UPTAKE AND RELEASE OF FUMIGANTS BY GRAIN: SORPTION/DESORPTION PHENOMENA

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ABSTRACT

Sorption/desorption behaviour of fumigants on the treated commodity has a major influence on the outcome, success or failure, of fumigation. In particular, this behaviour determines the concentration of active material in the gas phase during the treatment, the quantity of residual fumigant, and the rate of loss of fumigant after treatment. Factors which affect the magnitude and rate of sorption/desorption include the properties of the fumigant, the commodity being treated and its state of subdivision, the commodity temperature and moisture content (m.c.) or water activity, the fumigant concentration, and the history of the commodity including both previous changes in m.c. and previous treatments. There are few published quantitative studies of the effects of these factors on cereal grains. This report presents examples, largely from unpublished studies, which illustrate the effect of these factors on the behaviour of methyl bromide and phosphine with grains. Recent investigations have shown that the rate constant for sorption, an important parameter approximately describing the rate of loss of fumigant by reaction, doubles with a rise of 6.0 and 9.8°C or 2.8 and 3.0% m.c. for methyl bromide and phosphine, respectively. The rate constants for phosphine on unmilled rice and peanuts in shell can be estimated from those of the individual components (hull, bran, and milled rice or nuts and shell). Hull and shell are particularly sorptive relative to other components. There has been some progress in modelling particular sorption/desorption processes, but as yet there is no adequate description that incorporates the effects of all the factors involved.

INTRODUCTION

In a successful commodity fumigation, the fumigant concentration is maintained for long enough to eliminate the target organism or reduce its population to an acceptable level. Additionally, resulting residues and damage to the commodity must be within tolerable limits and there must be no

significant exposure of non-target organisms, including workers and other persons. Sorption/desorption phenomena play an important role in determining whether a treatment is successful according to these technical criteria.

In a truly gastight system, the sorption/desorption interaction between the fumigant and commodity principally determines the concentration achieved by a given quantity of fumigant and how this changes with time. In well-sealed systems, sorption is often the dominant cause of gas loss and even in highly leaky systems it may be important (e.g., Banks *et al.,* 1986). Sorption behaviour also influences the rate of forced or unassisted dispersion of fumigant through a grain mass (e.g., Berck, 1964). It thus largely determines the level of active material, the fumigant, experienced by the pests or other organisms under treatment. Sorption phenomena also affect the quality of the commodity, and determine the quantity of fixed and volatile residues formed and the time taken to remove unchanged fumigant from the commodity. Through influences on fumigant concentrations in free space and within the commodity, sorption behaviour directly affects the economics and the time taken to complete treatments.

Given the pivotal role that sorption/desorption phenomena play in fumigation technology, it is remarkable that they are so little studied. Good systematic, quantitative investigations are notably lacking. Most of the main influences on fumigant concentrations in treatments have long been recognised and understood empirically and qualitatively (e.g., Sinclair and Lindgren, 1958; Berck, 1964) and there were major quantitative studies in England in the 1950s and before (summarised in Banks, 1986), but there are not many recent studies.

This paper aims to build on the results of this earlier work and to present modern quantitative results on the influence of various factors on sorption behaviour. A comprehensive treatment is not feasible because of the range of durable commodities fumigated and the number of factors involved. Here, illustrative examples only are presented. Most of these are taken from recent unpublished work from the CSIRO Division of Entomology Stored Grain Research Laboratory. The examples show the magnitude and range of sorption behaviour exhibited by the common fumigants, phosphine and methyl bromide, largely on cereal grains and at $>15^{\circ}$C. The mathematical equations and constants used to describe the observations follow those in Banks (1986). Most of the discussion given below involves the observed influence of particular factors on the loss rate constant, k. This is the slope of the semilogarithmic plot of concentration of fumigant in the gas phase in a fumigation against time, after an initial diffusion-controlled part of the process has finished. It is a major determinant of the ct-product obtained and the fixed residues arising from a treatment. The influence of the following factors are considered in relation to sorption behaviour (uptake of fumigant from the gas phase):

- Fumigant
- Concentration effects
- Temperature
- Relative humidity (r.h.) or m.c.
- State of subdivision
- Component parts

Each of these factors has a sufficient effect in some situations to cause excessive loss of some fumigants. Fumigation failures may result unless their influence is appreciated and allowed for. Furthermore, it is important to be aware of the range of effects that can be found with a specific combination of fumigant and commodity, under apparently identical conditions. It is becoming apparent, at least with phosphine, that different grain samples may behave very differently with regard to sorption (Banks, 1990), to the extent that fumigation failures will occur if extreme, not average behaviour occurs. Some data on this are presented below.

UPTAKE OF FUMIGANT BY GRAIN
General considerations

Typical sorption curves for the fumigants phosphine and methyl bromide on wheat in a closed system are given in Fig. 1. A curve for dichloromethane, a material of similar molecular weight and properties to methyl bromide, but of low reactivity, is given for comparison. The forms of these curves are representative of those obtained in a wide variety of combinations of fumigant and treated commodities in gastight enclosures. The curves for dichloromethane and methyl bromide exhibit an initial rapid loss of fumigant from the gas phase as fumigant enters the grain and is physically sorbed in the grain matrix. This is less pronounced for the phosphine curve shown in Fig. 1. An initial rapid loss is frequently observed for phosphine, though to a much lesser extent than for methyl bromide. The process is reversible. Equilibrium is approximately achieved within about 8 hours under the conditions used. It will be noted that this period is often a significant fraction of the total fumigation time which may be 24 hours or less with methyl bromide on durables, and frequently much less with perishable commodities such as fresh fruit.

The initial rapid uptake of gas is recognised as being controlled by diffusion (Noack *et al.* 1984; Banks, 1986) with the speed with which it occurs described by a diffusion constant, D, for travel of fumigant within the grain particle and a capacity function, C_S, which gives the concentration within the particle at equilibrium with the external concentration. Banks (1986) discusses these parameters and gives some quantitative estimates of their values.
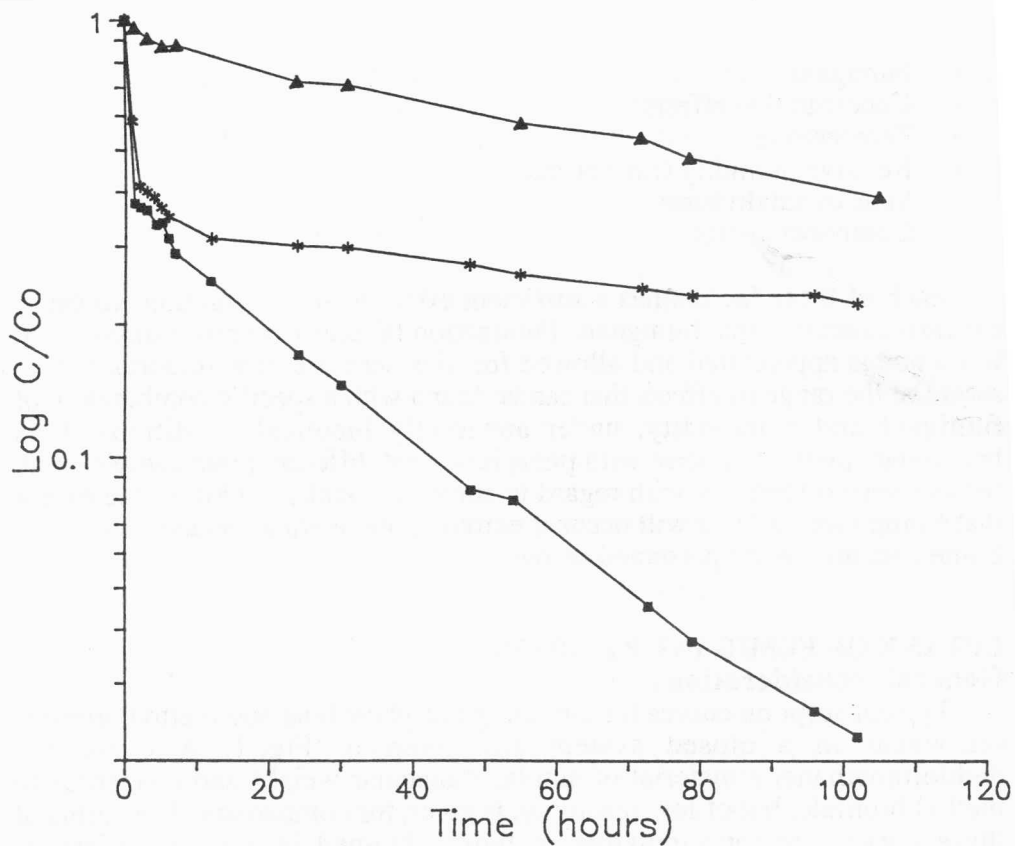
243

Fig. 1: Typical sorption curves for fumigants and similar chemical compounds on grain. Upper curve phosphine at $1 \, g \, m^{-3}$ initial concentration, middle curve dichloromethane at $60 \, g \, m^{-3}$ initial concentration, lower curve methyl bromide at $60 \, g \, m^{-3}$ initial concentration, all at 25°C, 60% r.h. and 95% filling ratio (H.J. Banks and J.A. Cassells, unpublished).

It will be noted that the value of D is unlikely to vary substantially with different fumigants. The value can be expected to be proportional to the square root of the molecular weight of the fumigant. This value only has a narrow range because of the nature of fumigants. The capacity function does vary much more widely. The general shape of the early part of a sorption curve can thus be expected to be similar for different fumigants, though the extent to which reversible sorption occurs will vary.

The curves for methyl bromide and phosphine uptake in Fig. 1 show further loss after the initial sorption equilibrium is approached. Since both these compounds react with grain constituents true equilibrium is never achieved. Reaction comes to dominate the overall kinetics of loss and the concentration continues to decline semilogarithmically with time. This process

is not found significantly with the relatively unreactive dichloromethane. Most of the discussion below concerns the influence of various factors on the sorbtion rate constant, k, calculated from the slope as in Appendix 1.

Effect of grain type on uptake

Reactivities of different fumigated grains differ widely with both methyl bromide and phosphine. This results in widely different ct-products under standard conditions of dosage. This difference in sorption is recognised for methyl bromide, resulting in different dosage recommendations for different commodities (e.g., Anon, 1989). At present this is not allowed for in phosphine dosage recommendations, although it is apparent that sorption in some cases (e.g. on paddy rice) with standard dosages may lead to potentially inadequate treatments (e.g., Annis, 1990).

Table 1 shows the variation in ct-products obtained with several commodities treated under standard conditions with methyl bromide. Another aspect of the same phenomenon is illustrated in Table 2 which shows the proportion of the original gas phase concentration of either methyl bromide or phosphine remaining after a period with a range of commodities. These values incorporate both the initial loss and that subsequently due to reaction. The effect of the initial rapid sorption is particularly obvious in the data for methyl bromide uptake where more than half the original dosage is absorbed in the first 8 hr with several of the commodities shown, but a lower fraction is lost in the subsequent 16 hr. The very low fraction of phosphine remaining with paddy rice and sunflower is also notable. In both cases, these losses are sufficient to give rise to fumigation failure under normal dosages. The high sorption of methyl bromide by faba beans is also remarkable.

Table 1: Effect of different sorption behaviours on the ct-product achieved after 24 hr in gastight systems (load: 0.5 kg product per litre, 25°C, 30 mg L^{-1} methyl bromide applied dosage, data of Soma et al., 1978).

Commodity	Moisture content (%)	ct-product (g hr m^{-3})
Red bean	12.4	800
Coffee bean	9.0	700
Wheat	11.8	460
Sorghum	11.9	260
Maize	13.0	240
Soybean	11.6	228
Buckwheat	15.0	190

Table 2: Percentage of initial concentration of phosphine or methyl bromide remaining in the gas phase after set periods in a closed system containing various commodities (25°C, 60% r.h., 95% filling ratio)

| Commodity | % of fumigant remaining in the gas phase | | | |
| | Phosphine | | Methyl bromide | |
	1 day	5 days	8 hr	24 hr
Wheat	78	56	32	18
Barley	74	55	48	35
Paddy rice	44	9	17	11
Sorghum	59	29	18	10
Faba beans	44	13	8	<1
Field peas	84	62	71	48
Canola	64	28	31	18
Safflower	20	2	7	5

Variation in rate of uptake with temperature and moisture content

The rate of reaction of the commodity with fumigant is strongly dependent on both temperature and m.c. or prevailing humidity.

The effect of temperature on the sorption rate constant, k, can be conveniently represented by an Arrhenius plot, where $\ln k$ is presented as a function of reciprocal of absolute temperature. This approach, also used by Noack *et al.* (1984), gives an approximately linear trend for both methyl bromide and phosphine uptake on wheat (Figs. 2 and 3) corresponding to apparent activation energies of 60.0 and 70.0 MJ kg-mol^{-1}, respectively.

The effect of m.c. is much more complex. For a single wheat sample, the value of k is approximately semilogarithmic with water activity for both methyl bromide and phosphine (Figs. 4 and 5). However, there is about a twofold variation in k for wheat samples of a given m.c.. This is shown in Fig. 6 where values of k were determined for a large number of freshly harvested wheat samples. The determinations were made on the samples taken directly from deliveries by producers without adjustment of m.c.. No data are available on this type of variation for methyl bromide uptake.

Wide variation in uptake of phosphine between samples of the same grain makes study difficult. Causes of the variability are still being sought. However, it has been found that moisture history of the grain influences rate of uptake. This is illustrated in Fig. 7, which shows k values for subsamples of a sample of freshly harvested paddy rice at various stages after gentle drying by exposure to dry air at 25°C and then rewetting slightly by addition of water in a sealed system. The k value is observed to rise upon wetting, but subsequently declines to below that of the drier sample. This trend suggests the value is still changing 27 days after the moisture change. Similar changes
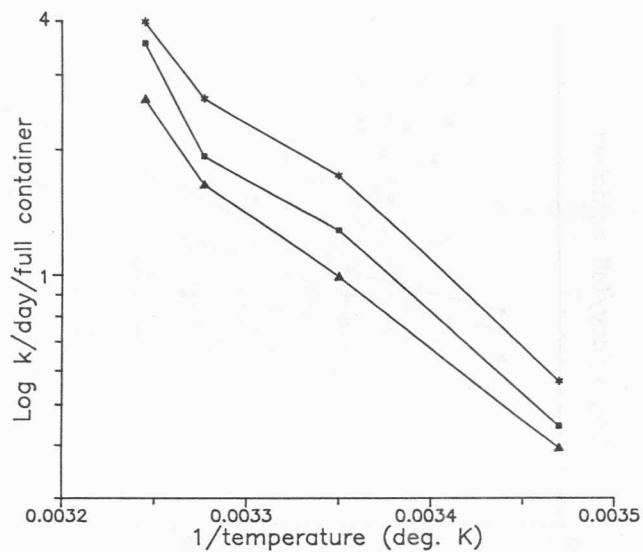
246

Fig. 2: Influence of temperature on methyl bromide sorption rate constant (k) on wheat at 60% r.h., presented as an Arrhenius plot. Upper, middle and lower curves for 5, 20 and 60 g m^{-3} initial concentration, respectively (H.J. Banks and J.A. Cassells, unpublished).
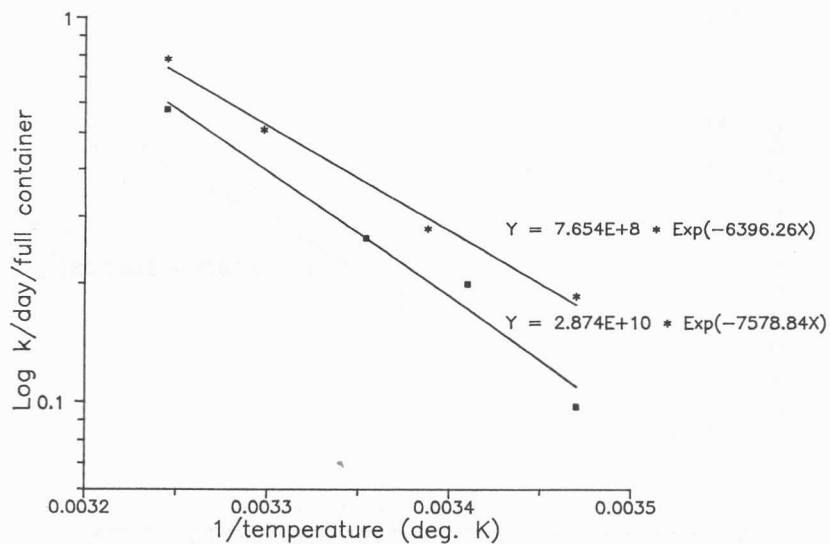

Fig. 3: Influence of temperature on phosphine sorption rate constant (k) on two samples of wheat (Australian Standard White, 1987 and 1990 harvests) at 60% r.h. and 1 g m^{-3} initial dosage, presented as an Arrhenius plot (H.J. Banks and J.A. Cassells unpublished).

247
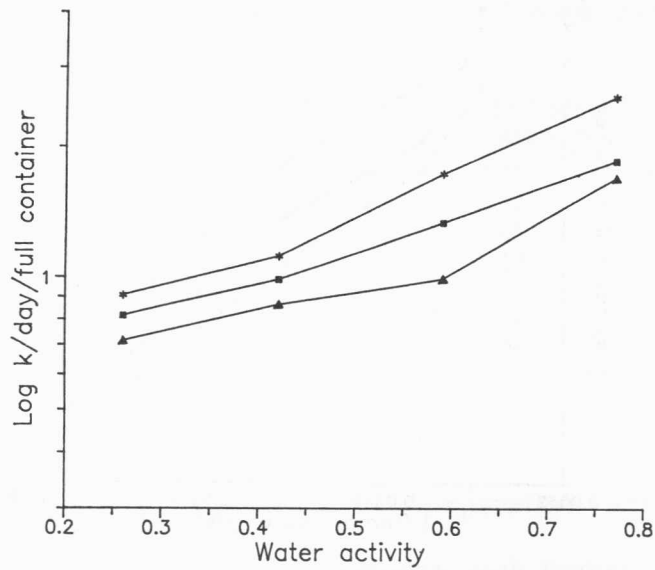
Fig. 4: Influence of water activity on methyl bromide sorption rate constant (k) for wheat at 25°C. Upper, middle and lower curves for 5, 20 and 60 g m^{-3} initial concentration, respectively (H.J. Banks and J.A. Cassells, unpublished).
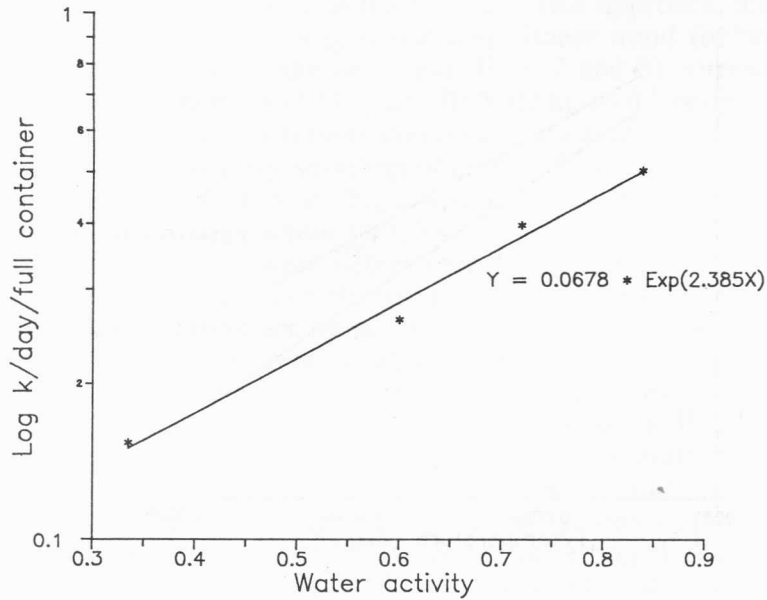

$$Y = 0.0678 * Exp(2.385X)$$

Fig. 5: Influence of water activity on phosphine sorption rate constant (k) for a sample of wheat at 25°C, 1 g m^{-3} initial concentration (H.J. Banks and J.A. Cassells, unpublished).
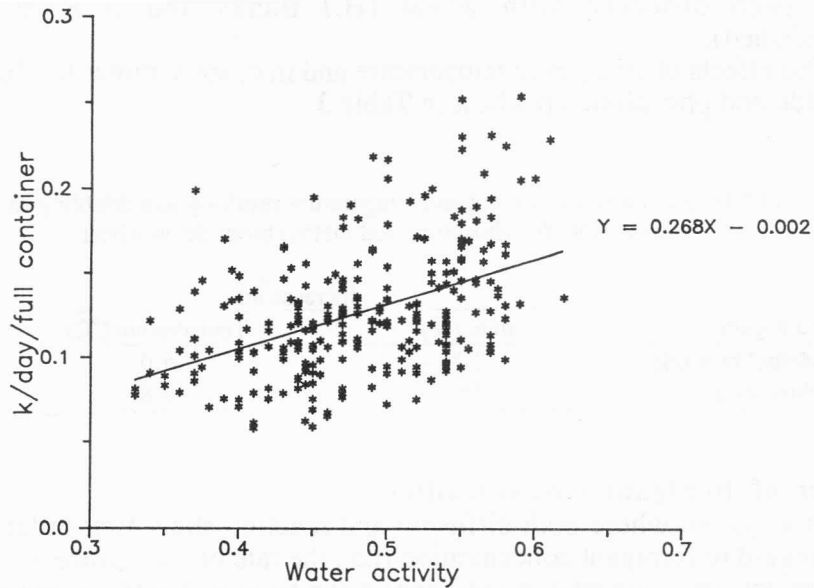
248

Fig. 6: Variation in sorption rate constant (k) for phosphine on samples of freshly harvested Australian wheat at 25°C, as a function of water activity (H.J. Banks and J.A. Cassells, unpublished).
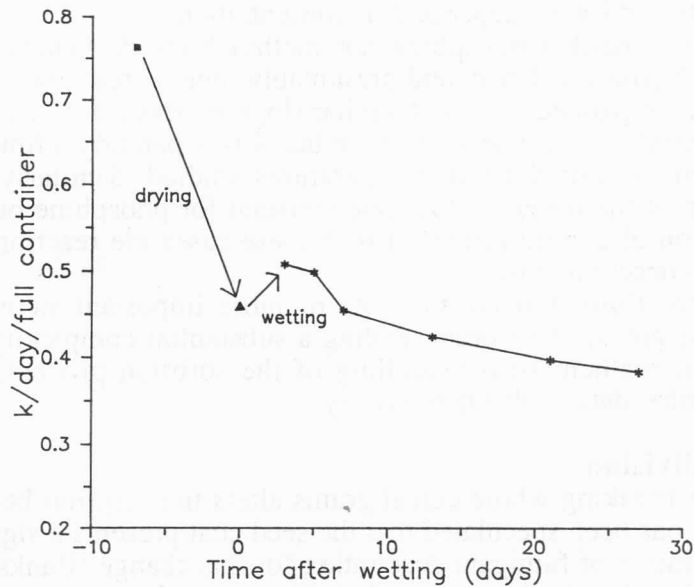

Fig. 7: Changes in sorption rate constant (k) for phosphine on a sample of paddy rice, (cv. Pelde). The freshly harvested sample was air-dried at 25°C from about 17-12.6% m.c. and then rewetted to 13.5% with water and held under sealed conditions (H.J. Banks and A. Kumanovska, unpublished).

249

have been observed with wheat (H.J. Banks and A. Kumanovska, unpublished).

The effects of changes in temperature and m.c. are summarised for methyl bromide and phosphine on wheat in Table 3.

Table 3: Change in moisture content and temperature resulting in a doubling of sorption rate constant for phosphine and methyl bromide on wheat

Fumigant	Increase in:	
	m.c. (%)	Temperature (°C)
Methyl bromide	2.8	6.0
Phosphine	3.0	9.8

Effect of fumigant concentration

In a system where both diffusion and reaction show first order kinetics with regard to fumigant concentration (i.e., the rate of each process is directly proportional to fumigant concentration) it can be expected that sorption curves for different concentrations of fumigant will be superimposable when concentration is expressed as a fraction of that initially present. An example of this is shown for methyl bromide sorption on sultanas (Fig. 8). This also implies that values of k are independent of concentration.

Unfortunately, neither phosphine nor methyl bromide behave in this simple way with wheat and rice, and presumably other cereal grains. Fig. 2 shows three, well separated curves of similar slope for three different methyl bromide concentrations on wheat, showing that k is apparently a function of concentration at each of the four temperatures studied. Similarly, Fig. 9 shows variation of the observed loss rate constant for phosphine on paddy rice as a function of concentration. In both these cases the reaction rate is higher at lower concentrations.

These observations indicate that one or more important steps in the sorption process are not first order, adding a substantial complexity to the already difficult mathematical modelling of the sorption process. Banks (1986) gives further data on this nonlinearity.

State of subdivision

Grinding or breaking whole cereal grains alters the sorption behaviour substantially. It has been speculated that the seed coat presents a significant barrier to penetration of fumigant accounting for this change (Banks 1986). However, it is clear that this is not the only influence and it may even make no difference at all.
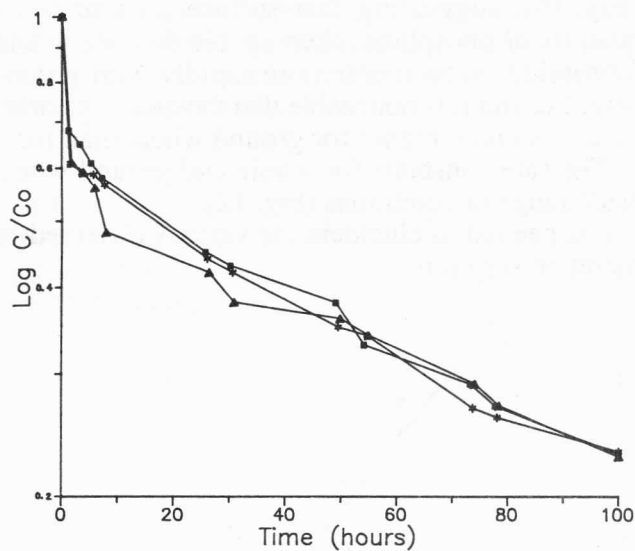
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Fig. 8: Sorption curves for methyl bromide on unprocessed sultanas at 25°C, 60% r.h., 95% filling ratio for 5 (■), 20 (*) and 60 (▲) g m^{-3} initial concentration (H.J. Banks and S.J. Hilton, unpublished).
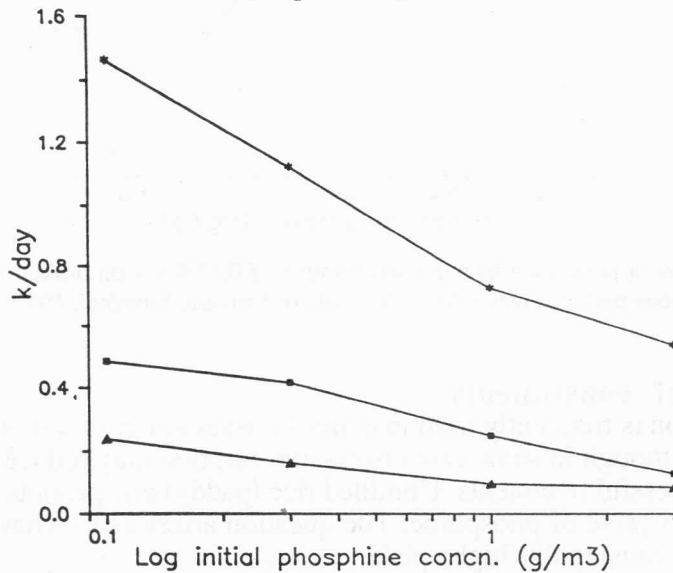

Fig. 9: Rate constants (k) for phosphine sorption on paddy rice (cv. Pelde) at 25°C, 60% r.h. at various filling ratios (25%, lowest curve; 50%, middle curve; 95%, upper curve) as a function of initial concentration (H.J. Banks and A. Kumanovska, unpublished).

251

Phosphine sorption on broken milled rice is strongly dependent on particle size (Fig. 10), suggesting that surface area of the particle may influence the quantity of phosphine taken up. No data are available for other grains. Methyl bromide reacts much more rapidly with ground wheat than intact kernels (Fig. 11) and it is noticeable that the quantity sorbed in the early part of the exposure is much higher for ground wheat than for intact kernels (about double). The rate constants for whole and ground wheat are linearly related over a wide range of conditions (Fig. 12).

Further work is needed to elucidate the various observed influences of state of subdivision on sorption.
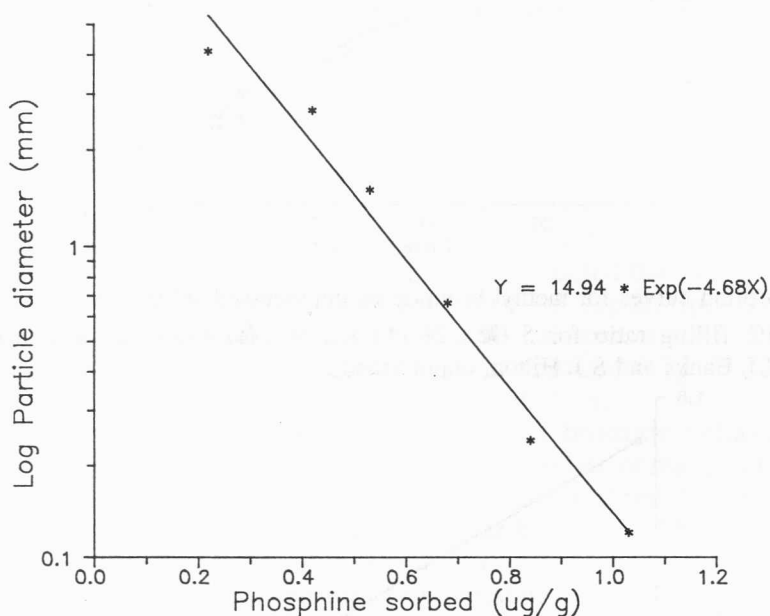

Fig. 10: Sorption of phosphine from a concentration of 0.37% v/v on broken white rice of various particle sizes after 48 hr. (data of Sato and Suwanai, 1974).

Influence of constituents

Fumigation is frequently used to control infestation in stored whole grains and legumes, though in some cases excessive sorption may reduce chances of routinely successful treatments. Unmilled rice (paddy) and peanuts in shell are particularly sorptive of phosphine. The question arises as to what part of the commodity is causing this high uptake.

Tables 4 and 5 show observed loss rate constants for paddy rice and peanuts in shell and calculated rate constants based on contributions from individual components in proportion to their presence by weight in the unhusked commodity. It can be seen that agreement between observed and

252

calculated is surprisingly good, given the difficulties of obtaining consistent sorption results with phosphine and the non-linear influence of concentration on sorption kinetics. The substantial contribution of rice hull and peanut shell to the overall sorption is noteworthy.

Table 4: Observed loss rate constants for phosphine (initial concentration 0.3 g m^{-3}, 25°C, 0.60 a$_w$) on paddy rice (cv. Pelde) and its milled products as compared with values calculated from the combination of values from the individual milling fractions (H.J. Banks and J.A. Cassells, unpublished)

Material	Observed[a] loss rate (d^{-1})	Calculated[a, b] loss rate (d^{-1})
Paddy	2.96	1.85
Brown rice	0.71	0.59
Hull	6.15	
White rice	0.38	
Bran	2.75	

[a]Rate constant per kg for a full system
[b]Calculated on the basis of 1 kg paddy giving 0.79 kg brown rice and 0.21 kg husk and 1 kg brown rice giving 0.91 kg white rice and 0.09 kg bran.
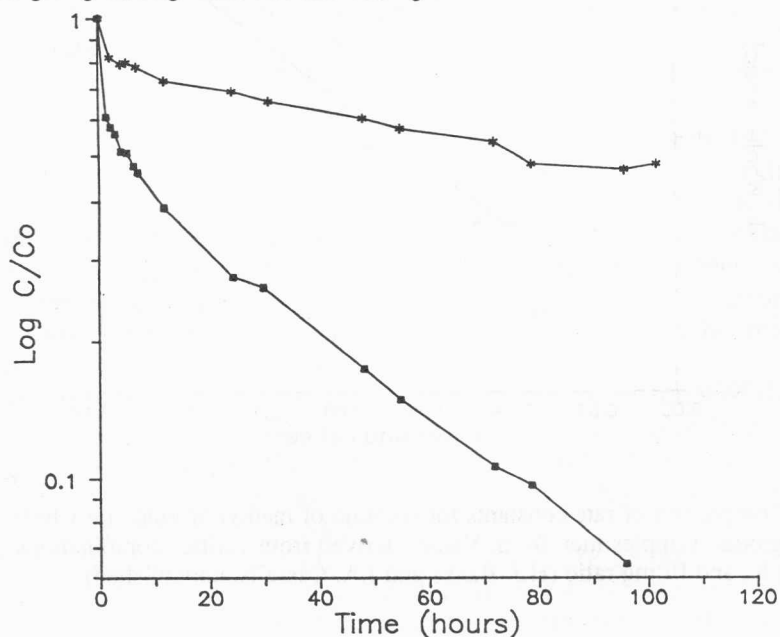

Fig. 11: Influence of grinding on the sorption curves for methyl bromide on wheat. Upper curve are whole wheat, lower curve are ground sample of the same wheat; both at 25°C, 10% r.h. with 60 g m^{-3} initial concentration (H.J. Banks and J.A. Cassells, unpublished).

Table 5: Observed sorption rate constants for phosphine on two varieties of peanuts in shell and shelled and for the husks, and calculated sorption rate constants for nuts in shell from data for isolated nuts and shell (15°C, 8.5% m.c., 0.05 g m^{-3} initial concentration) (H.J. Banks and J.A. Cassells, unpublished)

| | White Spanish | | Virginia Bunch | |
	Observed sorption rate[a]	Calculated sorption rate[b]	Observed sorption rate[a]	Calculated sorption rate[b]
Nuts in shell	1.50	1.66	0.984	1.24
Shell	5.01		2.12	
Nuts	0.540		1.028	

[a] Sorption rate constants given per day per kg for a full system
[b] Calculated on the basis of 1 kg of White Spanish peanuts yielding 0.75 kg nuts and 0.25 kg shell and 1 kg Virginia Bunch giving 0.80 kg nuts and 0.20 kg shell.
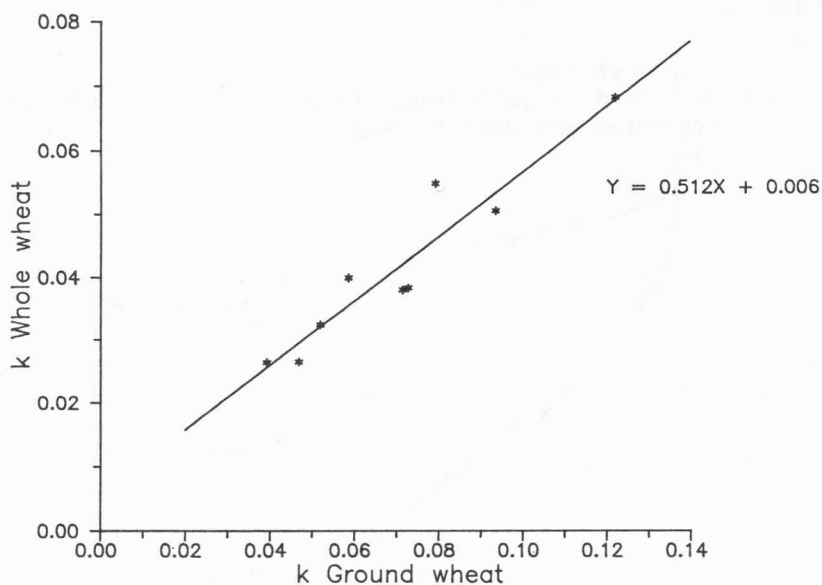

Fig. 12: Comparison of rate constants for sorption of methyl bromide on whole wheat and ground samples therefrom. Values derived from various combinations of dosage, r.h., and filling ratio (H.J. Banks and J.A. Cassells, unpublished).

Influence of exposure time and multiple treatments

It may be expected that the capacity for grain to react with fumigant will become exhausted if large quantities of fumigant are used over a long period or the grain is subjected to a series of dosages.

254

This does not appear to be so for methyl bromide on cereal grain, at least up to the limit set by the 50 ppm tolerance for bromide residues. Multiple dosing at normal rates add similar quantities of residue for each application, showing no change in capacity and kinetics. However, with phosphine exposures there is some evidence that the reactive capacity may be used up to some extent. Repeated fumigation of paddy rice leads to a decreased rate constant for sorption (Fig. 13). A much less pronounced decrease is observed for wheat (H.J. Banks and A. Kumanovska, unpublished).

While repeated exposure to phosphine may alter the kinetics of reaction with the grain, there is evidence that long exposures, such as may be experienced with the SIROFLO, technique, do not result in higher quantities of unchanged, sorbed phosphine. Fig. 14 shows quantities of sorbed phosphine in wheat, determined by the Brockwell (1978) method, resulting from continuous exposure of up to 6 months to two set phosphine concentrations. There was no obvious change in sorbed phosphine with duration of exposure. The phosphine levels in the grain were approximately proportional to the concentration applied.

RELEASE OF FUMIGANTS FROM GRAIN

Desorption phenomena have not been studied in nearly as much detail as sorption. Thus, there is no good quantitative data available on effects of substrate history, m.c., state of subdivision and many of the other factors influencing sorption behaviour for cereal grains.

Banks (1986) reviewed published literature on mathematical and quantitative descriptions of desorption. In general, desorption is diffusion-controlled with some studies on temperature dependence of the diffusion coefficient. Desorption from grains closely follows the form expected of diffusion of a substance, initially at even concentration throughout a spherical particle, into air containing a chemically-negligible concentration of the. Banks (1986) gives examples of this. The loss of methyl bromide from apples follows the same form (Fig. 15).

In the case of the reactive fumigant, methyl bromide, most of the sorbed unchanged material reacts with the grain constituents to give fixed residues and only a small fraction of the sorbed material desorbs during airing (Banks, 1986). Thus, the kinetics of loss of sorbed methyl bromide are generally similar in sealed and unsealed systems.

The quantitative data available on desorption are generally inadequate. Systematic studies are urgently needed in view of the importance of desorption to crucial aspects of fumigation technology: worker safety and levels of fumigant remaining in the product. Good data on kinetics of phosphine desorption from treated grain and similar durable foodstuffs are notably lacking.
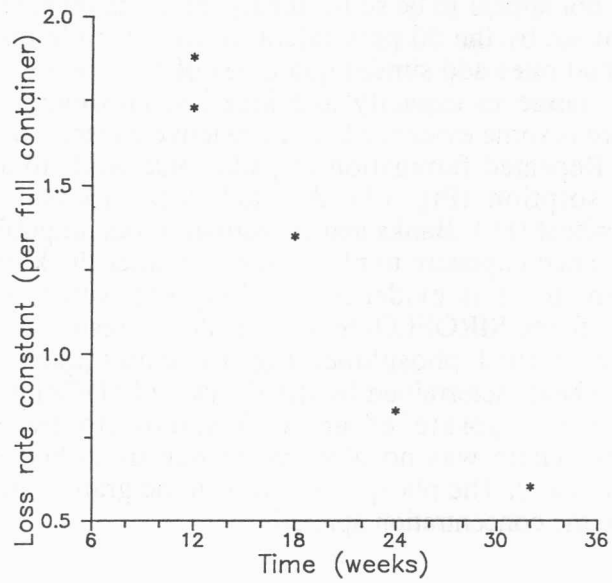
Fig. 13: Decrease in sorption rate constant for phosphine on paddy rice as a result of successive fumigations with 1 g m^{-3} phosphine (25°C, 60% r.h.) (H.J. Banks and A. Kumanovska, unpublished).
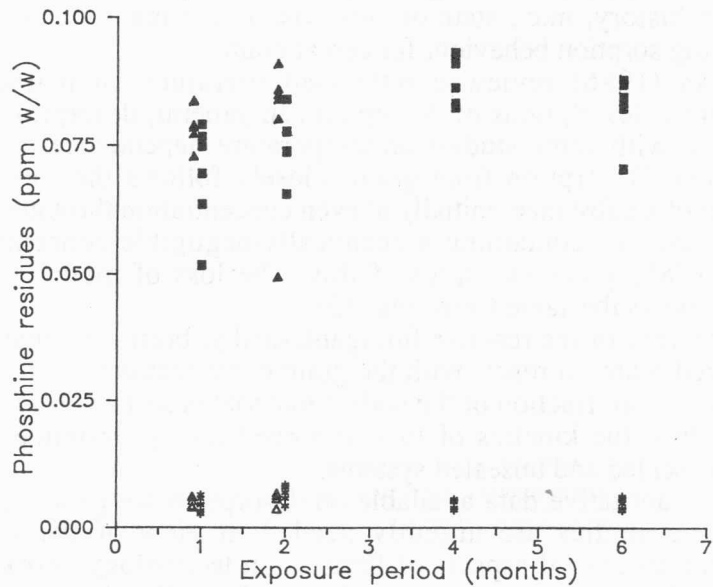
Fig. 14: Phosphine residues remaining in wheat (25°C, about 0.7 a$_w$) exposed continuously to 1 g m^{-3} (▲,■) or 0.1 g m^{-3} (Δ,✳) phosphine in air after airing for 24 hr (H.J. Banks and J.A. Cassells, unpublished).
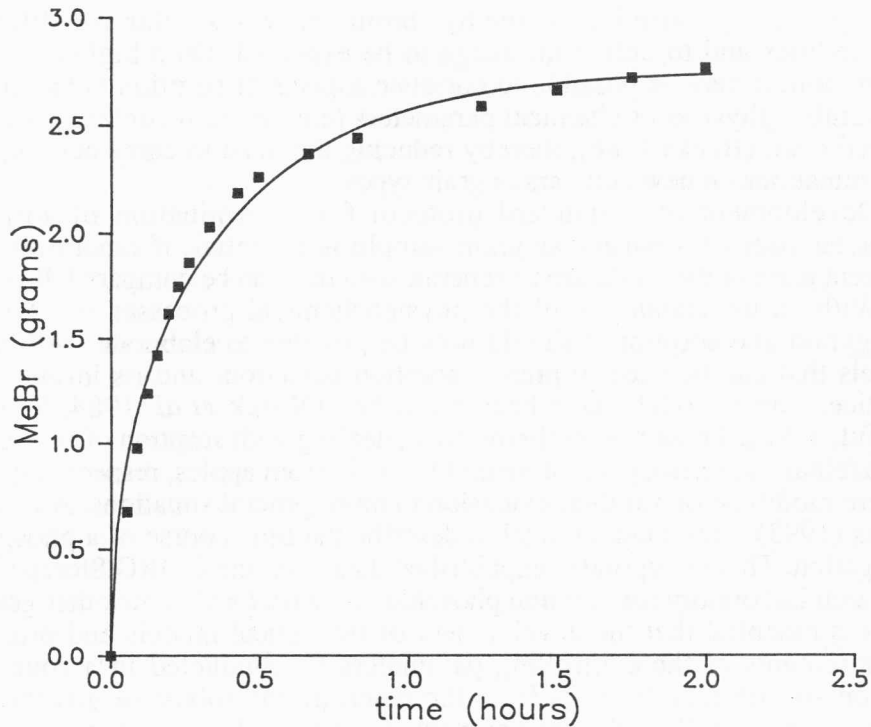
256

Fig. 15: Cumulative loss of methyl bromide from fumigated apples ventilated at 5 air changes per hour, fitted to loss curve expected for diffusion-controlled loss from a spherical particle (data of Sell and Moffitt, 1990).

CONCLUSION

The examples given here illustrate the complexity of sorption/desorption phenomena on grain with fumigants. Some progress has been made since the review of Banks (1986) in improving a quantitative understanding of these processes and, in particular, demonstrating which of the many factors involved in determining rates and quantities of fumigant sorption are dominant under particular conditions. It is clear that there is still much to be done in order to get a good working understanding of sorption to a level where quantitative data can be used reliably for prediction and decision-making in fumigation practice. In particular, the range of grains and similar commodities studied needs to be increased to gain a better measure of the range of values of the loss rate constant, diffusion coefficient and sorption capacities that occur. Local cultivars and grains produced under a variety of growing conditions need to be checked for abnormal sorption behaviour. The influence of m.c. and temperature needs further study. There is also a need to develop generalisable conclusions to reduce the complexity to manageable levels. Thus, it would be useful to show if the influence of temperature and water

257

activity on, say, sorption of methyl bromide, was similar for different commodities and to define the range to be expected. On a higher level of integration, it may be possible to correlate aspects of sorption behaviour to measurable physical or chemical parameters (e.g., protein content, hardness of seed coat, (Banks 1986), thereby reducing the need to carry out sorption determinations on new cultivars or grain types.

Development of a standard protocol for determination of sorption characteristics of a particular grain sample is essential, if laboratories in different parts of the world are to generate data that can be compared directly.

With an understanding of the physicochemical processes involved in fumigation and sorption it should now be possible to elaborate well-based models that can be used to predict sorption behaviour and its influence in practice. Some models have been published (Noack *et al.* 1984, Sell and Moffitt, 1990). These are semi-empirical, dealing with sorption of phosphine on hazelnuts and desorption of methyl bromide from apples, respectively, and require modification for their extension to more general situations. Annis and Banks (1993), presented a model to describe the time course of a phosphine fumigation. This incorporates unpublished data from the CSIRO Stored Grain Research Laboratory for sorption phosphine on wheat and some other grains.

It is essential that the development of theoretical models and practical measurements of the controlling parameters be conducted in a concerted fashion so that each benefits from the other, giving robust results that are usable in practice. With the development of computer-based expert systems, it should be possible to use mathematically complex models to produce practically simple decision recommendations (e.g., dosage rate for particular situations, allowing for commodity, temperature, m.c., target pest etc.) without necessitating fumigators to perform difficult calculations from a confusing array of data. Quantitative sorption data will certainly be required as input.

The use of fumigation is under threat in many parts of the world. Concerns include worker safety, environmental exposure of persons near fumigations, and environmental effects. Application of knowledge of sorption to improve fumigation technology, including prediction and minimisation of emissions from treatments, should help to counter those concerns. It is hoped that this will help preserve this most valuable technique for control of pests in food.

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Appendix 1 - Calculation of sorption rate constants

The slope of the line describing the semilogarithmic loss of concentration of fumigant in a sealed system with time, $d\ln (c/c_0)/dt$ was corrected for the filling ratio of the system, f, and the mass of commodity present to give the sorption rate constant, k, according to the following formula:

$$k = \frac{d\ln(c/c_0)}{dt} \frac{1}{f\rho_{bulk}}$$

where the filling ratio is given by the ratio of mass of commodity present in the system to the mass present when full and ρ_{bulk} is the bulk density of the commodity.