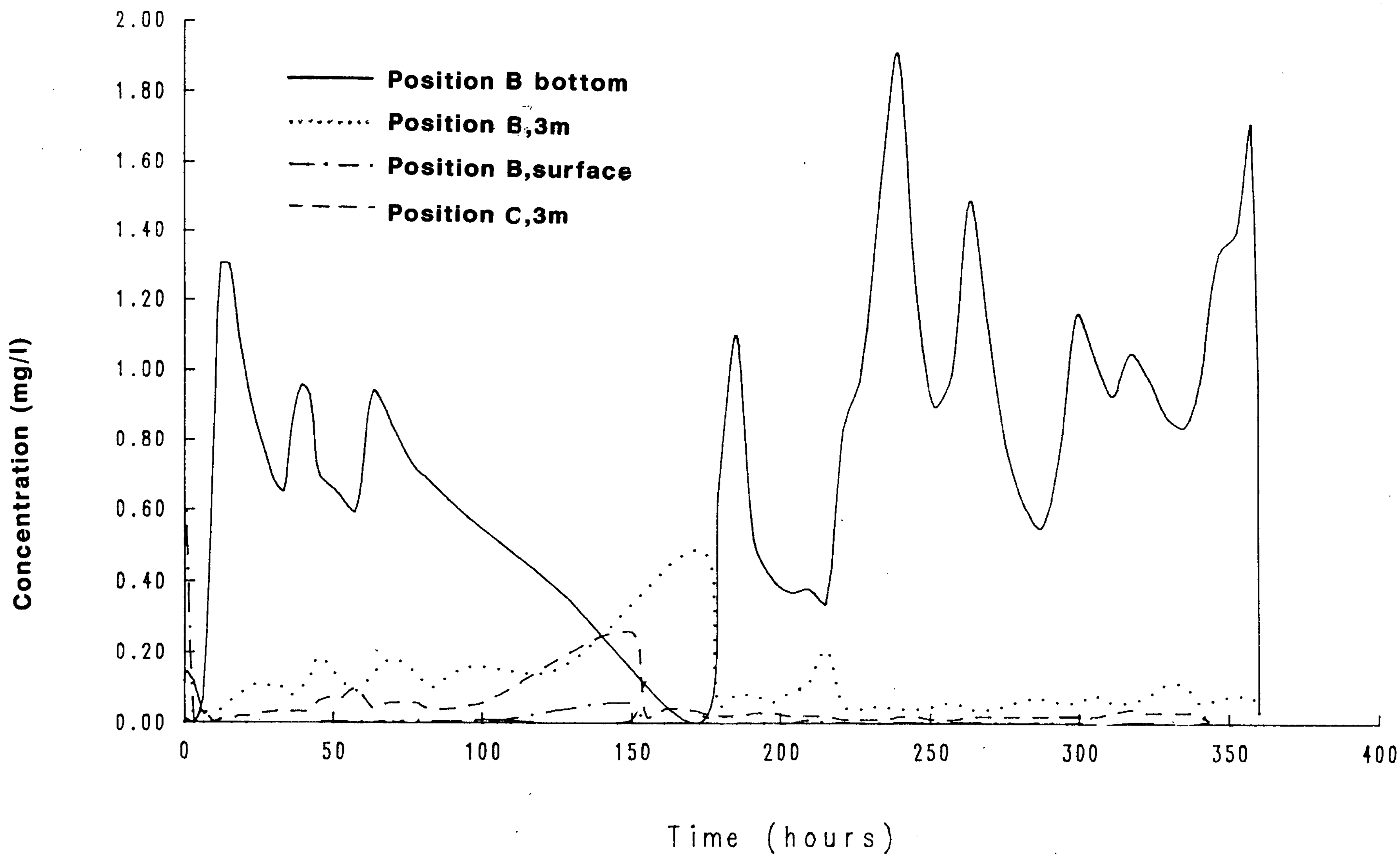


Fig. 18 Gas Concentration Profiles at the Worcestershire Site with a Single Probe to Dose a Localised Region of the Bulk with the Phosphine/Carbon Dioxide Mixture

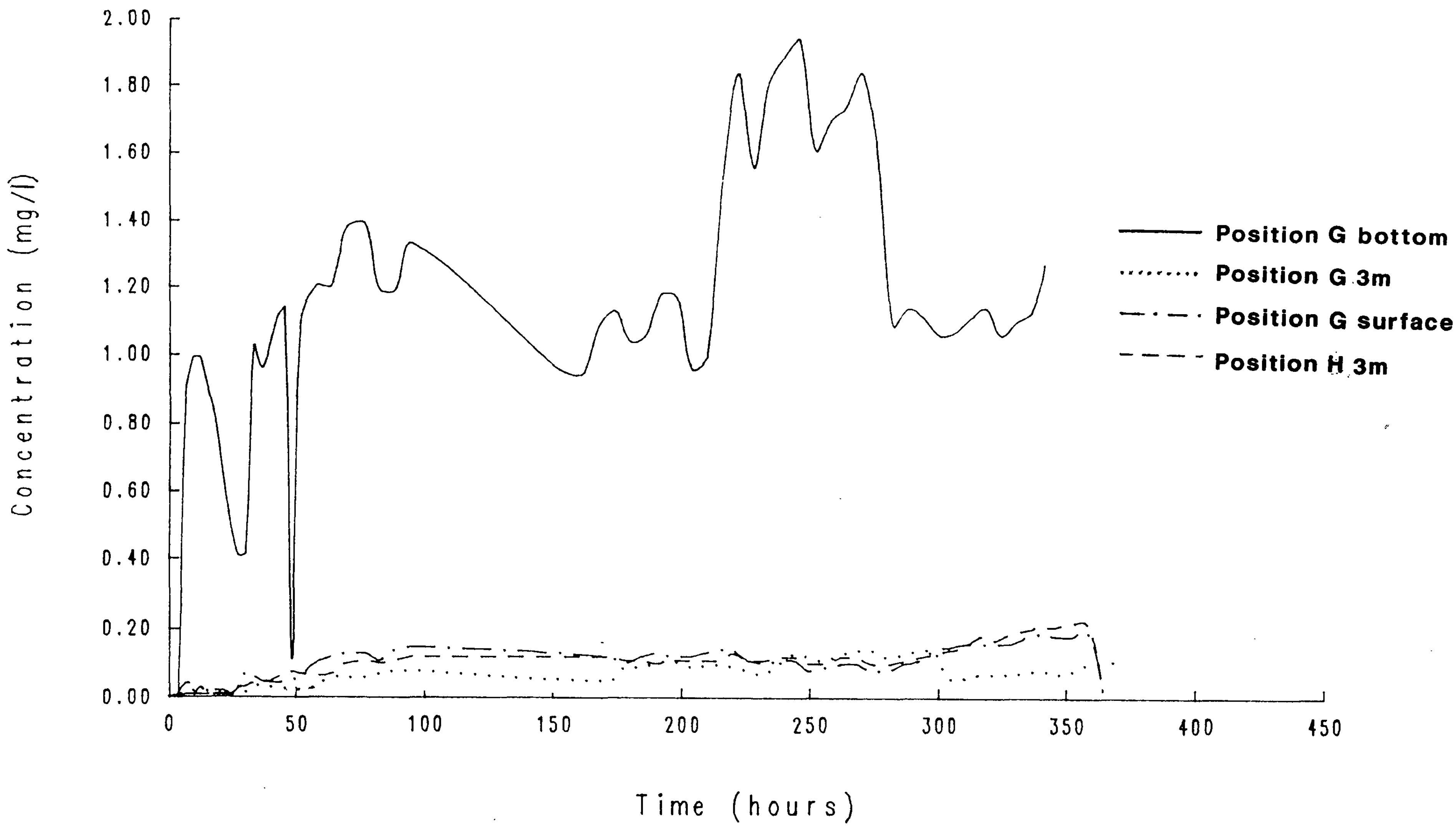


Fig. 19 Gas Concentration Profiles Obtained at Bottesford During the Commercial Fumigation of a 9500 tonne Bulk of Wheat by Surface Application of Phosphine

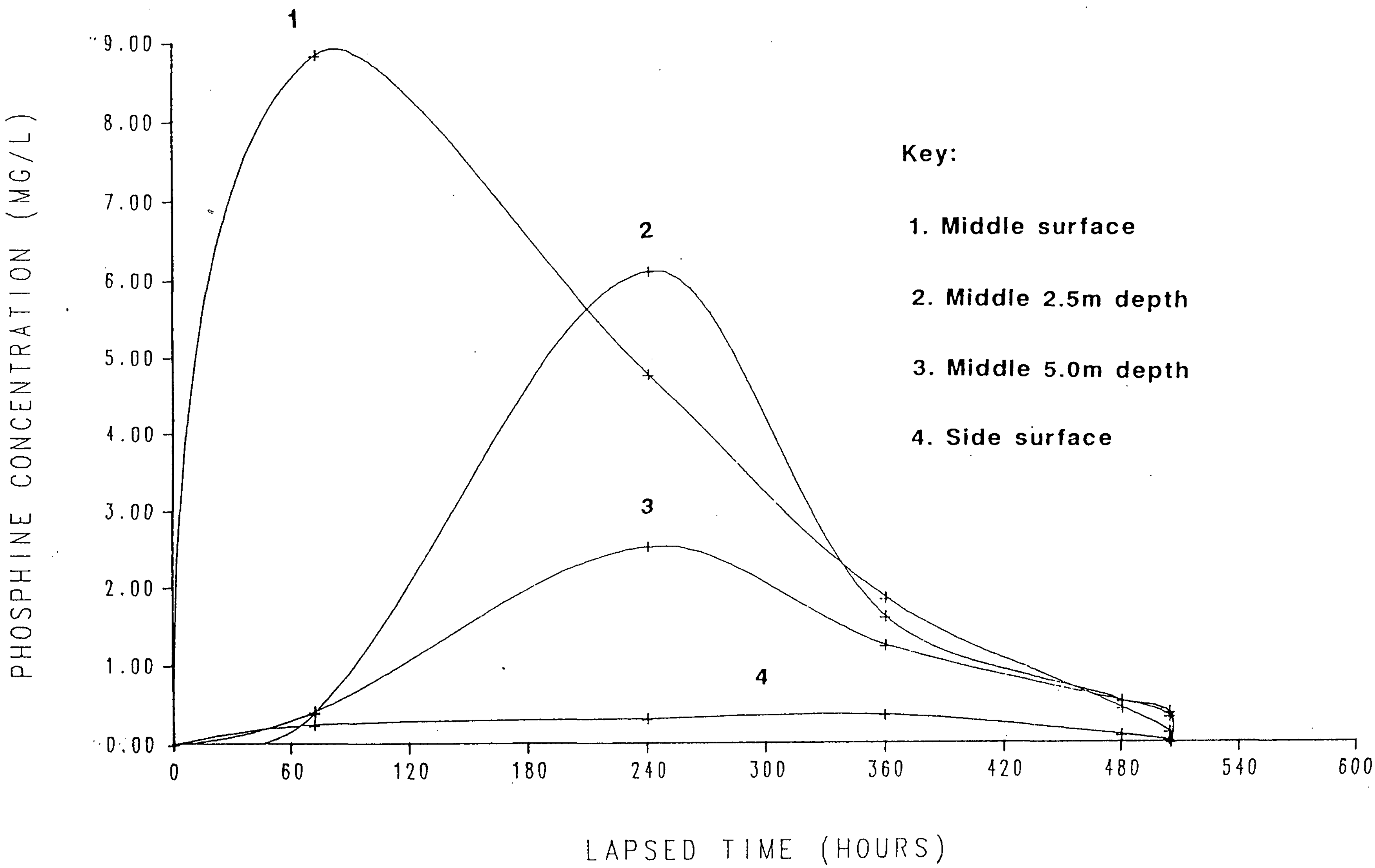


Fig. 20 Stain Length and CT Product for Three Different Concentrations of Phosphine Using Two Drager Tubes Joined Together

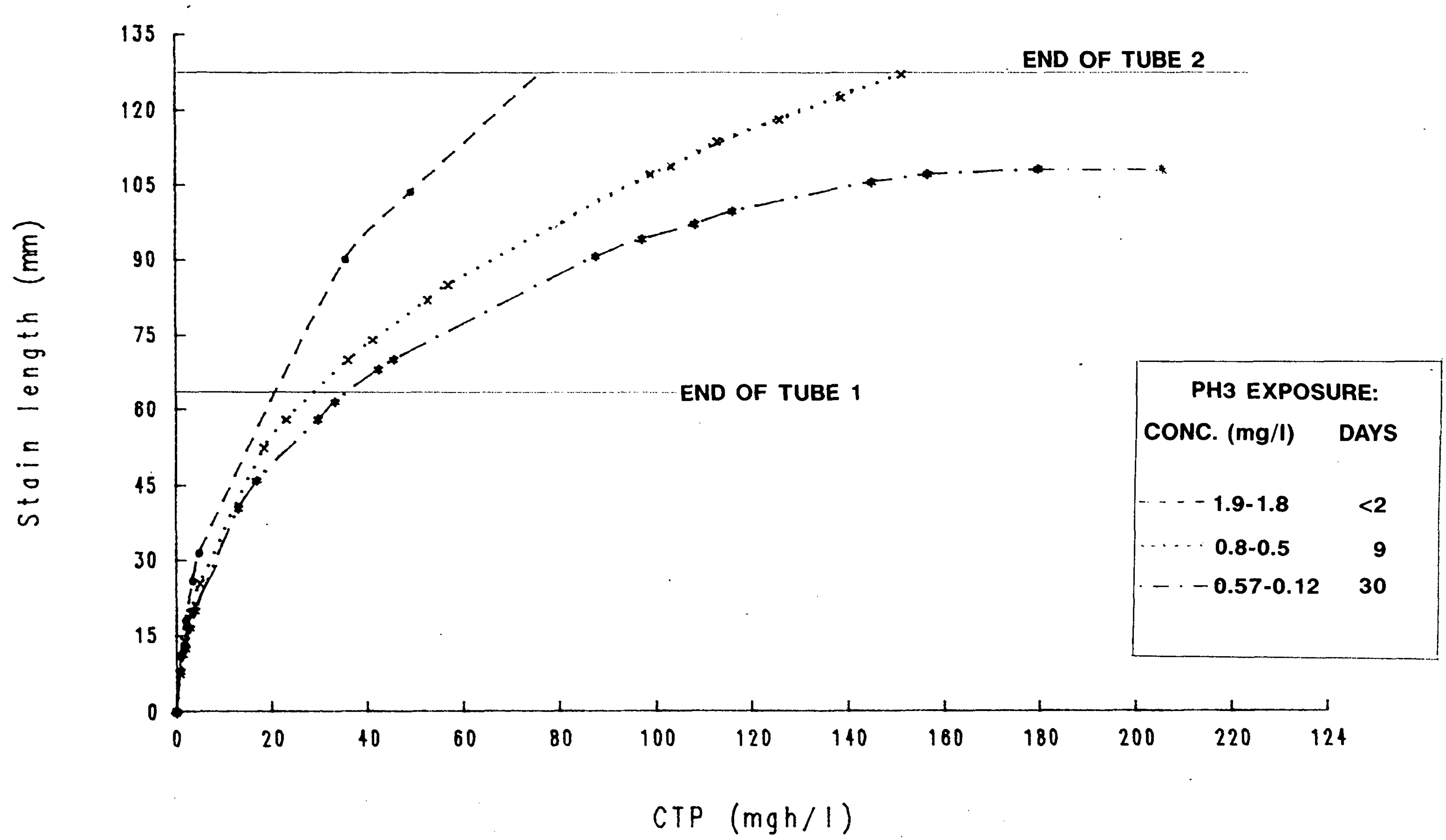


Fig. 21 Stain Length and CT Product for Four Different Concentrations of Phosphine Using Two Gastec Tubes Joined Together