

Behaviour of Gases in Grain Storages

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Abstract

Understanding gas behaviour is fundamental to theory and practice of both fumigation and controlled atmosphere (CA) techniques. The actual gaseous concentration to which pests are exposed determines the outcome of the treatment. This is affected by processes on three length scales, all of which interact to give the observed concentration distribution. On the molecular level, sorption/desorption and diffusional effects predominate; on the scale of the stored grains, forced or natural dispersion is important; and on the scale of the store itself, gas interchange with the environment is the main influence. This paper reviews progress towards a sound qualitative and quantitative appreciation of the fate of gases (CO₂, methyl bromide, nitrogen, oxygen, phosphine) applied to stored grain. Some of the sorption/desorption effects have been quantified recently, but new, unexpected observations relating to fumigant residues show that more work is required before an acceptable mathematical model for this can be elaborated. Larger scale phenomena are better understood qualitatively, although full-scale data for testing of theoretically based models are scarce. Examples are given of neglected and recently noted aspects of behaviour of gases in grain storages relevant to pest control by CA and fumigation, including evolution of methyl chloride during methyl bromide treatments and rapid sorption of phosphine by paddy rice.

A proper appreciation of the techniques of controlled atmospheres (CA) and fumigation must be based on an understanding of the behaviour of gases: how gases disperse in stores and interact with the commodity or pests. The objective is to be able to describe the variation in concentration over time of the active agent or agents at any point within the treatment enclosure, since the concentration-time regimen experienced by pests determines the success or failure of the treatment. Even in regions free of pests, it is necessary to know the concentration and its variation, as this affects production of residues, and gain or loss into regions that are infested or must otherwise be protected.

The problem of describing gas behaviour is complex. Relevant phenomena include sorp-

tion/desorption, diffusion, natural convection and, often, forced distribution. These phenomena, in turn, are influenced by factors such as the grain condition, type, history, grade, temperature, moisture content, etc., how the grain is stored (e.g. bag stack or bulk), shape of store, and external inputs such as gas quantities added, use of fans and environmental effects on the enclosure. Furthermore, there are interactions between the various phenomena. For instance, solar heating of an enclosure heats part of the stored commodity and alters internal convection currents, both of which will affect the rate and magnitude of sorption. Nevertheless, without knowledge of the details of the gas-related processes involved in fumigation and CA, treatments can at best be carried out only by recipe. They cannot be predictably optimised for new situations or changed regulations; treatment failures often cannot be explained and appropriate remedial action

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taken; particular instructions cannot be justified; and research and development of new techniques cannot be rationally planned or carried out.

This paper reviews current knowledge on the behaviour of gases relevant to CA and fumigation. Only processes involving cereal grain within an enclosure are considered. Related phenomena exterior to the enclosure — such as the fate of vented fumigant in the environment — are not considered. The processes described, in principle, operate with any stored commodity, though parameter values may change. A general outline of phenomena and leading references are given, rather than detail and a comprehensive review. Mathematical approaches to the description of gas behaviour in fumigation and CA will be referred to without mathematical detail. Many persons find mathematical modelling abstruse and of no obvious utility. However, it should be noted that it does provide a means of integrating knowledge into a formal framework and, inevitably, will affect thinking on fumigation and CA. Successes and failures in modelling serve to measure how close or far away we are to understanding real processes.

The descriptive system used in this paper is based on consideration of phenomena occurring on different 'length scales', usually in isolation. Various phenomena are influenced by different scales. Three scales are used, summarised in Table 1. These are: the 'molecular' scale, where chemical interactions and the movement of individual molecules are important; the 'grain' scale, where the arrangement of individual grains and local inhomogeneities are important; and the 'store' scale, where large-scale effects such as wind and fan-forced ventilation predominate. This view of gas behaviour is similar to that on which the mathematical modelling must be based. It should thus provide a common basis on which practitioners of CA and fumigations, and theoreticians, can talk.

Molecular Scale Phenomena

Phenomena of particular interest to fumigation and CA on the molecular length scale involve gas diffusion and film permeation, sorption/desorption effects and chemical reaction. All of these directly influence important variables such as the residues formed by treatments,

Table 1. Length-scales

Names used	Typical dimension (m)	Typical phenomena
Molecular scale	10^{-10} - 10^{-5}	Diffusion, chemical reaction, physical sorption
Grain scale	10^{-3} -1	Convection, boundary layer problems, local effects of inhomogeneities
Storage scale	10-100	Bulk air movement, environmental effects

the concentration of fumigant or CA composition experienced by target pests, and how rapidly gases are dissipated after a treatment.

Diffusion

The phenomenon of diffusion controls the travel of individual gas molecules over short distances, typically less than about 1 mm. The rate at which the gas disperses by diffusion depends on temperature and the environment, usually described in terms of the concentration gradient of the gas and a temperature-dependent diffusion coefficient, D . The magnitude of D has a major influence on fumigation and CA. It determines the rate at which gases travel into and within grains (and insects) and thus the rate at which fumigant molecules are taken out of the free gas phase, either temporarily, through reversible sorption, or permanently, by irreversible chemical reaction, giving alteration products or fixed residues of some kind. Removal from the free gas phase reduces the gas concentration available to act on pests. Note, however, that the magnitude of D does not directly determine the magnitude of a process such as sorption, only the rate of approach to completion. The desorption of CO_2 from grains (Fig. 1) is an example of a diffusion-controlled system.

In fumigation and CA, four principal values of D for a given gas are important: that in air; the effective value in grain in a grain mass; the apparent value within a grain; and the value for permeation through plastic film. Table 2 gives

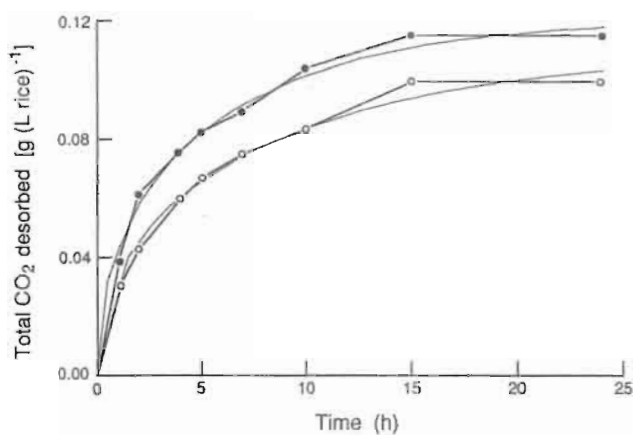


Fig. 1. Desorption of CO_2 from brown (O) and milled (●) rice (data of Mitsuda et al. 1973). Faint curves show fitted trend based on diffusion kinetics.

some values of D for the first three of these. The effective rate through bulk grain appears to be about one-third that in free air. It should be noted that the values of D given for travel within a single grain are derived from curve-fitting results of fumigations under controlled conditions. Because of the simplifications assumed in this analysis, the values obtained are approximate only. Nevertheless, they are the best estimates available until experiments conducted specifically to measure D are carried out. The effect of temperature on D for unrestricted gases is predictable theoretically. The variation with temperature for diffusion within a single grain has not been determined for any cereal but is known for phosphine into hazelnuts (Noack et al. 1984).

Permeation through films is of topical interest with the development of film packaging on both a small (ca 1 kg retail packs) and large

Table 2. Diffusion coefficients (m^2/s) for fumigants in grain and air (25°C)

Medium	PH_3	MeBr	CO_2
in air ^a	1.7×10^{-5}	0.94×10^{-5}	1.5×10^{-5}
in bulk grain ^b	5.3×10^{-6}	—	4.7×10^{-6}
within milled <i>japonica</i> rice ^c	5.9×10^{-12}	—	2.2×10^{-12}

^a Calculated from data in Weast (1986) and Barker (1974) using Graham's Law and assuming D proportional to absolute temperature.

^b from Barker (1974) and Singh et al. (1984) with adjustment for temperature. Values will include some contribution from sorption phenomena.

^c from data in Banks (1986), assuming rice to be of spherical grains, diameter 1.8 mm.

(ca 100 t bag stacks) scale as a means of protecting grain. The concentration of gases within the pack or enclosure is dependent on diffusion across the film and thus on the diffusion coefficient, in this situation referred to as the permeation coefficient or constant. A large number of films are available with a wide range of permeabilities to atmospheric gases. The permeation coefficients for fumigants are known for only a few films (Williams et al. 1980; Phillips and Nelson 1957), but those for atmospheric gases have been determined for a wide variety of membranes (Bixler and Smeeting 1971). These coefficients vary somewhat with both humidity and temperature but this variation is seldom described. It is small compared with the differences between films and the effect of thickness.

Grains appear to be solid particles. However, they are actually microporous, having small channels or pores running through them. The diameter of these pores has been estimated for wheat (10^{-8} – 10^{-4} m (Stawinski and Szot 1976)) and rice (half volume being less than 3.5×10^{-8} m (Mitsuda and Yamamoto 1980)). The effective diffusion coefficient for travel within a grain is a combination of diffusion through those pores and presumably from permeation through liquid and solid components and from physical sorption. The size of these pores is relevant to fumigation. It may restrict entry of large molecules. For instance, sulphur hexafluoride is almost completely unadsorbed (Fig. 2) suggesting that it cannot penetrate into the capillary space important for sorption of small fumigant molecules and atmospheric gases. Fumigants with boiling points at or above ambient temperatures, e.g. hydrogen cyanide, may liquefy within the pores ('capillary condensation') resulting in high losses through sorption. Overall, the effect of the microporous nature of grain in fumigation has largely been ignored, but deserves detailed research attention.

Sorption, Reaction, and Residues

The rate of uptake and release of gas into grain may be limited either by diffusion or by the rate of reaction with grain constituents. Thus, the loss of methyl bromide and phosphine from the gas phase of a closed system containing grain is typically very rapid, initially corresponding to diffusion-dependent uptake and declining to a semilogarithmic decay after a few hours (e.g. Figs 2 and 3) when reaction predominates.

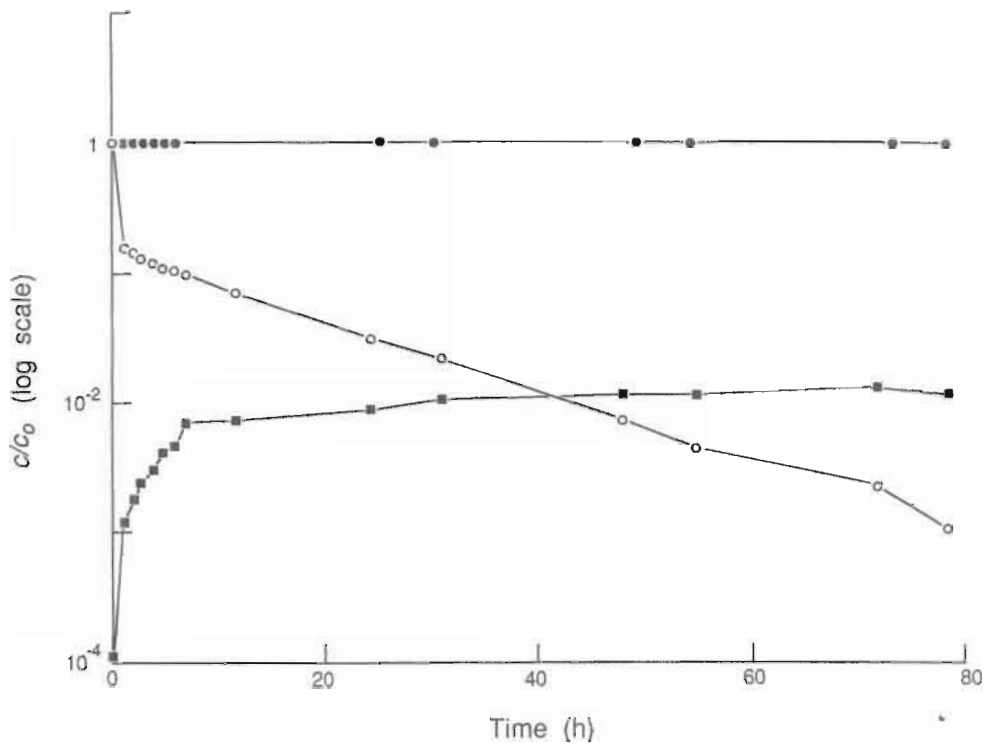


Fig. 2. Uptake of sulphur hexafluoride on whole wheat (●) and methyl bromide (○) with concurrent release of methyl chloride (■) by ground wheat. 25°C, 60% relative humidity (H.J. Banks and J.A. Gorman, unpublished data).

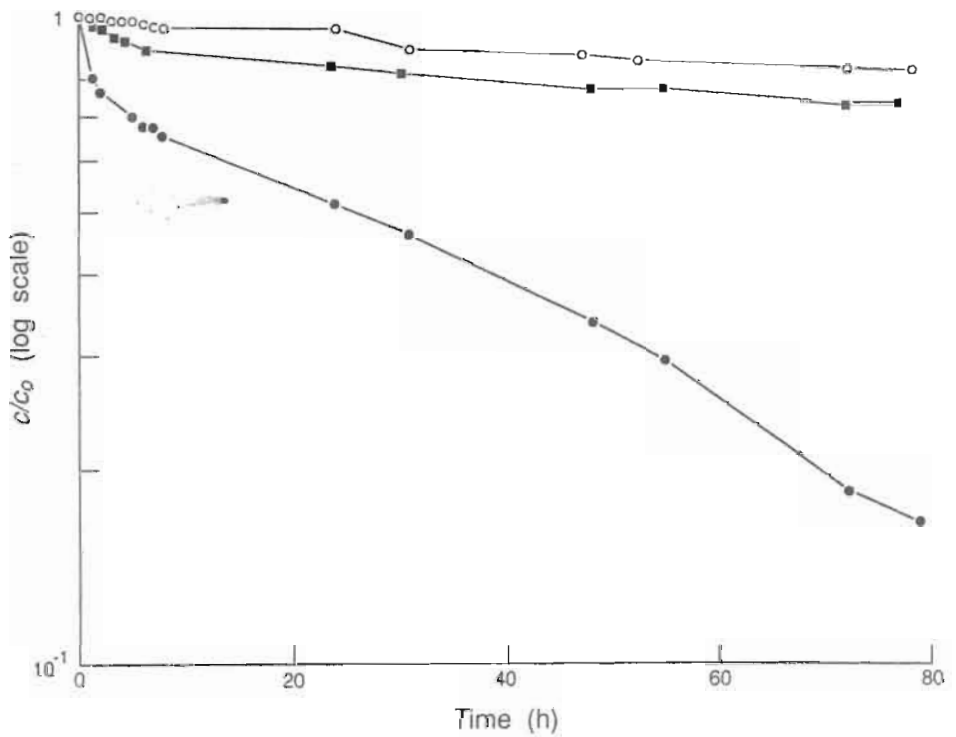


Fig. 3. Phosphine uptake by paddy (●), brown (■), and milled (○) rice. Initial dosage 3 g/m³, 25°C, 60% relative humidity with 70 g rice in 100 mL vessel (H.J. Banks and J.A. Gorman, unpublished data).

The magnitude of uptake of gas is determined by the type of grain, its condition, and the relative quantities of gas to grain. It is described by a mathematical expression, a 'sorption isotherm', relating the concentration in the gas phase to that in the solid. These are equivalent to the more familiar water sorption isotherms. Apparent sorption isotherms are available for methyl bromide and phosphine (see Banks 1986). In neither case are they truly sorption isotherms. Some of the material is taken up irreversibly and cannot be counted as unchanged, yet no allowance has been made for this. A crude isotherm has been given for CO_2 on rice (Mitsuda et al. 1973), but isotherms for oxygen or nitrogen on grain are not available.

Indeed, detailed data on uptake of oxygen and nitrogen into grain is generally not available, though it is known that some oxygen desorbs only slowly from grain (Bailey 1965). Complete desorption takes about 24 hours after the atmosphere is changed from air to nitrogen. After a rapid purge of a grain mass with nitrogen, if the system remains sealed, the interstitial

oxygen concentration will rise to about 1%. Carbon dioxide is absorbed more extensively on grain, with the rate apparently diffusion controlled. Uptake is complete in about 48 hours on wheat (e.g. Mitsuda et al. 1973). Crude figures are available for the quantity of CO_2 sorbed on several grains (Mitsuda et al. 1973), but systematic studies are lacking. Typically, about 10% of the applied CO_2 is absorbed by grains. In all probability, the mechanism of sorption is largely by reversible chemical bonding to basic groups in proteins (Mitsuda et al. 1975).

The uptake of phosphine has in the past been regarded as part simple reversible physical sorption and part loss by oxidation leading to innocuous residues of phosphorus oxyacids such as phosphate. The recent WHO review (Anon. 1988) discusses the fate of phosphine in these terms. However, some other pathways apparently operate too. Unchanged phosphine, or materials releasing unchanged phosphine on treatment, can be detected in grain long after exposure (Dumas 1980), suggesting that at least

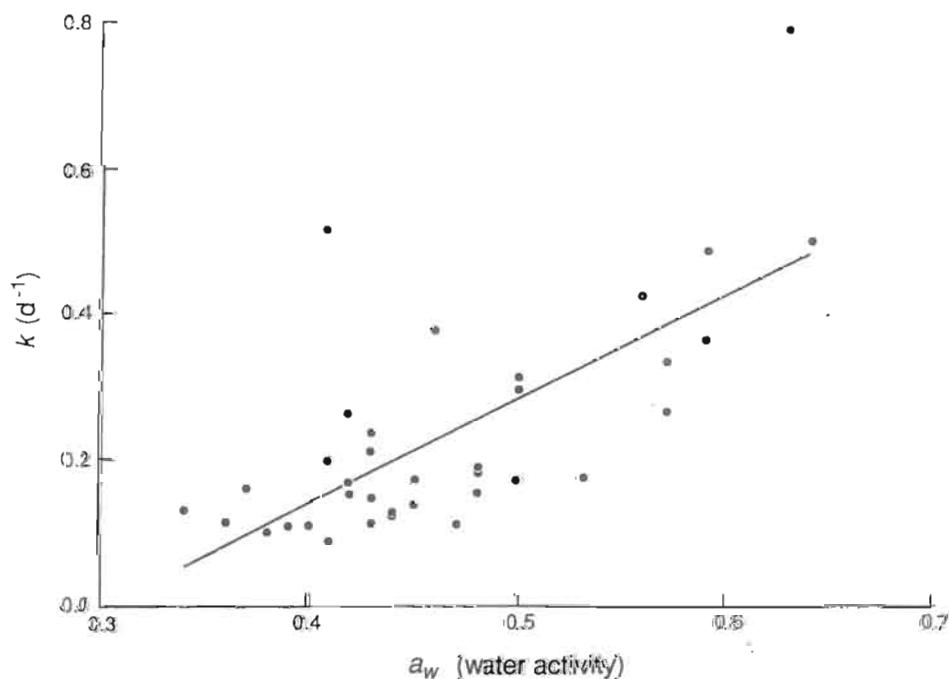


Fig. 4. Reaction rate constants (k) for sorption of phosphine on samples of wheat obtained soon after harvest from various receipt sites in New South Wales, shown as a function of water activity (a_w). Line shown corresponds to $k = 1.41 a_w - 0.43$ (H.J. Banks and C.M. Ahern, unpublished data).

some chemical reaction is involved in uptake. Phosphine can also bond to protein in some form, though this is a minor part of the total sorbed (Tkatchuk 1972). Phosphine also appears to react with several vegetable oils, causing them to solidify. Further research is needed on these aspects, as they are relevant both to understanding and quantifying of residues produced in phosphine treatments and to the kinetics of phosphine uptake and, more importantly, desorption. Without a satisfactory understanding of the reaction scheme, it is not possible to measure the fundamental parameters such as D and the isotherms.

The rate of phosphine sorption onto dry grains in general is similar in magnitude to losses expected from a well-sealed enclosure caused by environmental forces, i.e. 0.05–0.20 per day (see Fig. 4). However, the sorption rate is much less than the loss rate from poorly sealed systems in which phosphine is frequently used. As a result, loss rates have overshadowed sorption, and recommendations for phosphine use have ignored its effect. Nevertheless, allowance may have to be made for sorption in dosage schedules. Paddy rice, but not brown or milled rice (see Fig. 3), and high moisture grain, absorb phosphine very rapidly and, occasionally, so too do apparently normal samples of wheat (Fig. 5). Sorption onto paddy rice is so extensive that an adequate fumigation may not be achieved under normal dosages, even in a perfectly sealed system. The occasional occurrence of high sorption rates presents a clear demonstration of the need to monitor fumigations.

The sorption and residue production behaviour of methyl bromide has been extensively studied. Some progress has been made towards relating bromide ion concentration, produced as residue, with constituents of grain, in the hope of finding some measure of reactivity independent of grain type (see Banks 1986). However, most studies on methyl bromide sorption have not been sufficiently systematic to allow generalisation. Kinetic studies have hitherto assumed that loss of methyl bromide from the gas phase, after the initial rapid loss, directly reflects reaction of methyl bromide to give bromide residues. Unfortunately, methyl chloride is released during methyl bromide treatment of grain (Fig. 2 and Dennis et al. 1972). Unless special precautions are taken, usual analytical methods determine methyl

chloride erroneously as methyl bromide. This leads to incorrect residual methyl bromide estimations and incorrect reaction rate constants. Consequently, published rate constants (e.g. Scudamore and Heuser 1970) are likely to be incorrect, sometimes substantially so, and require checking. The continued production of methyl chloride from methyl bromide-treated materials can be quite prolonged, extending over several days. This is clearly relevant to studies on methyl bromide desorption, field quantitation of methyl bromide concentrations and on practical definition of ventilation periods after fumigation (methyl chloride is much less toxic to humans than methyl bromide). No desorption studies taking methyl chloride production into account are yet available.

Table 3 gives some typical rate constants for reaction of phosphine and methyl bromide with grains.

Table 3. Typical apparent first-order rate constants (per day) for sorption of fumigants on wheat and rice at 25°C, 60% relative humidity, for a full system (estimated from Banks 1986, and H.J. Banks and J.A. Gorman, unpublished data).

Commodities	PH ₃	MeBr
Whole wheat	0.4	0.6
Paddy rice	0.8	0.4
Milled rice	0.1	0.7

Grain Scale

The most intractable problems in gas behaviour occur over the grain length scale. This is because, at this scale, the effect of inhomogeneities become most apparent. With few exceptions, models of gas behaviour on the molecular and store length scales treat phenomena in what are considered to be homogeneous units. For instance, reaction rates are taken to apply to the grain, with due allowance for temperature and humidity, and grain is assumed to be uniformly porous throughout the store. In practice, even individual grains differ in properties and bulk grain includes regions containing different quantities of foreign matter, dust, hulls, etc., that substantially alter the properties of the region relative to clean grain (e.g. Lai and Fan 1976; Lai 1978).

These regions may well be of practical importance as they may be more easily colonised by

pests or affected by moulds, or even be created by the activities of the pests and moulds themselves. There is remarkably little documentation on how inhomogeneous the grain in store actually is, yet it is well known to those who store grain that variation within a bulk or bag stack can be dramatic. The presence, particularly of dust and matter other than whole grains, can cause major storage problems, as demonstrated by the better storage obtained when grain is cleaned (e.g. maize in 'Cyprus' bins (de Lima 1980)). Clearly, if mathematical treatment of gas behaviour is to be useful it must be able to illuminate what happens in other than perfectly clean grain. As yet, this has not been done (but see Lai 1978).

Study of the way that CAs are formed in grain can provide some demonstration of intermediate-scale problems that must be addressed. For instance, unexplained, inadequate penetration of regions of grain under fumigation is sometimes observed in practice, though the results are not usually published.

Fig. 6 shows, however, such a problem during

the purging of barley with nitrogen where there was slow displacement of oxygen in one region where husks may have accumulated.

Another area of concern on the intermediate scale involves the formation of 'havens', i.e., regions of the grain mass or enclosure under treatment where, because of dilution of the fumigant or CA through leakage of air into the region, pest control fails. Regions around poorly sealed valves in silo bins are an example of such havens (e.g. Bond et al. 1977). Here the chimney effect may draw in sufficient air to dilute the fumigant and allow pests to survive. Wind may displace fumigant from critical regions, such as from the windward corner of a bunker (Fig. 7). Where havens form by air ingress, this problem can, in theory, be overcome by maintaining a positive pressure differential with respect to the enclosure across all leaks at all times. This can be done either by adding sufficient gas continuously, as in the Siroflo system (Winks 1986), or on demand, as in some CA systems (Tranchino et al. 1980).

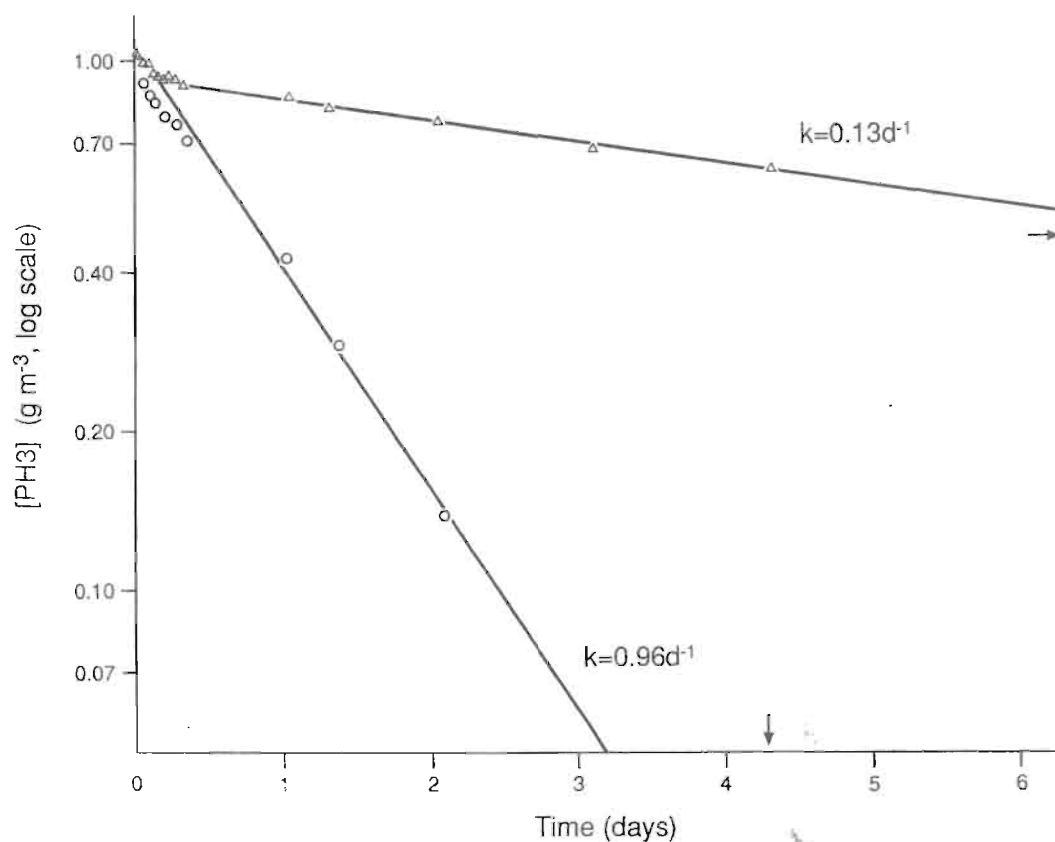


Fig. 5. Sorption of phosphine by a typical Australian wheat sample (Δ) and an exceptionally sorptive one (\circ). Both samples at 25°C and 12% moisture content (H.J. Banks, unpublished data).

No models have been published to predict the extent of dilution of internal gases by air leakage. Detailed field data on gas concentration distributions close to leaks are meagre, though reports of concentration data from treatments often give some unusually low readings in particular areas. These low readings will often occur close to the boundaries of an enclosure, a particularly important region, as invading pests are first likely to establish there and conditions may be particularly favourable to pests through moisture accumulation and segregation of chaff and other matter. The region is likely to be less accessible to introduced gases because of the very factors favouring the pests.

Store Scale

Gas interchange occurs between the storage atmosphere and the outside environment, usually typified as leakage, and there is gas transfer within the store controlled by natural convection and forced distribution. While these phenomena are well recognised, the magnitude of

their influence on concentrations within a store is often unknown to those practicing CA and fumigation. Full-scale practical observations have been very limited, but modelling has helped illustrate their effects. These large-scale phenomena, leakage and convection, interact, although mathematical modelling has so far treated them separately.

Gas Interchange with the External Environment

Leakage from an enclosure under CA or fumigation is affected by a number of factors, summarised in Table 4. Mathematical analyses of these effects and how they influence average gas concentrations within an enclosure has been given by Banks and Annis (1984a) and Barker (1974). The analyses indicate the magnitude of leakage expected from each factor in isolation. However, because distribution of leakage points is important, and there is as yet no suitable method for defining this distribution, or of treating combined effects, its predictions are approximate only. In poorly sealed enclosures, wind and the chimney effect are

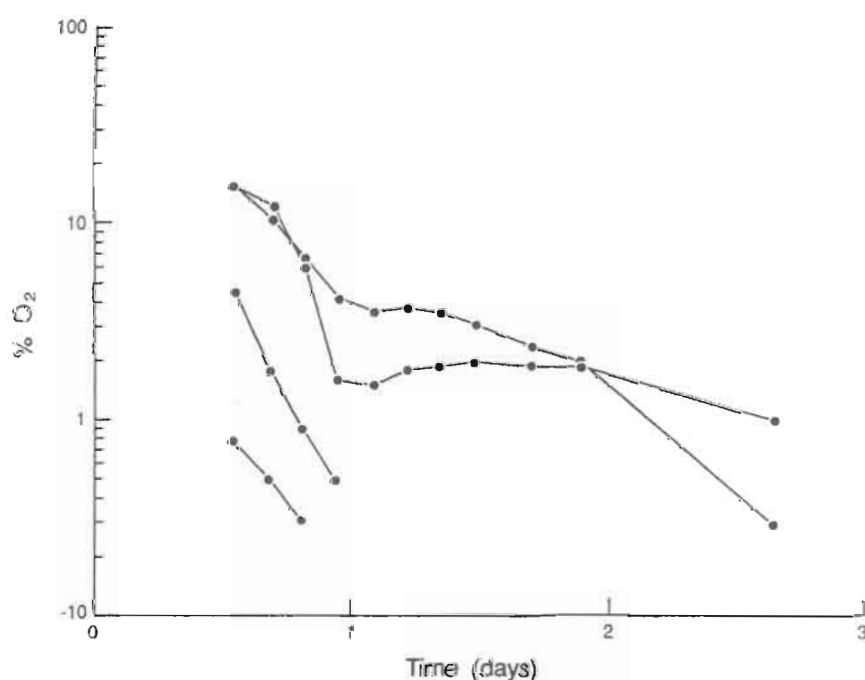


Fig. 6. Oxygen concentration history of some points close to the wall in a bin of barley purged with nitrogen, showing very slow displacement of oxygen. All other points measured in this experiment purged rapidly (< 24 hours) to below 1.0% O₂ (H.J. Banks and P.C. Annis, unpublished data).

Table 4. Environmental factors causing leakage from an enclosure. In approximate order of importance for a poorly sealed storage (after Banks and Annis 1984a).

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- Wind
 - Chimney effect
 - Temperature variation in the headspace
 - Barometric pressure variation
 - Temperature variation in the bulk
 - Permeation (plastic film enclosures only)
 - Diffusion
-

expected to be the main causes of gas loss, with temperature variation and sometimes barometric pressure effects predominating in well-sealed enclosures. In the limited published information available (see Banks and Annis 1984a), this appears to have generally been found to be so in practice.

Internal Distribution

The internal distribution of gases in an enclosure is largely determined by natural convection currents, unless some form of forced distribution is used. Diffusion can play only a minor role except over short distances (< 1 m). These convection currents result from differences in gas density at different points caused either by temperature or composition. For circulation to occur, the less-dense gas must be directly or indirectly below the more dense. If this is not so, the system is stable and no convection results. The surface-application technique for phosphine fumigation relies on convection to distribute the gas. Phosphine concentrations become even throughout the grain and headspace within large, well-sealed, shed-type stores in a few days (Banks and Annis 1984b). Structures that are tall and narrow tend to have less effective convection currents than squat structures, and adequate distribution may take weeks. In extreme cases, the gas is lost by sorption and leakage before adequate distribution can be achieved. Where internal convection

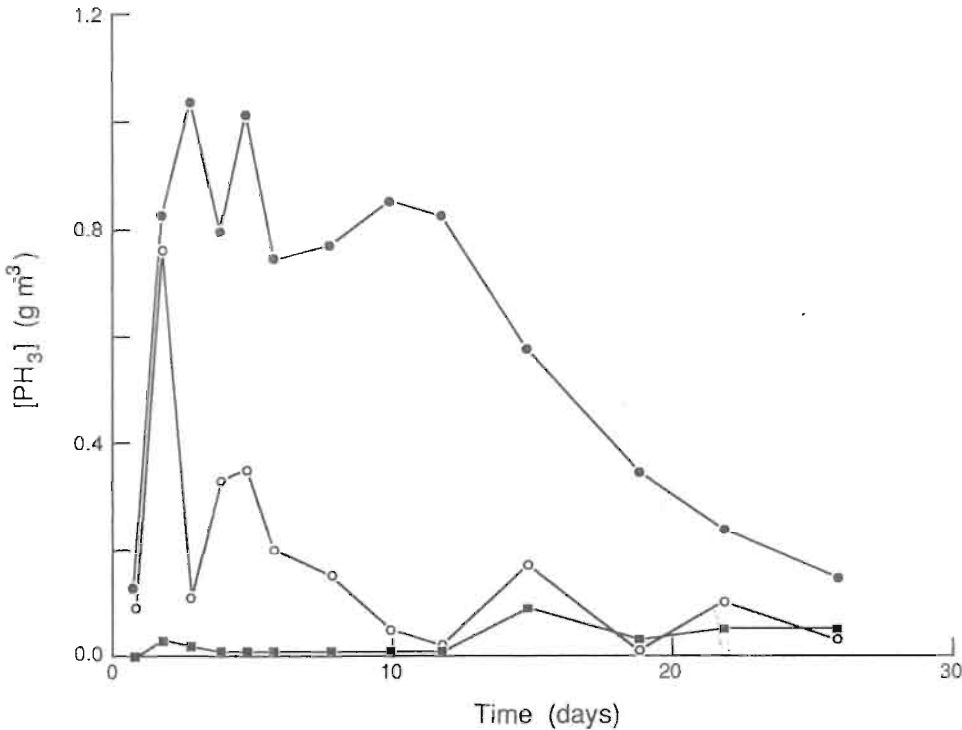


Fig. 7. Average concentrations of phosphine achieved in a bunker of wheat (●) dosed at 0.78 g/t compared with observations from the two windward corners (○, ■) where air ingress occurred (data from Banks and Sticka 1981).

currents are linked with leakage caused by the chimney effect, there may be no dispersion of phosphine in a particular direction. Conway and Mohiuddin (1984) and Banks (1977) demonstrated the chimney effect by creating a band of phosphine in the centre of a wheat bulk in a silo bin. In the former case, where the grain was cooler than the environment, the gas descended and was lost by leakage. In the latter case, with warmer grain, it rose. No significant internal movement occurred in the opposite direction in either case.

Ships' holds are especially difficult to fumigate effectively by a surface-application method without forced distribution (Leesch et al. 1986) as the convection currents that might otherwise distribute gas are weak; the colder gases are below the warmer ones in holds and so there is little driving force for convection. It should soon be possible to predict this type of behaviour in detail, given temperature data on the grain bulk and surroundings.

The mathematical treatment of natural convection in grain is complex and has been

restricted to description of movement of unadsorbed fumigants in two-dimensional, regularly shaped enclosures with constant temperature walls or ones undergoing a step change in temperature (Nguyen 1986). Leakage was not included. The models have not yet reached the level of development where predictions of behaviour of fumigants can be made for real three-dimensional systems with fumigants affected by sorption.

Forced distribution

Aeration systems that force air through grain are well known. The rate of air flow under pressure through particular grains is described by the Hückill coefficients as outlined by Hunter (1983). This equation underlies the various mathematical models that are available to calculate air flows for various arrangements of duct work and storage design. These models deal with discrete air fronts without dispersion, and do not include fumigant sorption/desorption phenomena. However, there is a

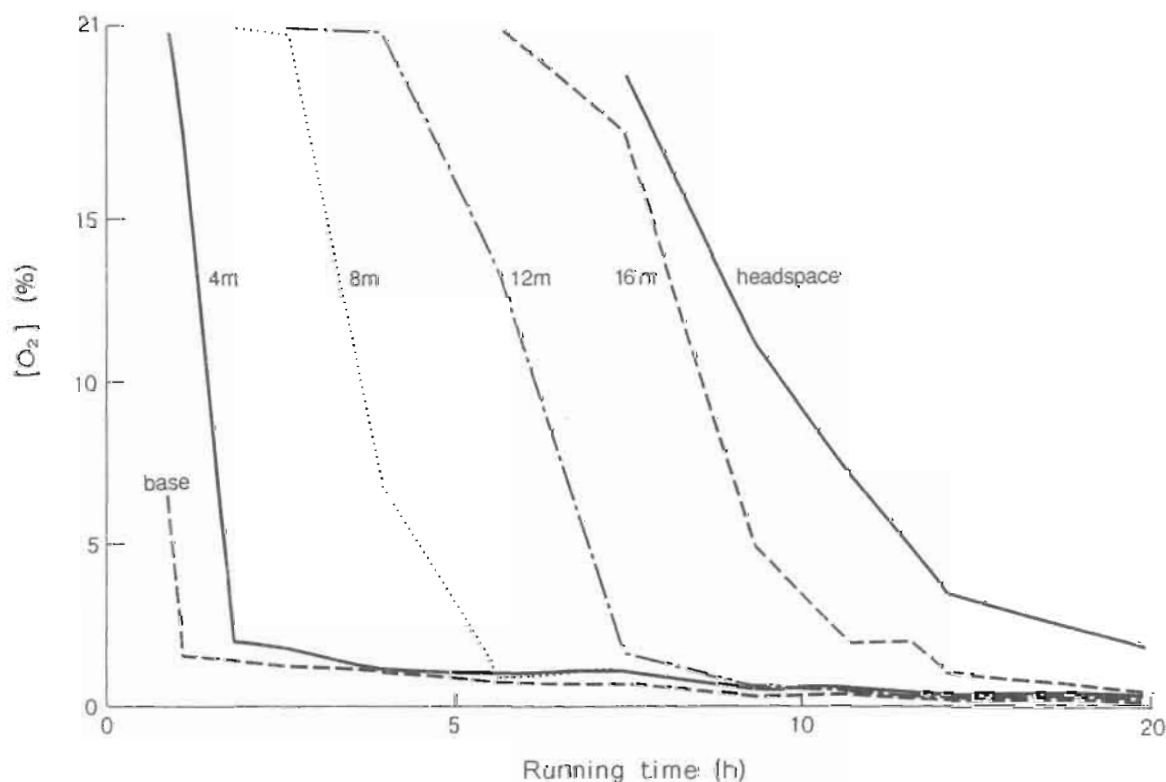


Fig. 8. Fall in oxygen content in a flat-bottomed 2000 t bin of wheat, diameter 13.9 m, at various points in the bin when purged from the base at 100 m³/hour with < 0.5% O₂ in 12% CO₂, balance inert gases (H.J. Banks, unpublished data). Position of sampling points; on bin centre line at heights above base as marked.

numerical model of the coupled heat and moisture transfer occurring during aeration that includes dispersive effects (Wilson 1988). Inclusion, at least theoretically, of fumigant effects into this model should be possible, though the relevant controlling parameter values may not yet be available.

In practice, gases under forced flow, such as during addition of controlled atmospheres, traverse a grain bulk in the mode known as 'disperse plug flow', with the initially sharp boundary between the existing interstitial atmosphere and introduced gas becoming more diffuse as the front proceeds. Fig. 8 shows the sigmoid concentration profile typical of such a front. Presumably, similar effects occur when fumigants are force distributed and mathematical models of the process should include a description of this dispersion.

Conclusion

This paper has given a brief overview of where we stand as regards understanding of gas behaviour in fumigation and CA and an indication of where we ought to be. The size and complexity of problems that need to be overcome, and the difficulty of their analysis, should not deter investigation, as the objective is worthwhile: rational and optimal use of CA and fumigation. However, a good strategy is required to attack it successfully. I believe that careful coordination is required between researchers involved in measurement and model development and persons who can gather data from full-scale treatments. Without this, models will be produced that do not reflect reality and much effort will be expended in unnecessary measurement.

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