Navarro, S. and Donahaye, E. [Eds.](1993) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Grain Storages, Winnipeg, Canada, June 1992, Caspit Press Ltd., Jerusalem, pp299-312.

A PREDICTIVE MODEL FOR PHOSPHINE CONCENTRATION IN GRAIN STORAGE STRUCTURES

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ABSTRACT

The average concentration of phosphine in a structure fumigated with phosphine released from a metallic phosphide preparation is determined by the interaction of several physical and chemical parameters. A stepwise mathematical model has been developed in which the time course of phosphine concentration is calculated from the amount of phosphide applied, the rate of phosphine liberation, total storage volume, degree of filling, gas loss due to leakage, and the amount of phosphine sorbed on the commodity. Corrections are made for the influences of temperature and moisture on the rate of phosphine liberation and sorption. The current model is based on the treatment of wheat but is easily adaptable to other commodities with known sorption characteristics. The model enables evaluation of application rates, for particular situations, against known toxicological objectives expressed as either target concentration-time products (Ct) or minimum concentrations after prescribed intervals of time and also rates of emission of phosphine into the atmosphere.

INTRODUCTION

Phosphine is one of the very few reliable fumigants available to the grain industry. Therefore it is important that it be used properly so that its value not be compromised by problems brought on by its misuse. The most obvious of these problems is development of resistance arising from significant survival of insects after populations have been subjected to sub-optimal dosages. A mathematical model has been developed to describe the time course of phosphine concentration, thereby making it possible to simulate many of the types of storage situations that may occur. The rationale of the model is very simple: the concentration of a gas in a sealed structure is determined only by the amount of gas added, the gas-space to which it is added, the amount of gas leaking out, the amount of air leaking in, and the amount of gas reacting with or sorbed onto solids within the structure.

The rate of phosphine production from a metal phosphide preparation can be determined in the laboratory under a range of well controlled conditions. It has been shown that the rate of liberation can be modelled satisfactorily using two simple equations: one for the early part of phosphine evolution and one for the latter part (Banks, 1991). The rate of evolution is controlled by the rate at which water becomes available for reaction. This, in turn, is determined by the absolute water content of the surrounding air (or the moisture content [m.c.] of the grain), and the rate of air flow over the preparation.

Leakage of phosphine outwards, and air inwards, is a function of the degree of sealing of the structure. Leakage will not only vary between structure types (Annis and Banks, 1993) but will also vary within a particular structure type due to differences in sealing, history of use, and local micro- and macro-meteorological conditions. Gas holding is also likely to vary temporally in the same structure due to the variable nature of meteorological conditions both on a day to day and seasonal basis. The true leak rate of a structure would be best measured using a non-sorbed tracer gas, but this is rarely possible. Approximations can be made from experience of a particular storage on the basis of typical observation of the decrease in fumigant concentration with time. Where this is not available, approximations of leakage can be made with reference to a pressure test standard. When there is no objective measurement of sealing, i.e., knowledge of the actual leak rate or a pressure test, it is possible to use a leakage rate typical of a type of storage structure (Table 1), modified by an expert view of its level of sealing.

Table 1: Typical gas leakage for a range of storage types (based on Annis and Banks, 1993).

Storage type	Typical leakage rate as % day^{-1} *
Unsealed structure	>10%, >100% possible
Sealed above ground rigid structure	5% at pressure test standard 5 - 10% marginally sub-standard
Sealed grain bunker	2-5%
Sealed bag stack	1-2%
Underground bunker	<1%

*Leakage rate is the volume of gas lost from the enclosure during one day, divided by the volume of gas contained and expressed as a percentage. For discussion of this rate constant and its use and derivation, see Banks and Annis (1984).

The gas volume within a filled storage structure can be determined from the structure volume, and the density and mass of material contained in the enclosure. The volume of a structure is frequently not known but can, of course, be estimated from its rated capacity. The mass of material in a storage is usually known, and when not known, it can be estimated if the filling ratio and structure volume are known. In fact, given two values out of total volume, gas volume, filling ratio and mass of commodity, it is possible to calculate the remainder if the type of commodity and its solid density are known.

Although sorption of phosphine by grains may be considerable, it is not well documented. There are reports showing that in particular cases, sorption may be the dominant cause of phosphine loss from sealed storage structures (Annis, 1990). General models of fumigant sorption exist (Banks, 1985); however, the parameters needed to apply these to the sorption of phosphine on a range of cereal products are not well established. It is, however, possible to use empirical models to describe phosphine sorption onto specific commodities in the laboratory (Banks, 1993). These models calculate the amount of phosphine sorbed with water activity, temperature and gas concentration.

In this paper, we will illustrate a model that uses four components, namely: rate of phosphine release, leakage, volume, and sorption, to predict the time course of a phosphine fumigation. Some simulation runs of field applications used for validation of the model are shown, and some of its past and current uses are discussed.

THE MODEL

The particular implementation of the model discussed here uses Microsoft "EXCEL" software as a convenient framework, permitting easy input, output and calculation. Implementation using other spreadsheet packages and languages is equally possible.

Inputs

The parameters needed to complete the calculations are given in Table 2. Many are derived from information supplied by the user and are easily changed. Others are incorporated in the programming of the model as they need to be changed less frequently.

Calculation

Calculation is by a simple stepwise process updating the amount of phosphine present at each finite time step, for, the current amount of phosphine gained during the production process. Phosphine production is calculated using the data of Banks (1991). Losses due to sorption are calculated on the basis of an empirical mathematical model describing the sorption observed by Banks (1993). These values were applied in the present model, along with loss due to leakage, to the amount of phosphine present as enclosure. The volume of a structure is frequently not known but can, of course, be estimated from its rated capacity. The mass of material in a storage is usually known, and when not known, it can be estimated if the filling ratio and structure volume are known. In fact, given two values out of total volume, gas volume, filling ratio and mass of commodity, it is possible to calculate the remainder if the type of commodity and its solid density are known.

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Table 2: Parameters used to run the model.

Group	**Parameter**	**Notes**
Volume related	Gas volume	*b*
	Structure volume	*b*
	Mass of commodity	*b*
	Filling ratio	*b*
	Commodity type	*a*
	Commodity density	*c*
Internal environment	Temperature	*a*
	Moisture content	*a*
	Water activity	*b*
	Moisture content/Water activity relationship	*c*
	Rate of air flow across phosphide preparation	*d*
Leak rate	Known or assumed by user	*b*
	From storage type	*b*
	Typical leak rates for storage types	*c*
Applied phosphine dose	Grams phosphine applied	*b*
	Grams phosphine per m^3 of total volume	*b*
	Grams phosphine per tonne of commodity	*b*
Sorption	Commodity	*a*
	Relationship between sorption, water activity and temperature	*c*
	Sorption factor relating sorption level to a standard sorption (currently average sorption for a sample of Australian wheats)	*a*
Control of model	Time step size	*e*

Notes

a Normally supplied by user, otherwise assumed value may not be appropriate.

b May be supplied by user or calculated by model if other adequate information is available.

c Values intrinsic to model may be modified in the light of new knowledge by expert user.

d Value changeable by user but usually not important as its value is not critical over a large range. Only needed where moisture availability is limiting.

e Model has been tested over a wide range of time steps. The only reason for varying is to conveniently change the length of the simulation.

first order decay constants for the length of the time step. The full set of parameters and equations used to simulate the fumigation of wheat with aluminium phosphide tablets are shown in Appendix 1.

Output

The output is designed to present results in a range of forms appropriate to the needs of several different types of users.

Graphical outputs

Concentration data

The estimated average concentration over time.

The maximum possible concentration, assuming no leakage or sorption.

Observed average concentration.

Ct *data*

The cumulative Ct product calculated by integration of the concentration curve.

Emitted phosphine

Emission in mass per unit time during the fumigation.

Cumulative emission during fumigation.

Biological data

Both the concentration data, and Ct data as graphical outputs indicate the approximate duration of the pupal stage of *Sitophilus* spp. under the temperature and moisture conditions of the simulation.

Numeric outputs

Concentration data

Phosphine concentration in g m^{-3} and ppm at specified times (5, 7, 10, 14, 21 and 28 days).

Ct *data*

The time to reach a preset Ct product, e.g., 150 g h r m^{-3}.

The Ct at 5 and 10 days.

An approximation of the pupal duration of *Sitophilus* spp. (see above).

Data values

A list of the supplied and calculated input values.

EXAMPLES OF VALIDATION

The model has been tested over a wide range of experimental and semi-commercial phosphine fumigations (30 individual treatments). In general, simulation of observed data is adequate for purposes such as estimating concentrations at pre-set times or calculating the time until Ct targets are met. The complete set of data required for a full simulation was rarely collected in these data sets. However, as the three examples of simulation runs presented here illustrate, the model can simulate concentration data over a wide range of conditions and storage types. This, however, requires a combination of known parameters and estimated parameters, e.g. Examples 1, 2, and 3, shown in Table 3. Good fits were obtained by minor adjustments of the controlling parameters. The examples shown have been selected from the much larger set to illustrate the good fit obtainable over a range of vastly different storages: very large and very small, sealed and unsealed.

Table 3: Parameters used. Example 1 - a small poorly sealed farm bin; Example 2 - a well sealed 16,000-tonne capacity horizontal storage; and Example 3 - a sealed drum.

	Example			Units
	1	2	3	
Grain mass	3.95	13,060	1.21	tonnes
Total volume	6.25	33,100	1.73	m^3
Filling ratio	1.0	0.59	1.0	
Commodity	wheat	wheat	wheat	
Temperature	20	20	18	°C
Moisture content	10	9.3	10	%
Leak rate	130	5.5	1.8	$\% d^{-1}$
Rate of air flow *	0.005	0.003	0.005	m^3h^{-1}
Sorption factor *	1	1.4	0.1	
Gas source	Tablets	Blankets	Pellets	
Total dose	10	26,395	0.1	g PH_3

* as defined in Table 2.

DISCUSSION

For a phosphine fumigation to be effective it is necessary to ensure that there is an adequate phosphine dosage available to the insects. So far, this paper has shown that many factors are likely to influence this in real fumigations. This is further complicated by the range of toxicological criteria that have been proposed as targets for efficacious phosphine fumigations. It is not the aim of this paper to discuss the magnitude of these targets as they vary among various researchers, regulatory bodies, fumigation manuals and insect species. A brief mention is made of their nature as this influences the nature of, and the motivation for, the model.

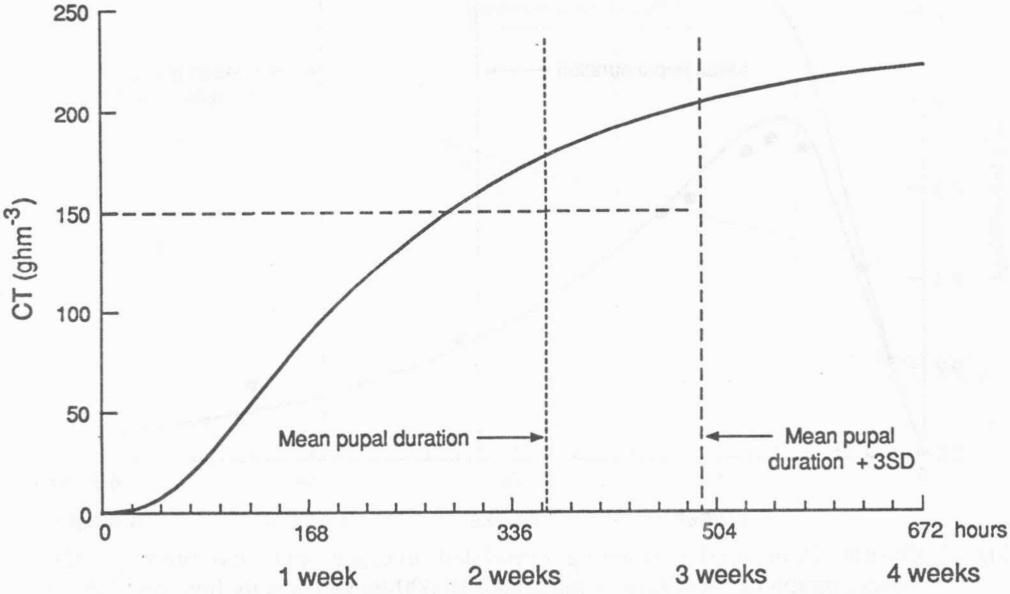

Fig. 1: Output from model showing simulated average Ct product in the sealed 16,000-tonne capacity horizontal storage described in Example 2.

Examples of toxicological targets for a phosphine fumigation

- A general target Ct product (e.g., 150 g h m^{-3} is often quoted). The Ct in reality is only a rough target as it is not truly independent of concentration, and different target Cts apply to different concentrations or exposure periods.
- A dosage in terms of Ct or concentration and time that will kill the most tolerant stage of the most tolerant species.
- A dosage-time combination designed to allow the development of a tolerant stage (e.g., pupae) to a susceptible stage (e.g., adults) and then to kill that stage.
- A minimum, above which the concentration has to be maintained for a defined period (e.g., 5 or 10 days).

The model shows that in the case of Example 2 a dose of two grams of phosphine per tonne stored will give a Ct of 150 g . h . m^{-3} (Fig. 1) in about 12 days and that a concentration of > 0.1 g . m^{-3} should be maintained for about 24 days (Fig. 2), both suggesting that the dose rate was adequate for

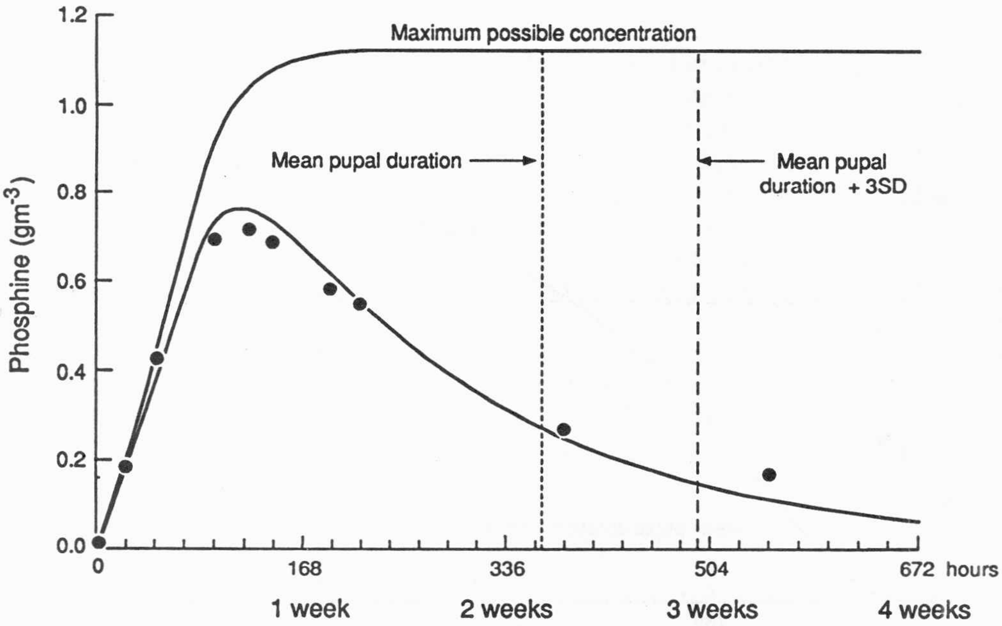

Fig. 2: Output from model showing simulated average and maximum possible concentration of phosphine in the sealed 16,000-tonne capacity horizontal storage described in Example 2. ● Observed average concentration during actual fumigation.

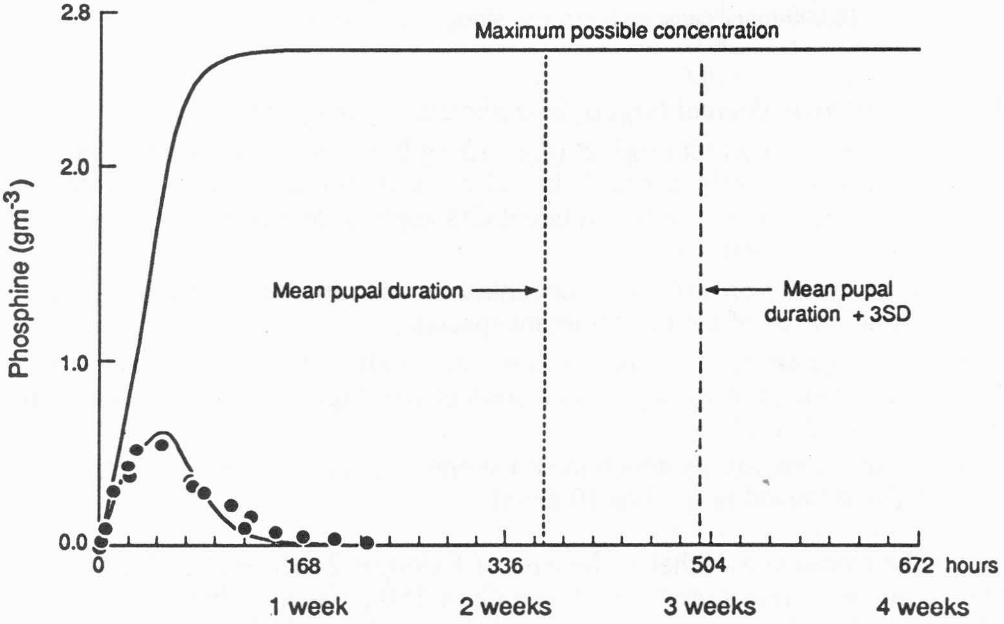

Fig. 3: Output from model showing simulated average and maximum possible concentration of phosphine in the poorly-sealed farm bin described in Example 1. ● Observed average concentration during actual fumigation.

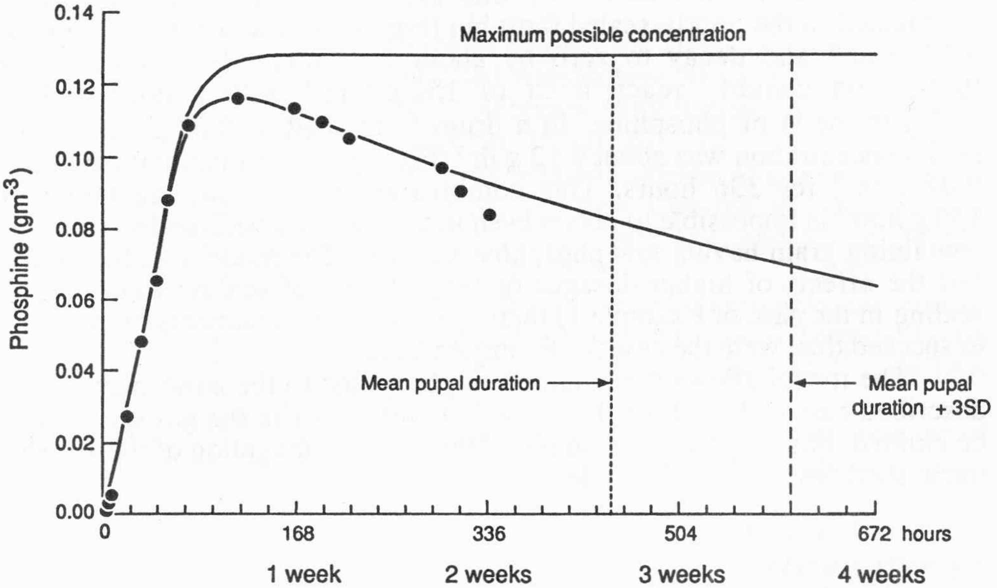

Fig. 4: Output from model showing simulated average and maximum possible concentration of phosphine in the well-sealed drum described in Example 3. ● Observed average concentration during actual fumigation.

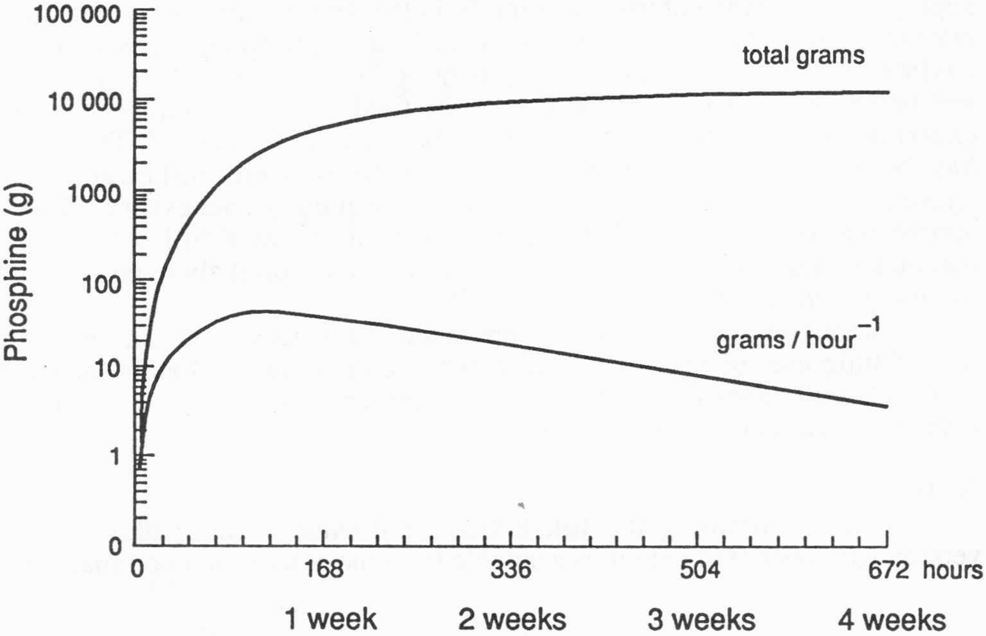

Fig. 5: Output from model showing simulated phosphine emissions to the atmosphere from a fumigation of the sealed 16,000-tonne capacity horizontal storage described in Example 2.

the particular circumstances of this fumigation. The concentrations maintained in the poorly-sealed farm bin (Fig. 3) peak at a concentration of 0.03 g.m^{-3} and decay to zero by about 200 hours. In this case, the fumigation cannot reach a Ct of 150 g.h.m^{-3} with a normal dose (2.5 g.tonne^{-1}) of phosphine. In a drum fumigated at 0.08 g.tonne^{-1} the peak concentration was about 0.12 g.m^{-3} (Fig. 4) and was maintained above 0.08 g.m^{-3} for 336 hours. This combination means that the target of 150 g.h.m^{-3} is impossible to obtain even in the case of a well-sealed structure containing grain having low phosphine sorption. The model can be used to test the effects of higher dosages or better levels of sealing (particularly sealing in the case of Example 1) thereby prescribing treatments more likely to succeed than were the case for Examples 1 and 3.

The model allows the emission of phosphine to the atmosphere to be described easily. Phosphine that is neither sorbed nor in the gas space must be emitted. Fig. 5 shows an example of this for the fumigation of the 16,000-tonne shed described in Example 2.

CONCLUSION

A model has been described that can be used to simulate successfully the average concentration of phosphine in a structure under fumigation using metallic phosphide preparations. The model has many types of output appropriate to a range of uses, varying from the determination of correct dose rates to the investigation of the amount and rate of phosphine released to the environment. The model allows treatment options to be tested theoretically, and hence optimised, before testing in the field. Thus, the number of field experiments needed to establish dosage schedules can be reduced. The model has been shown to match field observations well, although some approximation of input parameters is frequently necessary. These approximations are an essential part of the model, as a full set of input parameters has rarely been recorded in the past and is unlikely to be obtained routinely in the future.

Although the model is a good predictor of averages, in its current form, it is of little use for prediction under extreme conditions. Models for these more difficult cases are much more complex and are likely to require too many input parameters to be useful.

Note

A disk containing the full EXCEL software version, plus a basic version with restricted output, is available from the authors at a nominal cost.

REFERENCES

Annis, P.C. (1990) Sealed storage of bag-stacks: status of the technology. In: Fumigation and Controlled Atmosphere Storage of Grain: Proc. Int. Conf., Singapore, 14-18 February 1989 (Edited by Champ, B.R. *et al.*), ACIAR Proceedings No. 25, pp. 203-210.

Annis, P.C. and Banks, H.J. (1993) Is hermetic storage of grains feasible in modern agricultural systems. In: Pest Control and Sustainable Agriculture (Edited by Corey, S.A., Dall, D.J. and Milne, W.M.) CSIRO, Melbourne, Australia. pp. 479-482.

Banks, H.J. (1985) Sorption and desorption of fumigants on grains: mathematical description. In: Pesticides and Humid Tropical Grain Storage Systems (Edited by Champ, B.R. and Highley, E.), ACIAR Proceedings No. 14, pp. 179-193.

Banks, H.J. (1991) Influence of water and temperature on the release of phosphine from aluminium phosphide-containing formulations. *J. stored Prod. Res.*, **27**, 41-56.

Banks, H.J. (1993) Uptake and release of fumigants by grain: sorption/desorption phenomena. Proc. Int. Conf. Controlled Atmosphere and Fumigation in Grain Storages, Winnipeg, Canada, June 1992 [Edited by Navarro, S. and Donahaye, E.], Caspit Press Ltd., Jerusalem, pp. 241-260.

Banks, H.J. and Annis, P.C. (1984) Importance of processes of natural ventilation to fumigation and controlled atmosphere storage. In: Controlled Atmosphere and Fumigation in Grain Storages, (Edited by Ripp, B.E. *et al.*), pp. 299-323. Elsevier Sci. Publ. Co., Amsterdam, Holland.

APPENDIX 1 Calculations used for construction of the model

Symbols used

Symbol	Meaning	units
α	Constant of kinetics equation	m^3h^{-1}
β	Constant of kinetics equation	$m^6g^{-1}h^{-1}$
δG	Phosphine released during time step	g
δt	Time step	h
a	Constant for first evolution process	
A_1	Asymptote second process	g
A_2	Maximum evolution rate	$g\,h^{-1}$

A_w	Water activity	
C_t	Phosphine concentration at time t	$g\ m^{-3}$
D_{app}	Grams phosphine applied	g
e	Base of natural logarithm	
F_S	Sorption factor	
G_{dose}	Cumulative dosage (concentration by time product) at time t	$g\ h\ m^{-3}$
G_t	Mass of phosphine evolved at time t	g
H_{abs}	Absolute water content of air in contact with preparation	$g\ m^{-3}$
H_{rel}	Relative humidity	%
K_1	Index second production phase	
K_2	Air flow rate factor	
K_e	Leak rate	d^{-1}
K_s	Exponent in equation for sorption loss	d^{-1}
M_c	Moisture content	%
M_{cross}	Mass of phosphine evolved at change from process 1 to process 2	g
M_t	Mass of phosphine gas at time t	g
n	Exponent of equation for evolution process 1	
P_{dur}	Estimated duration of pupal stage of *S. oryzae* at T °C and H_{rel}	h
Q	Air flow across phosphide preparation	$m s^{-1}$
R_f	Filling ratio	
T	Temperature	℃
t_{50}	Time to 50% decomposition	h
t_{cross}	Time of change from process 1 to process 2	h
t_i	Current elapsed time from start of fumigation	h
t_{zero}	Time zero for evolution process 2	h
V	Gas volume	m^3

Initial pre-set values and calculations

Calculation of values related to the water content of the silo atmosphere and subsequently used for the calculation of phosphine production rates, sorbtion loss, and pupal duration.

$$H_{rel} = \frac{100(M_C - 4.85092)}{12.5982}$$

$$A_W = \frac{H_{rel}}{100}$$

$$H_{abs} = A_W\,(4.847 + 0.345T - 0.010167T^2 + 0.00017197T^3 + 0.0000017867T^4$$

Values of fixed parameters used to calculate phosphine production based on production from Phostoxin tablets

$\alpha = 0.00449$

$\beta = -0.0000325$

$n = 1.15$

$A_1 = 0.98$

$M_{cross} = 0.7$

$K_2 = 146.95$

Calculation of variable parameters used in the calculation of phosphine production

$$A_2 = \alpha H_{abs} + \beta H_{abs}^2$$

$$t_{50} = 0.5nA_2\left(1 - e^{-k_2 Q}\right)$$

$$a = \frac{0.5}{t_{50}^n}$$

$$t_{cross} = \left(\frac{M_{cross}}{a}\right)^{\frac{1}{n}}$$

$$K_1 = \frac{\left(ant_{cross}\right)^{n-1}}{1 - M_{cross}}$$

$$t_{zero} = \frac{\ln(1 - M_{cross}) + t_{cross}K_1}{K_1}$$

Calculation of the sorbtion constant

$$K_s = \frac{0.2785 R_f A_w F_s e^{20.4589-(639.78(t+273.16))}}{8.87073}$$

Calculation of the duration of the pupal stage

$$P_{dur} = 16.41 + (0.011H_{rel} + 4.727T - 0.4587T^2 + 0.01352T^3 - 0.0001301T^4)$$

Calculations used in the step-wise portion of the model

Equations used to update the mass of phosphine present at time t_{i-1} to that present at time t_i

$$t_i = t_{i-1} + \delta t$$

$$G_t = at_i^n \qquad t_i < t_{cross}$$

$$G_t = G_{dose}\left(1 - e^{-k_1(t_i - t_{zero})}\right) \qquad t_i \geq t_{cross}$$

$$\delta G = G_t - G_{t-1}$$

$$M_t = M_{t-1} + \delta G + e^{\delta t(K_e + K_s)}$$

$$C_t = \frac{M_t}{V}$$

Calculation of cumulative Ct product

$$D_t = D_{t-1} + 0.5\delta t(C_{t-1} + C_t)$$