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METHODS OF DISTRIBUTING PHOSPHINE IN BULK GRAIN

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METHODS OF DISTRIBUTING PHOSPHINE IN BULK GRAIN

by

B. CHAKRABARTI

National Fumigation Specialist, Pest Management Strategies Group,
Central Science Laboratory, London Road, Slough, Berks. SL3 7HJ

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CONTENTS

1. TERMS OF REFERENCE

The use of phosphine as a means of treating infestation of bulk grain is on the increase, and significant changes in traditional application methodology are being developed. This review seeks to collate the information currently available on the use of phosphine in grain storage practice. Although much has been published on the results of treatments with this fumigant, usually the operations described only relate to specific aspects of individual fumigation situations. There is an emerging need to bring together information on the more recent advances and on older methods. This at present exists in disparate and scattered accounts in trade and scientific publications and in unpublished reports.

Literature searches using computerised databases have been carried out to cover the period from 1970 to 1992 to supplement the research database and information available to the fumigation research team at the Central Science Laboratory (CSL), Slough.

2. INTRODUCTION

Since grain is the most important, and in terms of volume the most valuable, food resource in the UK, every effort must be made to preserve its full quality throughout the period necessary for storage prior to use. To ensure a regular supply for consumption, stocks are maintained world-wide between harvests and sometimes for even longer periods. Ideally, grain with very low moisture content placed in an infestation free, clean store should stay in good condition for a very long time. However, this is difficult to achieve in practice and the risk of introducing and spreading infestation from the usual movement of grain in the trade is a real threat. A light infestation may escape detection initially, but under favourable conditions pest species are capable of very rapid multiplication and can cause serious damage before being detected. Control can sometimes be achieved by the prophylactic use of contact insecticides though currently, because of fears over the presence of chemical residues in foods, other alternatives are being explored.

Fumigants are pesticides which act in the vapour phase in contrast to contact insecticides. Commodities can be treated *in situ* with fumigant which penetrates into the materials to be disinfested and diffuses away afterwards without leaving any appreciable residues. A successful fumigation, though dependent on various factors i.e. temperature, sorption, weather conditions etc. should destroy all the target pests including pre-adult stages.

No residual protection is imparted to the fumigated goods and it is always possible that reinfestation can occur immediately from outside sources if adequate precautions are not taken.

For bulk commodities such as grain, oilseeds etc. phosphine (hydrogen phosphide) is now the most commonly used fumigant world-wide. It was first introduced in the UK as a grain fumigant in 1954 after some initial development in Germany in the 1930s. Withdrawal of liquid fumigants in the 1980's from fumigation practice leaves phosphine as the fumigant of choice for most bulk commodity treatments. The use of certain formulations for the generation of phosphine so that no residues are left after treatment, and the introduction of cylinder-based supplies of gas, which avoid the use of solid formulations altogether, make this fumigant an even more attractive option for disinfestation. Moreover laboratory toxicity work has shown (Reynolds *et al.*, 1967; Howe, 1973; Bell, 1976; 1979; Winks, 1984; Winks and Waterford, 1986; Price and Mills, 1988; Bell, 1992) that quite low concentrations of phosphine are effective against insects provided the exposure period is sufficiently prolonged.

3. CHEMICAL DETAILS

3.1 Active ingredients and chemical reactions:

The chemical formula for phosphine or hydrogen phosphide is PH_3 and for fumigation purposes the gas is usually generated from either aluminium phosphide, AlP or magnesium phosphide, Mg_3P_2 (introduced in the USA in 1979) as follows:

$$AlP + 3H_2O \rightarrow Al(OH)_3 + PH_3$$
$$Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2PH_3$$

Phosphine preparations when exposed to moist air break down releasing phosphine gas. Aluminium phosphide formulations generate phosphine over a period of several days depending on the temperature and relative humidity. Magnesium phosphide formulations break down more quickly but can still require over 48 hours at low temperatures.

Phosphine is a colourless gas with a carbide or garlic-like smell. It is about 1.2 times heavier than air and is spontaneously flammable at or above 1.79% by volume in air (25.32 g/m^3).

3.2 Formulations:

Phosphine-producing formulations are made and marketed in various countries. Most of these formulations are mixtures of metal phosphides with materials such as ammonium carbamate, urea and paraffin to regulate the speed of decomposition for the release of phosphine and thus to suppress flammability. Apart from the solid formulations, phosphine is also mixed with liquid carbon dioxide and put in pressure vessels for marketing.

Formulations and the countries where these are manufactured are listed below:

Product	Weight	PH_3 released	Produced in countries						
	(g)	(g)	Brazil	China	Germany	India	USA	Australia	UK
Pellet	0.6	0.2	✓	✓	✓	✓	✓		
Tablet (flat)	3.0	1.0	✓	✓	✓	✓	✓		
Tablet (round)	3.0	1.0					✓		
Sachet (Bag)	34.0	11.0			✓	✓			
Bag-blanket	3400.0	1100.0			✓				
Bag-chain	340.0	113.0			✓				
Bag-belt	136.0	45.0			✓				
Plate	117.0	33.0			✓				
Strip	2340.0	660.0			✓				
PH_3/CO_2	30,000.0	780.0						✓	*

✓ commercially available

* Limited quantities available for experimental purposes.

3.3 Status of formulations in the UK:

"Phostoxin" tablets, pellets and "Detia Gas-Ex B" sachets from Detia Degesch, Germany and "Phostek" tablets and pellets from Anglo Oil, Brazil are cleared for use in the UK by the Pesticides Safety Directorate. More recently, approval for "Fumitoxin" tablets produced in China has also been granted. The British Oxygen Company (BOC) has taken a patent for the phosphine/carbon dioxide (PH_3/CO_2) mixture but it is not yet cleared for general use.

4. STORAGE STRUCTURES FOR BULK GRAIN IN THE UK

Storage structures are of various types; barns, sheds, bins or silos of many sizes, shapes and types of construction.

4.1 On-farm storages:

A considerable amount of cereal grain grown in the UK is stored on farms, in bins from 100 - 300 tonnes capacity and in floor stores of 200 - 800 tonnes capacity. Generally, farm storage facilities are not constructed with gas retention in mind. Free-standing farm bins are often constructed with rubberised sealant at the joints and a deliberate gap at the eaves for ventilation. Conical roofs may serve only to keep water out. Rubberised seals at the joints crack after a few years and unless regularly treated, cause problems for grain storage by harbouring residual infestations.

Sometimes several bins are served by a single ventilation fan connected by a complicated branching duct system. Lever-operated flaps are used for the isolation of individual bins and these do not make a gas-tight seal.

4.2 Commercial storages:

Deep silo bins of 250 to upwards of 2000 tonnes and floor stores from 500 - 60,000 tonnes capacity are used by merchants and for the storage of grain by the Intervention Board. Purpose-built floor stores are a comparatively recent development, but even these are not constructed for gas retention. Often a building constructed for a quite different purpose is used for grain storage. Aircraft hangers or old munitions factories are examples of such buildings used for bulk grain storage and have many disadvantages. Internal stanchions at regular intervals throughout the building create problems in covering the grain surface for fumigation, and on-floor aeration ducting is easily damaged during grain loading or unloading operations.

4.3 Leakage and sealing:

Leakage is primarily dependent on the surface area of the enclosure. The larger the structure becomes, the smaller is the surface area to volume ratio. If linear dimensions are doubled, there is an eight fold increase in volume but the surface area will only increase fourfold (Bell *et al.*, 1992). Thus per unit volume, the proportion of gas that is likely to be lost by leakage from the structure is halved.

The effect of environmental factors such as wind and temperature which influence the retention of gas in a storage structure can be minimised by sealing and painting (Banks, 1985). Methods were developed for sealing various storages of 15,000 - 300,000 tonnes capacity and successful fumigation could be achieved in structures thus modified (Williams, 1985). The sealed structures could be pressure tested to assess the gas retaining capabilities (Banks and Annis, 1980; Viljoen, 1988). Even mud structures for grain storage can be made suitable for fumigation using polythene liners (Chaudhry and Anwar, 1988). In Germany, the walls on all four sides of flat stores are lined with polythene sheets before being filled with grain (Mills, K. A. personal communication). Studies have been carried out on the use of natural gas movements for the distribution of phosphine in sealed storages and on localised concentration movements of phosphine through a bulk under reasonably gas-tight conditions (Banks and Desmarchelier, 1979).

5. TRANSPORTATION OF BULK GRAIN

For trading, grain in general is removed from the storage either by auger, sucker-blower, front loader, bucket elevator or poured by gravity on a conveyer belt. Nationally and internationally the movements of grain are facilitated by transferring from one form of transportation to another such as trucks, railcars, barges, coasters and ocean vessels.

6. INFESTATION

The fully formed grain can withstand rigours of drought, intense cold, hot weather and physical disturbance quite well. However, as a seed, the food it carries for the new plant is attractive to such pests and diseases as moulds, mites, insects and rodents from which it has to be protected.

The development of grain-infesting insects and mites is dependent on temperature and moisture content of the commodity. It is claimed that most insect pests develop slowly or not at all below 15°C and cannot survive in temperatures above 40°C (Howe, 1965; Evans 1986; Fields, 1992). However, there are notable differences between species.

6.1 Major insects in wheat and barley:

The importance of major pest species present in cereal grain varies depending on the temperature, storage and handling conditions. Imported pest species from tropical regions have become established in favourable conditions which prevail in flour or provender mills in temperate countries.

Oryzaephilus surinamensis, *Sitophilus granarius*, *Cryptolestes ferrugineus*, *Rhyzopertha dominica* and *Tribolium castaneum* are important pests in wheat and barley, but in differing circumstances. *R. dominica* is associated particularly with warm climates such as Pakistan, India and Australia (Champ, 1981) whereas *S. granarius* and *O. surinamensis* are largely prevalent in grains stored in the cooler areas of Europe. *C. ferrugineus* is also a widespread pest in Europe and is the principal grain pest in Canada. *T. castaneum* occurs over a wide range of climatic conditions although is less often found in cooler regions except in heated premises. Moths such as *Ephestia elutella, E. kuehniella, E. cautella* and *Plodia interpunctella* frequently occur on cereals, the former two in temperate zones and the latter two in warmer climates. All these species except *E. cautella* are adapted to survival in cold climates (Cox and Bell, 1991).

Mites because of their small size are easily overlooked. Apart from causing serious damage to the germ of the grain, they can spread fungal infections throughout the bulk, taint the grain and cause allergies to workers handling the grain (Hughes, 1976). The species *Acarus siro* and *Glycyphagus destructor* are the most common on grain in the UK (Prickett, 1988).

6.2 Economic significance of grain infestation:

The major effect of insect attack is loss of quality due to the changes resulting from heating, moisture migration, sprouting, mould attack etc. Infested grain may be downgraded or be rejected entirely and may yield less flour with excessive amounts of insect fragments.

For imports and exports, phytosanitary standards are applied amongst trading nations, and buyers may impose penalties when insects are discovered at the port of entry by charging for fumigation. While loading a ship, the cost of turn-round of a rejected truck-load of grain can be considerable.

6.3 Phosphine toxicity and resistance:

The susceptibilities of insect species to phosphine vary widely and also there is a considerable variation between developmental stages (Winks, 1986). Long exposures to low concentrations are more effective than short exposures to high concentrations. For mites, two phosphine fumigations were suggested (Bowley and Bell, 1981) at an interval of 3-4 weeks, a long enough time for tolerant stages to reach a more susceptible stage. In the presence of phosphine both susceptible (Hole *et al.*, 1976) and resistant strains (Price and Mills, 1988) continue to develop, and high natural tolerances thus can be overcome by longer exposures. Some pre-adult stages of the grain weevil, *S. granarius* and several species of moths and mites are very tolerant to phosphine, particularly at low temperatures. The dosages for different species, expressed as the period of exposure needed with a temperature range, are given in Table 1.

7. CURRENT METHODS OF CONTROL USING PHOSPHINE

The method of inserting packets of aluminium phosphide formulations as a fumigant in grain was first established in Germany around 1937. Later, in the 50s, the present-day formulations of tablets and pellets were developed.

The efficacy of a fumigation depends on the type and condition of the grain (Harein, 1959). Grain in the UK is dried to 15-16% moisture content before being stored. Out of an estimated 23 million tonnes harvested in 1984, 90% was stored for a period of time in farm grain stores (Taylor and Sly, 1986). With a store infestation rate of about ten per cent for *O. surinamensis* alone, an estimated two million tonnes of cereals were at risk and this was equivalent to the total tonnage of grain requiring phytosanitary inspection prior to export from the UK in 1984/85 (Wilkin and Hurlock, 1986).

The structures used for grain storage are diverse and the shape, size and construction of each storage facility demands a very different approach to dosing and there may then be further problems in achieving and maintaining an adequate concentration of phosphine over the period necessary for the control of insects and mites. The low molecular weight and low boiling point of phosphine promote rapid diffusion and penetration into the grain (Heseltine and Thompson, 1957; McGregor, 1961; Rout and Mohanty, 1967). These characteristics are useful for treating large bulks of grain and also grain in ships' holds (Davis and Barrett, 1986). However, these desirable properties of phosphine may also promote leakage if the storage structure is not gas-tight.

The standard of gas-tightness recommended by the Australian Agricultural Committee (Winks *et al.*, 1980) for fumigation with phosphine can be used as a guideline for fumigations world-wide. It requires structures from 300 to 10,000 tonnes capacity to be sealed in such a way that when these are full with grain and are subjected to a tiny increase in pressure, the time taken for an internal pressure drop from 500 Pa (2 inch water gauge) to 250 Pa (1 inch water gauge) should not be less than 5 minutes. Except in some welded steel bins, this standard of gas-tightness cannot be achieved in UK storage structures. So, the basic objective of fumigation which is to control all stages of the pest species present, is from the outset difficult to achieve. High dosage rates do not compensate for inadequate sealing or leakage, and may contribute to an increase in resistance levels.

7.1 Grain stored in farm bins and farm floor-stores:

The recommended method for the fumigation of grain stored on floors or in shallow bins is by inserting phosphide preparations into the grain. A calculated dose, to give 3-5g of phosphine per tonne of grain, comprised of tablets, pellets, stringed bags or sachets, is usually distributed evenly in a matrix. Formulations are inserted into the grain at different depths and covered by polythene sheeting of 70-125 micron thickness.

A specially designed probe for insertion of tablets is available which consists of a number of tubular sections which can be screwed together to obtain different lengths. A counter on the top via which tablets are delivered to the probe, registers the number of tablets added. In practice, however, simple metal tubes 1.5-3 metres in length and of 25mm diameter are used for the insertion of tablets depending on the depth of the grain bulk. The tablets are dropped down the tubes by hand, often as the tube is slowly raised to spread the dosage throughout the depth probed.

For bags, hooked probes were designed for pushing into the grain but in practice grain in floor-stores or small bins is treated by distributing strings of 10 bags and burying these about 15-20 cm into the grain, leaving a marker for recovery of the spent bags after treatment. The dosage rate remains the same as for tablets, 3-5g of phosphine per tonne of grain. Sometimes part of the dose is applied into the aeration duct or into the auger hole for the better distribution of gas. After dosing, the grain is carefully covered with clear low density polyethylene (LDPE) sheeting to allow generated gas to diffuse within the grain rather than escape from the surface. Aeration ducts and all other openings are also sealed with care. Using standard sealing methods it is difficult to maintain phosphine concentrations above the minimum level for effective action for the 16 days required at temperatures below 15°C to control all stages of *S. granarius* (the most phosphine-tolerant of the common grain pests in the UK), and also required for low temperature control of imported phosphine-resistant populations.

7.2 Grain in large bulks on floor-stores:

Purpose-built stores incorporate aeration systems for grain drying and cooling. These comprise either channels underneath metal grids flush to the floor, or lengths of on-the-floor perforated cylindrical or arched metal ducting. The latter system is more common for storage in large aircraft hangars or in similar improvised storage facilities. Air is fed under the grain either by an individual blower for each duct, or by a large fan supplying many ducts via a plenum chamber.

A problem commonly encountered in large bulks of grain is that phosphine concentrations tend to be slow to build up at deeper levels. It is very common for a small upward draught in a bulk of grain to be apparent during treatments. This may be caused either by poor sealing of the ducts, or by grain temperatures being higher than ambient in winter months. A strategy of placing one third of the calculated dose into the ducts and the rest on the surface, buried in the conventional way, has proved beneficial (Bell *et al.*, 1991).

For large bulks there are no effective methods in use for fumigating localised infestations or hot-spots. These could be treated in the past with liquid fumigant mixtures made up of various proportions of ethylene dichloride and carbon tetrachloride. A diameter twice that identified for the hot-spot was treated with the mixture, and usually successful control was obtained. The mixture was withdrawn from use in the 80's by an EC directive because of concerns over its chronic toxicity to humans. Since this time hot-spots have been treated with one of the available aluminium phosphide preparations in the expectation of achieving a similar level of control to liquid fumigants. Unfortunately, because of rapid diffusion and leakage of phosphine, this has not been the case and there has been the risk of selecting for phosphine-resistant strains because of the exposure of pests to sublethal dosages (Chakrabarti *et al.*, 1990). With this problem in mind it has been recommended that for localised infestation, in absence of any new development, the whole bulk is to be fumigated with phosphine.

7.3 Grain stored in deep silo bins:

Although it has been claimed by the manufacturers of aluminium phosphide preparations, that phosphine travels 3 metres per day up to 20 metres deep in a grain silo, in practice this hardly ever seems to be achieved. To enable a successful treatment to be carried out, infested grain must be turned from one bin to another. During conveying, either pellets, round tablets or sachets generating 0.2g, 1.0 g and 11g of phosphine respectively are added to the grain. The round tablets are an aluminium phosphide preparation similar to the previously described flat tablets. These were developed in the USA to use with automatic dispensers described below but are not labelled for use in the UK. Provided the amount of grain and rate of turning are known, the total dose necessary can be calculated. Portions of the total dose are added to the grain stream at intervals until the bin is full. Any of the formulations can be applied by dropping them through a manhole or inspection-cover at the top of the bin or preferably on the moving grain just before it enters the bin.

In the case of Phostoxin pellets and round tablets an automatic dispenser is available. This is electrically operated and delivers pellets at pre-selected fixed intervals. The intervals can be adjusted on the machine so that the rate of application can be geared to the rate of flow of the grain. The dispenser has a built-in safety cut-off, and the delivery of pellets stops if the grain flow is impaired.

'Detia' bags are added by hand through the opening on the top cover of the bin or on to the conveyer. An accurate count of bags must be kept so that these can be retrieved during the later transfer of the grain using a wire screen.

It is preferable to complete the fumigation of each bin by turning in one working shift but if this cannot be done the manufacturer recommends that a metre of grain without the addition of fumigant is run on to the top and the bin left sealed overnight. Any bin requiring more than two days to fill should not be fumigated by continuous addition into the grain stream.

To contain phosphine for the required period, up to 16 days for *S. granarius* infestation, every effort is necessary to seal the bin top, bottom and all the cracks and crevices in the sides. This practice for silo bin fumigation is, however, no longer encouraged due mainly to the high concentration that can rapidly develop in parts of the work place during application. It is also difficult to remove all the residues during turning and cleaning processes and to keep the phosphine level below the Occupational Exposure Standard (OES) during such operations.

7.4 Grain in barges or ships' holds:

A bulk for export may include grain from numerous sources where a variety of preventative measures e.g. pesticides or fumigant treatments may have taken place. The importing country usually demands a phytosanitary certificate stating that the grain is free of infestation. It is not always possible to screen the grain before loading. If infestation is identified while loading the ship or when the 'hold' is full, there is no alternative but to fumigate the whole bulk. Treatments on board ship resemble the fumigation of bulk grain on floor-stores but feature some differences, notably a better seal and deeper grain layer. Phosphine and methyl bromide are both used in ships' holds, depending on their availability and local regulations in the receiving country, and also according to the contract between the trading parties. However, phosphine is the fumigant of choice for in-transit fumigation of grain in ships' holds.

Ships and barges are of welded steel construction and when the covers are fitted with gaskets the holds make excellent fumigation chambers. However, the fumigation operation for ships' holds or barges is a very specialised technique. The British Pest Control Association have a separate module in their operators training programme to cover the needs of in-ship fumigation. The United Nations International Maritime Organisation (IMO) has issued a circular on the safe use of pesticides in ships (Anon 1984) which includes in-transit shipboard fumigation of grain. Further amendments to this section have been made in 1993 and are likely to be published shortly. In practice, a fumigator is advised to seek the services of a marine surveyor for the pre-fumigation inspection of the ship. In his report the marine surveyor should identify the areas of weaknesses which are to be sealed and made good. He also should say whether the vessel is fit for a fumigation treatment.

Most of the original development work for the in-transit ship-board fumigation of grain was carried out in the USA and this work forms the basis for much of the current methodology. The depth of grain in a ship's hold can be between 15-20 metres. Under these conditions it is difficult for phosphine to penetrate to the bottom by dosing at the surface. In a tanker hold of 17.7m depth, applying a dose of about $1 g/m^3$ by probing tablets to 4.3m resulted in sufficient gas penetrating to 9m depth but concentrations remained low at 17m depth even after 24 days (Redlinger *et al.*, 1982). However, the distribution of phosphine was improved progressively (a) when tablets were applied in layers during loading instead of surface dosing (Redlinger *et al.*, 1979), or (b) by the use of perforated plastic tubing of about 10 cm diameter, as used for drainage. Long lengths of tubing were laid at the bottom of the holds before loading and connected to vertical pipes run down the sides which opened above the surface of the grain when the hold was filled. Part of the dose of the aluminium phosphide preparation was mixed with grain and poured into the vertical tube, the rest of the dose was distributed on the grain and was pushed just under the surface. The method, known as the "J System", uses a fan to re-circulate phosphine through the grain via the pre-positioned plastic tubing. Rapid and uniform distribution of phosphine was achieved by this process (Leesch *et al.*, 1986) which is now widely used for pre-planned, in-ship in-transit fumigation with phosphine.

Even against susceptible insects, if a voyage is less than 5 days or if the grain temperature is lower than 10°C, in-transit fumigation with aluminium phosphide preparations is not currently recommended. The parameters for in-ship fumigation will be re-assessed when the HGCA funded project 0017/1/92 (control of grain pests with phosphine at temperatures below 10°C) is completed. However, if the grain is very cold or very dry solid formulations may not react completely and as a result if the method used does not allow the residues to be removed before discharge, may cause hazard while unloading.

Safety aspects of in-transit shipboard fumigation are fully described in the IMO recommendations (Anon, 1984) which are currently being revised.

The master of the ship has the responsibility to decide whether a fumigation can be carried out or not. In addition to arranging for an inspection and tests for leakage by a qualified marine surveyor, the fumigator-in-charge should

(a) notify the port authority before fumigation,
(b) check all the living quarters and engine room for any gas leakage for at least 48 hours after dosing,
(c) train two members of ship's crew so that they can use gas detection and respiratory protective equipment,
(d) provide at least one gas detection kit and two gas masks with phosphine canisters,
(e) request the master to notify the port authority at the destination at least 24 hours before arrival that an in-transit fumigation has been carried out.

8. NEW DEVELOPMENTS IN PHOSPHINE FUMIGATION

8.1 Research-led developments:

Existing methods of fumigating bulk grain have many shortcomings. In floor-stored grain with surface dosing (Fig. 1), the gas often disappears from the enclosure before it has time to reach the bottom (Table 2). Work at CSL established that by the distribution of solid formulations of metal phosphides on the surface and in the ducts in a fairly modern, purpose-built floor-store (Fig. 2), the distribution of phosphine could be improved considerably (Table 3).

A cylinder-based phosphine formulation was developed by CSL in the mid 80's in collaboration with BOC Special Gases Division (Chakrabarti *et al.*, 1987). Using this formulation both the concentration and exposure time can be varied easily before and during fumigation to maintain an even concentration of phosphine throughout the grain bulk for the duration of the treatment. The formulation consists of 3% v/v (2.6% w/w) phosphine in liquid carbon dioxide. Work with the mixture has progressed to the point when it could be marketed commercially but it still awaits registration with the Pesticides Safety Directorate, MAFF. In Australia, entomologists at the Commonwealth Scientific and Industrial Research Organisation have developed in collaboration with industry an essentially similar system independently of the work at CSL, and have patented it as "Siroflo" (Winks, 1990) and this is now in commercial use in Australia.

In this system a low concentration of phosphine gas, 2-3% in carbon dioxide, from cylinders is mixed with an air stream. The air-gas mixture under pressure is fed continuously into the base of a storage structure at very low concentrations until the gas spreads evenly throughout the entire grain mass to reach a controlled minimum level.

8.1.a Field trials by the CSL research team:

The procedures followed during large scale field trials on commercially-stored bulk grain warrant description in some detail. The standard sampling procedure for each trial is to trace a diagonal across the grain bulk using string from the far back corner of the bay to the front corner, or the start of the slope near the front. At each of these two positions and at the centre of the diagonal which coincides with the centre of the bulk, nylon gas sampling lines of 3 mm outside diameter are inserted to the bottom of the bulk, to the midpoint between bottom and surface, and to just below the surface. Further lines may be placed at the mid points of the back or sides of the store and down the slope at the front, if present. All lines are run from the bulk to a mobile laboratory housing analytical equipment stationed nearby. Samples of grain are taken to check the grain moisture content and for use as controls for subsequent analysis of residues.

When a bioassay is required for the investigation, up to 50 cages containing 3-5 week old immature stages of a standard stock of the grain weevil, *Sitophilus granarius* reared at 25°C, 60-70% rh in the laboratory are inserted in the grain alongside the gas sampling positions and elsewhere to supplement the information obtained on gas distribution and treatment efficacy. The cages are held in threaded cage holders linked to rod spacers which are inserted at metre intervals to depths of up to 6 metres. Thermocouples are attached to the rods to obtain a representative profile of the temperatures within the bulk.

Efforts are then made to seal the bulk prior to dosing. The ventilation system beneath the bulk is sealed off as far as possible by gluing polythene sheets across the hatch plates along the main plenum duct if present, leaving a corner free for insertion of fumigant sachets or dosing lines, and also by sheeting any fan present. Lightweight laminated sheets of low permeability to phosphine are placed on the grain surface and pushed into the grain round the sides of the bulk to achieve a good seal. Sheets are overlapped, gluing, taping or stapling all joins and taking special care to provide a good seal at the edges by weighting down with chains. For dosing with solid formulation, the centre joins are completed after dosing and sealing the aeration ducts and probing or digging in the required surface dosage of solid formulation. For tests on the cylinder-based phosphine carbon dioxide mixture, dosing lines are run to the aeration ducts from cylinders located outside the store or away from the grain and all sealing is accomplished before any introduction of gas.

In trials with the mixture, the gas supply from standard size J cylinders is monitored both by weight and flow rate. A cylinder containing 30 kg of 2.6% w/w of phosphine/carbon dioxide (PH_3/CO_2) mixture is fitted with a finned CO_2 regulator with the outlet pressure set to 100 psi, which is connected to a small (1200 litres) cylinder to act as a pressure stabilising reservoir. This in turn is connected to the dosing probe via a flow meter fitted with a needle valve (Fig. 3) to control the flow. The total dose calculated at the rate of 5 g per tonne is used to determine the number of cylinders required. For each the flow-rate is set to 700-750 ml/min for the 16-day duration of the test, this total amount being applied through one or more flow meters. A flow-through system of dosing is wholly dependent on the stability of the flow, which once set should be evenly maintained throughout the fumigation. The means of achieving such conditions has been substantially accomplished but there is room for further improvement (Table 4).

The concentration of phosphine is monitored using a Hewlett Packard 5880 gas chromatograph (GC) installed in a mobile laboratory which can be parked near the structures to be fumigated. The GC is fitted with a flame photometric detector, an automatic gas sampling valve and two 16-port stream selection valves. Gas for analysis is drawn through each of the gas sampling lines in turn using a diaphragm pump controlled by a thermal mass flow controller and each sample is injected into the GC at a pre-set interval. Once programmed, the GC can be left unattended for several days.

A comparison of the concentration-time products (CTPs) obtained by dosing both on the surface and in the ducts with those obtained by introducing PH_3/CO_2 mixture in the ducts is given in Table 4.

8.1.b Fumigation of grain in a bin using PH_3/CO_2:

The cylinder-based formulation was used to dose a free-standing bin on a concrete base. The bin standing 6 m high at the eaves and 5 m in diameter, contained 145 tonnes of feed wheat.

Two sets of gas sampling lines were inserted at different depths, at the centre and half a metre away from the edge of the bin near the hatch. The aeration duct, gaps around the eaves and the surface of the grain were sealed with polythene sheets and a cylinder of 2.6% w/w PH_3/CO_2 mixture was set up to supply a total dosage rate of 5 g/tonne via the plenum duct at the base of the silo. In this case in calm weather conditions the CTPs after 16 days were fairly high (Table 5) and flow rates could have been reduced, but in adverse weather conditions the fumigation exposure time could have been extended or the flow rate altered as necessary.

8.1.c Fumigation of localised infestations in a large bulk (hot-spots):

Early attempts to treat hot-spots with aluminium phosphide preparations failed because it was found difficult, if not impossible, to contain phosphine in the affected area for the necessary period (Chakrabarti *et al.*, 1990). A number of trials then were conducted with the cylinder-based formulation and the procedure was modified from trial to trial. One of these procedures, as the data obtained below suggest, would probably be suitable with some modifications.

Two hypothetical hot-spots, each of 1 m diameter and at a depth of about 2 m to 3 m from the surface were dosed differently to assess the horizontal and vertical distributions of phosphine. In one, all four dosing probes of 6 mm OD stainless steel tubing were pushed in and around the hot-spot to a depth of 2 m from the surface (Fig. 4a). In the other, all the four dosing points were placed vertically through the hot-spot at different depths of 0.5 m, 1.5 m, 2.5 m and 3.5 m from the surface (Fig. 4b). Dosing, at the rate of 5 g per tonne, was done from J-size cylinders and the gas concentrations were monitored using the GC in the mobile laboratory. Typical plots of concentration levels at a range of depths at two corresponding points (Fig. 5) of the hot-spots show the distribution patterns of phosphine obtained with the different dosing methods. The horizontally spread dosing method maintained an effective concentration level around the hot-spot throughout the treatment.

8.2 Industry-led progress

8.2.a Fumigation of floor-stores and barges:

A new process, introduced by the French Company, La Desinsectisation Moderne (DM), and now being used for some in-ship fumigations in the UK, uses patented "Fumisleeves" which are made of fine mesh woven nylon with a lay-flat width of 11 cm and of length 6 or 8 m with one end closed. For dosing, these are slid over sections of 50 mm diameter UPVC piping which are pushed up to 6 m into the grain. Tablets or pellets are dropped into the sleeve through the UPVC pipe by means of a plastic funnel while the pipe is being gradually withdrawn. The tablets are held at different depths by the collapsed sleeve. Probing is done in a matrix according to the dosage necessary for the bulk. Excess lengths of the sleeves are tied in a knot and are left on the surface of the grain as markers. The technique is suitable for use in deep floor stores and in smaller ships holds. On ships, mechanically operated "MacGregor" hatch covers with gasket linings can provide a virtually gas tight seal for fumigation. At the end of the treatment the sleeves are pulled out and the residues are disposed of, leaving no powder behind in the grain.

8.2.b. Fumigation of grain in floor-stores or in a silo using the Phyto-Explo system:

A novel method of dosing has been developed by "Desinsectisation Moderne" for use in deeper grain bulks. The process is called the Phyto-Explo System and is a patented method for the introduction and distribution of phosphine or any other fumigant in bulk cereals.

In this process an expandable, corrugated shaft of about 63 mm diameter, wholly or partially perforated, is slid over a metal pipe and fitted to metal probe which is introduced into the grain using a pneumatic hammer. When it reaches the desired depth, the probe is withdrawn leaving the shaft expanded in position (Fig. 6). Aluminium phosphide tablets or pellets are put in nylon sleeves and introduced into the shaft. Phosphine generated in the shaft spreads in the grain mass through the perforations in the shaft and if the seal is adequate, will spread evenly throughout the bulk. For a large bulk of grain in a floor-store, a number of shafts in a matrix may assist distribution (Igrox Limited, 1993). A further refinement has been the use of fans to draw phosphine generated on the surface into the grain mass to speed gas distribution.

In a recent trial, a 7000 tonne bulk of wheat in a floor-store was treated with phosphine using the Phyto-Explo system. The grain bulk was contained by corrugated iron walls on three sides, sloping down to the floor at the front. There did not appear to be any sealant at the joints and the walls were far from gas-tight. The outer wall of the store was constructed of corrugated aluminium sheeting and there was a gap of 0.5m from the grain retaining walls. The surface of the bulk was very uneven with several peaks and troughs and the depths of grain ranged from 3 - 8 metres.

Altogether six shafts were introduced into the grain from the surface each with only the bottom half metre perforated, 4 in the front half and the other two in the back half of the grain. Each shaft was positioned halfway between the wall and the centre of the store (Fig. 7). The shafts were linked in pairs to a fan with the air-inlet attached to a perforated suction pipe laid along the ridge of the grain under the sheeting.

The grain mass was dosed along the centre of the ridge with 'Detia' bag-chains at the rate of about 1.7g/tonne of phosphine and was covered with 150 micron polythene sheeting with the fans underneath. The edges of the sheeting were buried under grain all the way round and joints were rolled and then stapled together.

After dosing, the use of the fans to inject phosphine was continued for 4 days and the gas concentrations were monitored on-line from 23 positions using a Hewlett Packard 5880 gas chromatograph fitted with a flame-photometric detector and housed in a purpose-built mobile laboratory (Table 6). The sheeting near the ridge of the bulk was slit open after 12 days and an additional dose of about 0.5g/tonne was introduced only to the area adjacent to the four shafts near the slope to extend the treatment period. Then the bulk was resealed, the fans connected to the four shafts were switched on and the test was continued up to 15 days.

In spite of the surface dosing method, concentrations of phosphine were generally lower near the surface. The highest CTP was recorded near the highest peak of the bulk (Table 7), probably because of proximity to a dosing point. Positions C, D and H were all on one side of the store and recorded lower concentrations. This indicated a possible wind effect and after day 7 CTPs at D and H showed little increase (Table 7). The lowest CTP occurred near the surface at J but could have been the result of a damaged line. From the data it is apparent that good gas distribution can be achieved by the Phyto-Explo System. However, to retain phosphine at the desired level for the required period to kill tolerant strains without redosing, a more gas-tight store would be necessary.

For tall silos, fan-assisted circulation of the gas through a single shaft with partial perforation is essential to achieve even distribution due to the strong upward movement of air frequently experienced with this type of silo. In this situation the fumigant is introduced into the head space rather than into the bulk. In this way, the spent phosphide residues can be retrieved easily at the end of the treatment or if necessary, a fumigation can be extended by further introduction of formulation into the head space. However, if the structure is not sound, the use of a fan will cause leakage and dilution of the gas.

The system may also be useful for hot-spot treatment but no work has been done in this area. If the required dosage is split by half and applied in two doses at an interval of 7 days, the phosphine concentration may be maintained for the necessary period.

8.2.c. In-transit in-ship fumigation

The fumigation procedure for the treatment of cereal grain in ship's holds developed by Desinsectisation Moderne is very different to those currently practised which have already been described in Section 7.4.

The fumigation procedure is similar to that for floor-stored grain (8.2.a and b) but with three extra points on safety.

i) After an initial survey the holds are treated with a thermally generated insecticide fog. Apart from effects on crawling and flying insects, this helps to find the gaps and escape points for the fumigant so that these can be sealed before loading.

ii) At the end of the fumigation treatment, the fumisleeves containing the spent aluminium phosphide residues are taken out of the corrugated shafts.

iii) Before the vessel is due for arrival at the port, de-gassing of the bulk is carried out by connecting a suction pump to a shaft for forcing air through the bulk (Zakladnoi *et al.,* 1991; Bannikov *et al.,* 1991; Belobrov, 1991).

9. DISCUSSION

Now that methyl bromide has been listed in the Montreal Protocol as an ozone depleting chemical, phosphine is the only toxicologically and environmentally acceptable fumigant available for the disinfestation of stored food commodities. It is imperative that in order to maximise the usefulness of phosphine, its methods of application, retention in a structure, distribution in a bulk and subsequent removal are evaluated critically. In addition, attempts to extend its use into new situations arising because of changes in storage practices or loss of previously used control agents are generating a number of problems. Some pests are tolerant of exposure to phosphine at particular stages of development (Bell, 1976) and their control requires extended exposure periods, especially at low temperatures. This problem may further be compounded by the presence of resistance in pest populations (Mills *et al.,* 1990).

In practical terms the approach should be to fumigate at a sufficient dosage to guarantee the control of the most tolerant strains of the most tolerant species, so that the doses would be sufficient for all other pests, including resistant strains. At present, with the methods of treating bulk grain relying on dosing the surface only, there is little likelihood with most application methods of achieving the necessary concentrations at all positions for the required exposure period, especially where the grain is deep, and where sealing of the walls and surface of the bulk is difficult. Increased dosage in a leaky situation, instead of controlling a population may cause selection pressure for resistance.

9.1 Dosing via the ventilation system

Dosing in the ventilation ducts as well as the surface is a useful technique to improve gas distribution but to benefit from this, fairly well-sealed storage structures are needed.

It is emerging from the field trials that the 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. As the size of the bulk decreases, the surface area to volume ratio increases progressively and proportionally the rate of leakage increases. Although it is evident that dosing both on the surface and in the ventilation ducts improves gas distribution, it needs to be conducted with some degree of caution. Phosphine usually diffuses away as it evolves from the phosphide preparations but the risk of high concentrations of gas building up in the confined space within a duct remains. The proportion of the dose applied within a duct is therefore to be calculated so that the concentration of phosphine in the free space does not exceed the flammability threshold of 1.79% by volume.

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 "Siroflo" system already in use in Australia incorporates a cylinder-based 2-3% 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.

9.2 Use of a cylinder-based gas supply

The cylinder-based formulation of PH_3/CO_2 mixture needs to be registered under the Food and Environmental Protection Act before it can be marketed in the UK for commercial use. The registration process is now being started but may take some time.

It proved possible with this formulation to remain within the existing recommended dosage level of up to 5 g per tonne by setting a steady gas flow to run continuously throughout a 16-day exposure. Initial problems encountered for the maintenance of a steady flow over the period have been resolved by the use of a secondary cylinder for stabilising the pressures. The process of continuous dosing using the PH_3/CO_2 mixture through the plenum duct at the base of a silo will not only make a fumigation operation simpler but will also ensure complete eradication of the pest population.

Successful treatments of localised infestation in a large bulk can also be achieved by the use of the cylinder-based formulation of phosphine. The horizontal spread of a number of probes in and around a hypothetical 'hot-spot' in a large grain bulk gave a better distribution of phosphine at the centre than spreading probes vertically (Fig. 5). The commercial significance of this development is that in most situations the enormous cost of treating the whole bulk can be avoided. Another added advantage of using the PH_3/CO_2 mixture is that unlike tablets and pellets it cannot leave any spent residues in the grain.

9.3 Developments with solid formulations

If the solid phosphide preparations in bags or packets can be recovered after the treatment, the risk of leaving spent residues in the bulk will be minimal. However when tablets or pellets are probed into the grain, residues with about 1-2% undecomposed metal phosphides are left behind at the end of the treatment. When the grain is disturbed, phosphine starts evolving from the remaining phosphides. This may cause operator hazard and in certain circumstances rejection of the consignment due to smell. The use of "fumisleeves" to extract the residues after treatment is a considerable advancement over the existing methods. By this technique tablets can be placed several metres deep in floor-stored bulks, coasters, farm-bins and barges and the residues can be retrieved for disposal afterwards. Although this will improve the distribution of phosphine, the success of a fumigation operation is still dependent on the gas-proofing of the structure.

In the French DM "Phyto-Explo" system which has been further developed in the UK by Igrox Ltd., introduction of perforated shafts to almost any desired depth for dosing into large grain bulks e.g. deep floor-stores, ship's holds or tall silos, assists in the distribution of phosphine throughout the bulk. Fan-assisted circulation through a shaft improves gas distribution but if the structure is not sound, the forced movement of phosphine will increase leakage, so that redosing may be necessary half way through the fumigation. Using this system the phosphide preparations can be placed above the surface of the bulk and need not come in contact with the grain mass at all so that residues can be withdrawn and safely disposed of at the end of the treatment. Treatment of hot-spots is a possibility by this technique and needs to be explored.

9.4 Resistance

Resistance to phosphine is an established fact and a constant watch on the spread of resistant populations needs to be maintained. Gas-tightness of a structure, under dosing, leakage and poor gas distribution are some important factors for creating situations for resistant insects to survive and develop resistant populations. Early detection of resistance is vital as now there are means of achieving extended exposures to achieve control. Utmost care from all sides of the industry is necessary to retain the effectiveness of the only fumigant available for the total disinfestation of grain for the foreseeable future.

10. CONCLUSIONS

10.1 Phosphine will kill all stages of all stored grain pests if at a given temperature a certain level of fumigant is maintained for a certain level of time.

10.2 The most common reason for ineffective treatment is that the fumigant is not distributed evenly throughout all parts of the bulk of the grain or other product, and also it is often not fumigated for long enough. This results in surviving adults or surviving juvenile stages which lead to re-infestation and also contribute to the development of resistance.

10.3 Phosphine has traditionally been used as a treatment to cure a problem and as a last resort. With improved application techniques which can ensure complete eradication, and with an increasing requirement for nil or low residues of contact pesticides, it can now be considered as an economical routine preventative treatment option.

10.4 Existing structures and storage facilities need to be sealed to a reasonable degree of gas-tightness. Fumigation must be taken into consideration in the construction of future grain storage facilities.

10.5 By dosing solid formulations both on the surface and in the ducts of floor-stored grain, the gas distribution in existing structures can be improved considerably.

10.6 It is possible to maintain adequate concentrations of phosphine regardless of weather conditions in bins and floor-stores using the PH_3/CO_2 mixture from cylinders. The formulation of 2.6% w/w phosphine in liquid carbon dioxide is not yet commercially available.

10.7 Use of a continuous flow of gas from the cylinder-based source enables localised areas of large bulks to be treated and provides a means of disinfesting 'hot spots'.

10.8 If the tablets or pellets are dosed directly into the grain, the small amount of un-decomposed aluminium phosphide remaining at the end of the treatment may cause a hazard while handling and the grain consignment may sometimes be rejected on the grounds of a smell of phosphine persisting in the grain.

10.9 The careful use of phosphide formulations in bags or the use of fumisleeves can eliminate the presence of residues in the grain mass. The use of fumisleeves offers the prospect of better distribution of phosphine in a bulk.

10.10 Similarly, the Phyto-Explo system further enhances the use of the fumisleeves. In addition to retrieving residues, the gas distribution can be improved by natural or forced air circulation through shafts sunk in the grain.

10.11 This review is intended to provide the reader with information regarding developments in methods and technology to assist in the better use of the fumigant. Current HGCA research into use of phosphine at low temperatures will further assist this process.

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Table 1

Minimum exposure periods (days) required for control of all stages of the stored product pests listed, based on a stable phosphine concentration of 1.0g/m^3. This dose is recommended for good conditions and the dosage applied will usually need to be increased considerably in leaky situations.

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	Lesser 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	8
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.

Table 2

Surface dosing with a 'Detia' bag blanket in fumigating cereals (wheat) in bulk.

Position	Depth from the surface m	CTP gh/m^3
A	Bottom, 3	12
	1.4	16
	Surface	
		18
B	Bottom, 2	
	1	322
		287
	Surface	
		264
C	Bottom, 2.4	
	1.4	55
		65
	Surface	
		72
D	Bottom, 2.5	
		97
	Surface	
		277
E	Bottom, 3	
	1.5	11
		9
F	Bottom, 2.5	
		0.8
	Surface	
		8.0

Table 3

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

Position	Depth in grain (m)	7-day Ct product (gh/m^3)	14-day Ct product (gh/m^3)	Total Ct product (gh/m^3)
A, front corner on slope	0.5	118	224	282
	1.5 (bottom)	122	244	256
B, on diagonal between A and C	0.5	327	391	395
	1.5	319	418	426
	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 between C and E	Surface	255	260	260
	0.5	187	206	206
	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 near bulkhead	Surface	380	388	389
	0.5	746	855	865
	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 4

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

Position	Depth (m)	Bags in surface and ducts Ct product gh/m^3	PH_3/CO_2 in ducts Ct product gh/m^3
A, rear corner	Surface	128	318
	1.0	130	264
	2.5 (bottom)	122	297
B, centre	Surface	143	169
	1.0	110	152
	2.0	88	93
	2.5 (bottom)	72	50
C, front corner	Surface	47	215
	1.0	23	121
	2.0 (bottom)	30	56
D, back centre	Surface	154	214
	1.0	160	188
	2.0 (bottom)	277	114
E, highest point of bulk	Surface	136	412
	1.0	141	453
	2.0	153	484
	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	104
	2.0 (bottom)	99	100

Table 5

Positions of sampling lines with concentration-time products in a silo when treated with PH_3/CO_2 mixture.

Position	Depth from surface, m.	CTP after 16 days (gh/m^3)
Centre	Bottom, 5	376
	4	464
	3	232
	2	241
	1	152
	Surface	250
Side	5	523
	4	363
	3	208
	2	240
	1	206
	0.5	208
	Surface	202
East	0.5	147
West	0.5	159
North	0.5	108
South	0.5	92
Auger hole		3591
Duct to fan		25

Table 6

Phosphine concentrations at different positions on the 12th day before redosing and on the 15th day before the termination of the test using the Phyto-Explo system.

Position	Depth from surface, m.	Phosphine concn. g/m^3	
		12th day	15th day
A	3.25	0.148	1.080
	1.0	0.197	0.309
B	4.5	0.032	0.890
	1.0	0.003	0.328
C	3.5	0.002	0.176
	1.0	0.002	0.335
D	4.0	0.001	0.064
	1.0	0.002	0.070
E	6.0	0.038	0.025
	3.0	0.036	0.006
F	3.5	0.200	0.045
	1.0	0.182	0.035
G	6.0	0.019	0.116
	3.0	0.022	0.028
H	4.0	0	0.033
	1.0	0	0.177
I	4.0	0.083	0.011
	1.0	0.063	0.213
J	4.0	0.015	0.209
	0.5	0.017	
Highest peak In duct.		0.245	
		0.236	

Table 7

The position of sample lines and CTPs at 7, 12 and 15 days in the test using the Phyto-Explo system.

Position	Depth from surface, m	CTP (gh/m^3)			Remarks
		7 days	12 days	15 days	
A	3.25	133	186	249	
	1.0	66	104	123	
B	4.5	152	186	211	
	1.0	136	157	166	
C	3.5	103	104	230	
	1.0	88	90	108	
D	4.0	105	107	116	
	1.0	83	86	88	
E	6.0	134	166	167	
	3.0	117	138	139	
F	3.5	116	157	161	
	1.0	109	149	152	
G	6.0	79	101	106	Line blocked
	3.0	159	193	205	
H	4.0	59	59	68	
	1.0	43	47	53	
I	4.0	135	171	184	
	1.0	126	141	153	
J	4.0	102	156	168	
	0.5	11	25	26	Line damaged, later restored
Highest peak	0.5	350	420	423	
In duct		160	198	232	

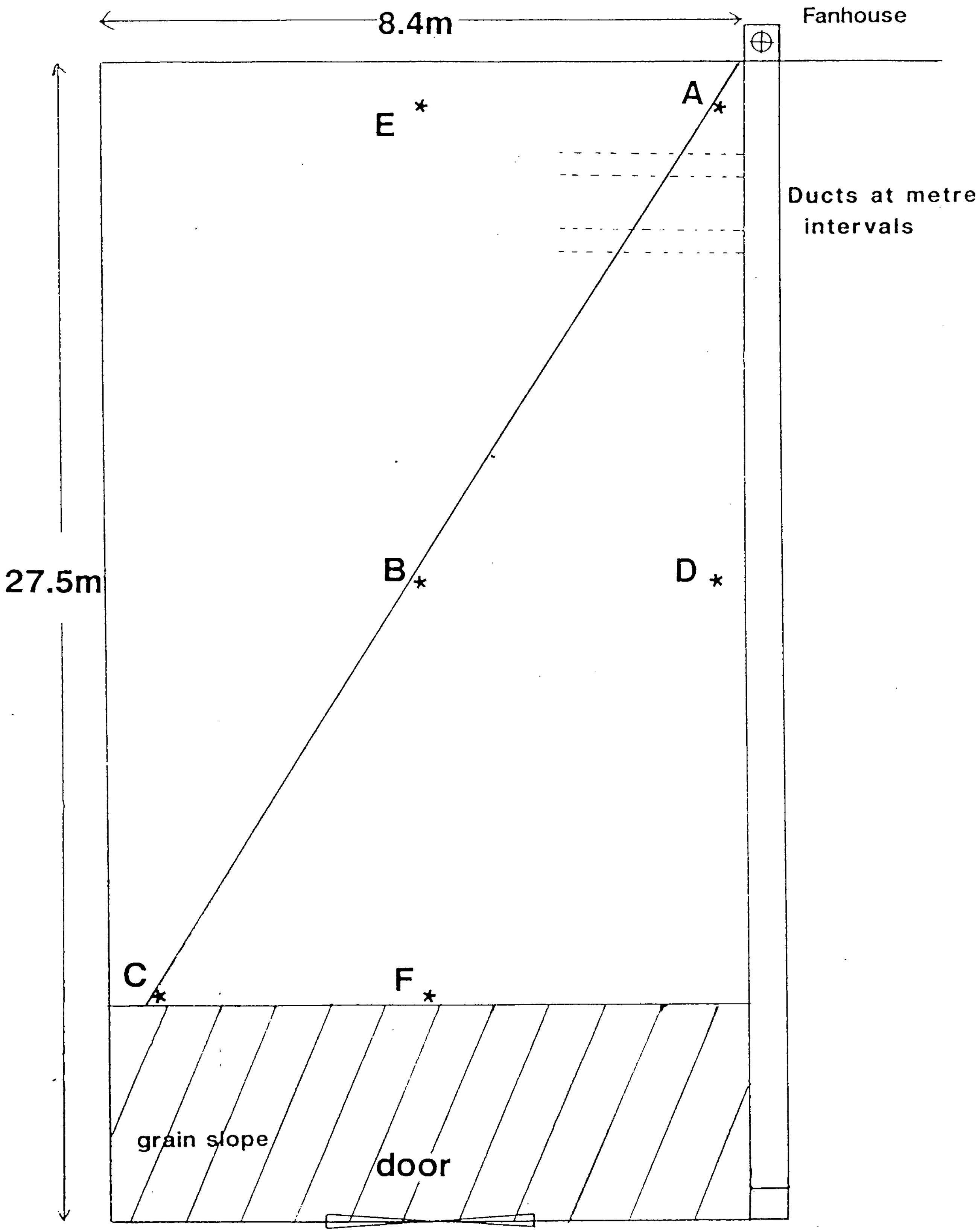


Fig. 1 Plan of the site showing gas sampling positions

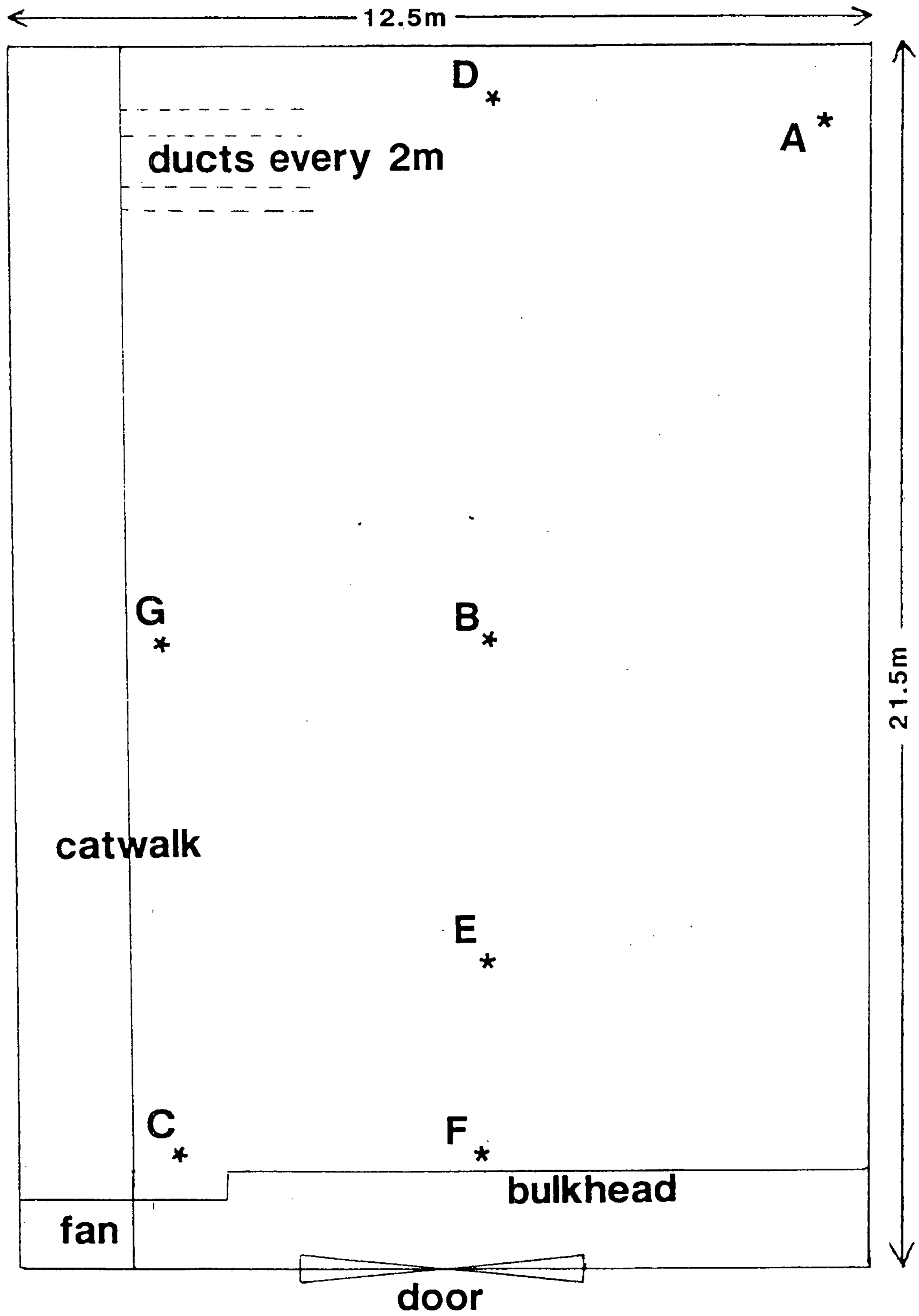


Fig. 2 Plan of the site showing sampling positions

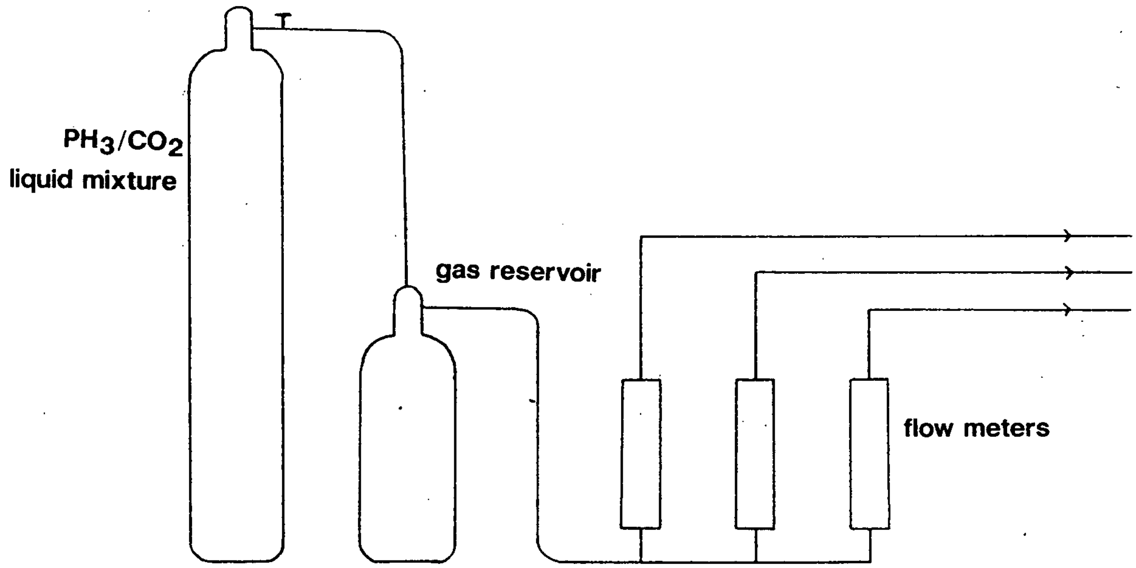
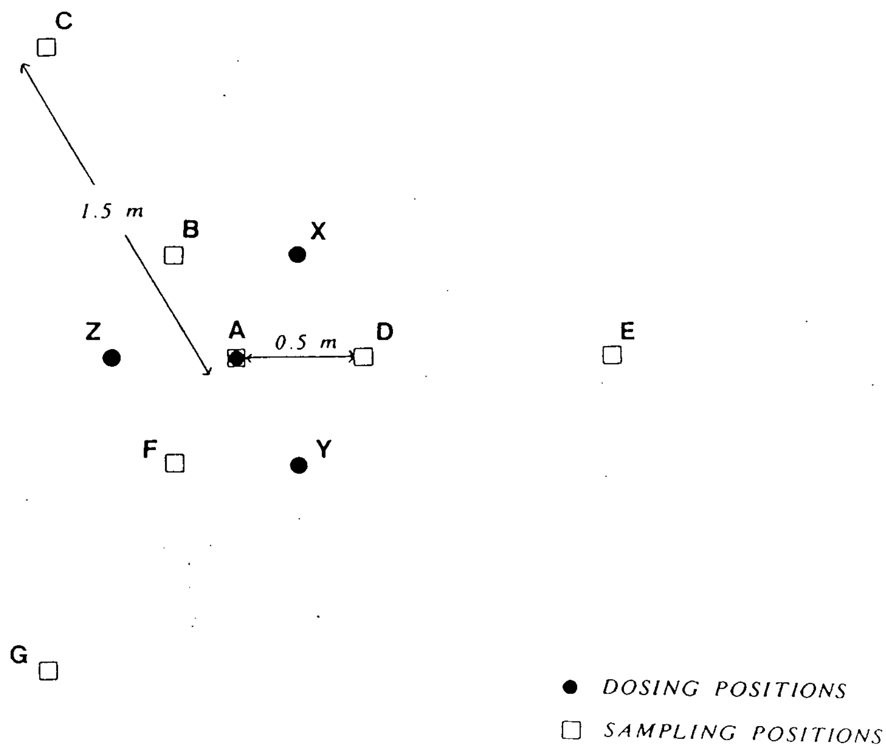


Fig. 3 Flow diagram for dosing phosphine/carbon dioxide mixture

a)



b)

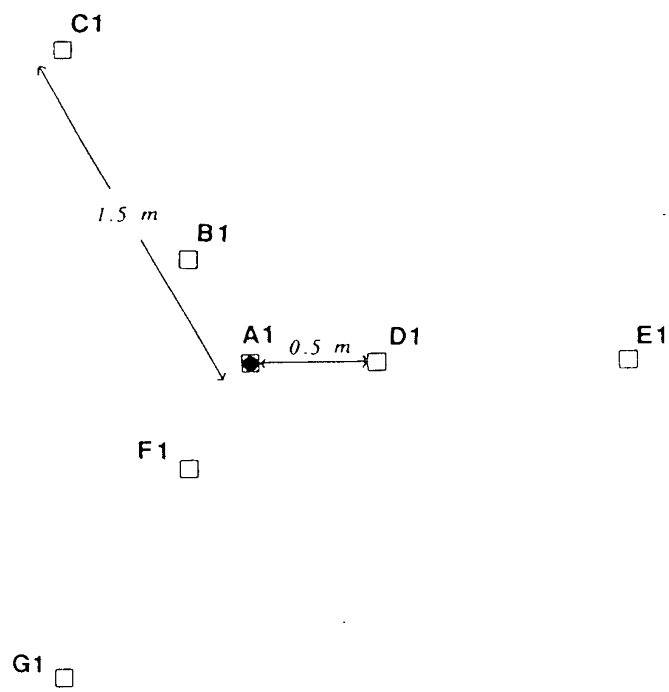


Fig. 4 Treatment of a hypothetical hot spot with the PH_3/CO_2 mixture with a) a horizontal and b) a vertical distribution of dosing probes

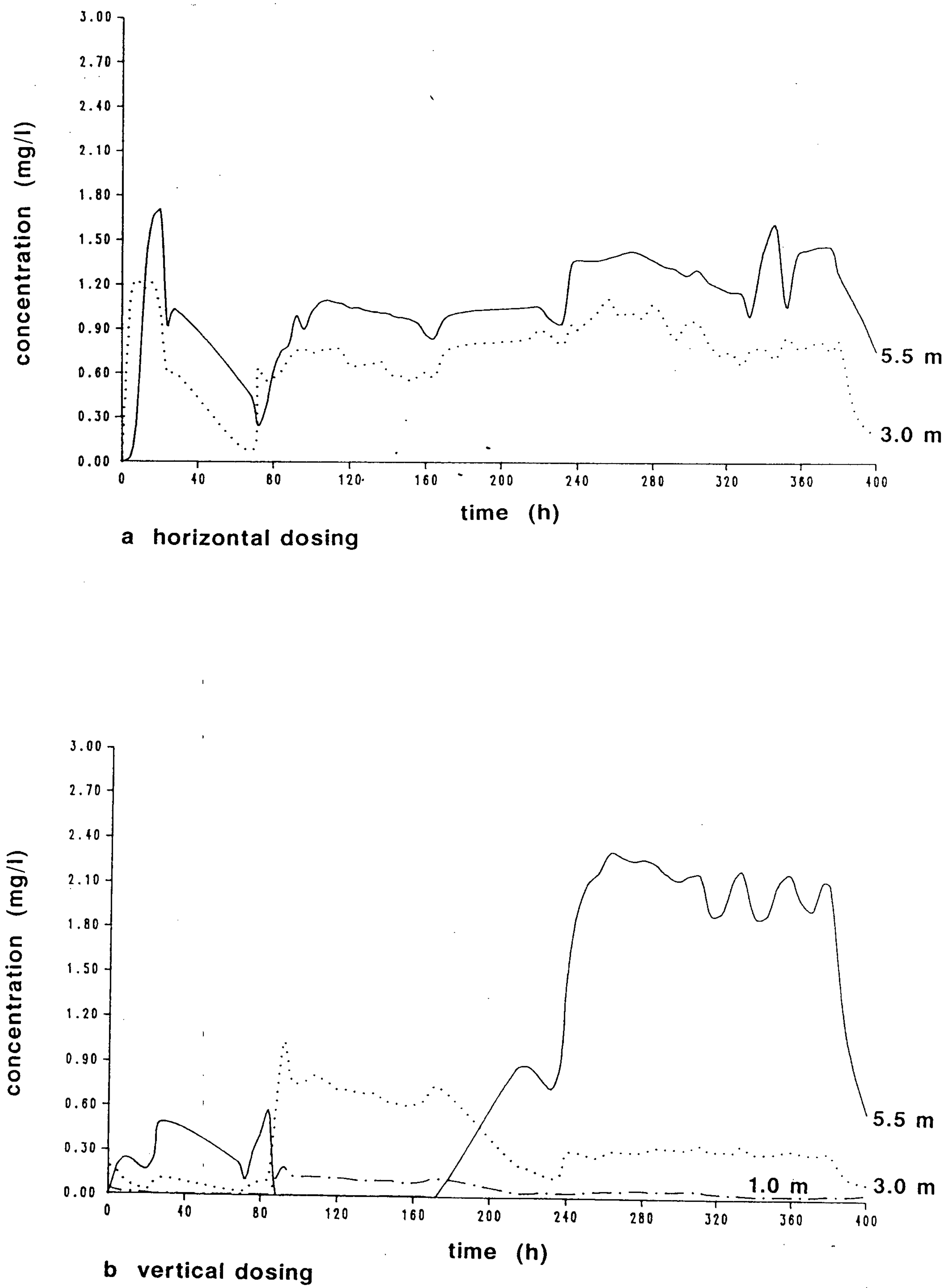


Fig. 5 Concentration v. time at the B positions in Figure 4

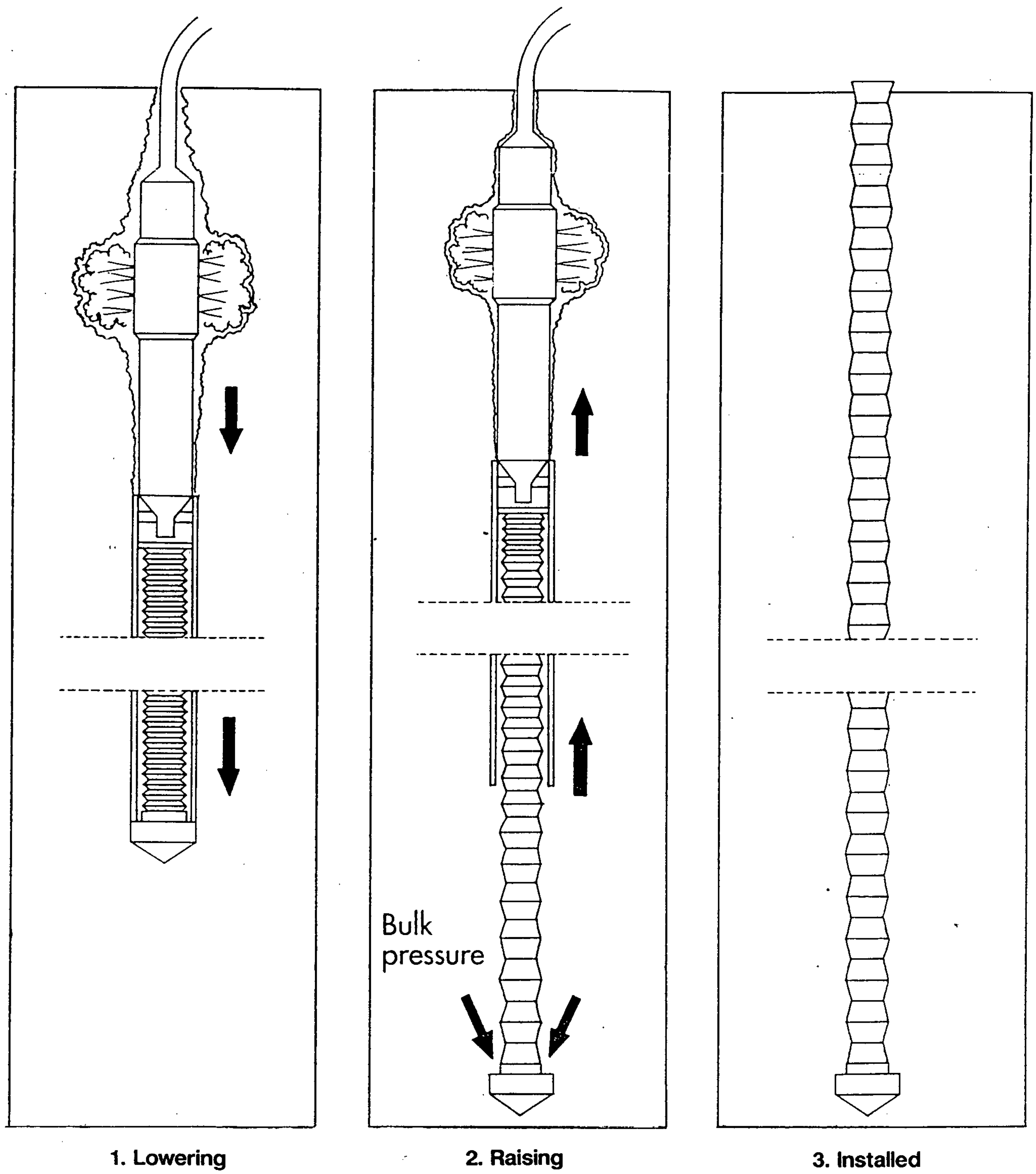
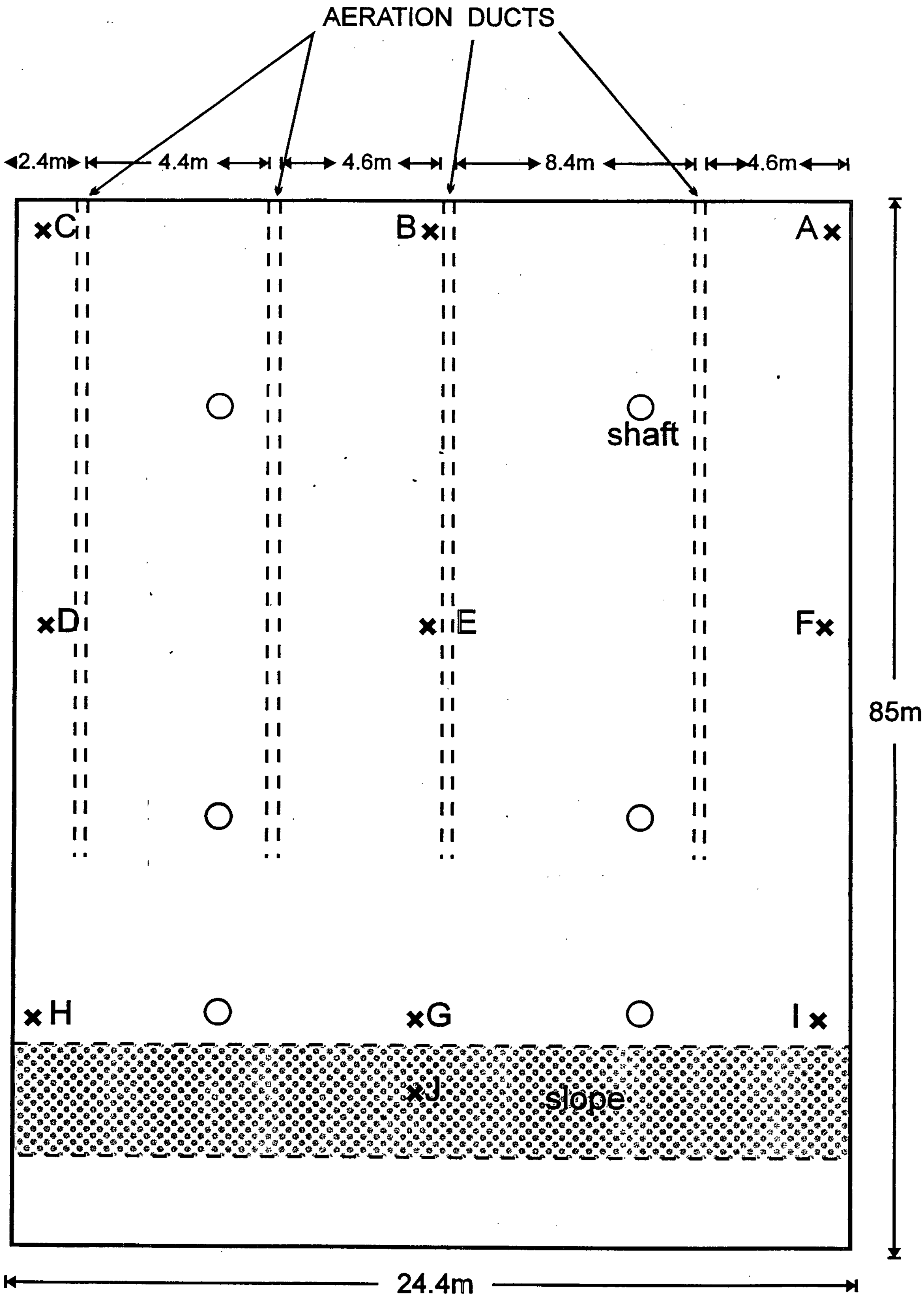


Fig. 6 Principle of fumigation shaft installation



NOT TO SCALE

Fig.7 Gas sampling and shaft positions with aeration ducts marked with dotted lines.