Descriptive Model of Phosphine Concentrations and Emission Rates During Controlled Aeration of Fumigated Tobacco Warehouses[1]

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ABSTRACT A model was developed to describe the emission of phosphine gas from the interior of a tobacco warehouse to the outside during controlled aeration after fumigation of the warehouse. We used a fan/stack exhaust system to control the aeration, but other systems can be used. Model inputs include phosphine concentrations in the warehouse just prior to aeration, warehouse characteristics, and characteristics of the system used to release phosphine. Model outputs for any time during aeration include the emission rate of phosphine from the warehouse, the phosphine concentration remaining in the warehouse, and suggested exhaust rates that help fumigators comply with regulatory standards on phosphine emission rates. (Exhaust rate refers to release of air/phosphine mixture from the warehouse [=volume/time], but phosphine emission rate refers to the amount of phosphine [=mass/time]). The model also calculates how much exhaust rates can be increased at regular time intervals to hasten aeration without exceeding the initial phosphine emission rate. The model can be used by fumigators to comply with regulatory standards on phosphine emissions, and by regulators to assess that compliance. Diffusion of phosphine from the packaged tobacco (cases) into the freespace of the warehouse and its impact on the model are discussed.

KEY WORDS Aeration, degassing, phosphine, tobacco warehouse, fumigation

Fumigation with phosphine gas is the preferred means of insect control in many stored commodities throughout the world. It is the only widely accepted method in the United States, and much of the world, for rapidly disinfesting large tobacco warehouses of the cigarette beetle, *Lasioderma serricorne* (F.).

A typical fumigation includes a 4-day fumigation period during which the warehouse is totally sealed, followed by a 3-day aeration period. Tobacco warehouses were originally built well away from communities, but community expansion has now reached many warehouses. Therefore, the conventional practice of aerating warehouses by simultaneously opening all doors and vents can release large concentrations of phosphine toward nearby human populations. Phosphine dissipates rapidly (Fluck and Novobilsky 1973) and is not known to be a serious health threat, but new government regulations limit phosphine emissions.

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Many states are starting to regulate the emission of airborne chemicals including phosphine. The amended North Carolina Air Pollution Control Requirements (Section 15 NCAC 2D) limit phosphine concentrations beyond property boundaries to $\leq$ 0.1 ppm. The state of Virginia's standard is more stringent at $\leq$ 0.025 ppm. These regulations are meant to deal with the health and safety of citizens near warehouse fumigations rather than with environmental contamination.

The total amount of phosphine released during aeration is the same regardless of how aeration is accomplished. However, with conventional aeration the fastest release of phosphine is during the first few minutes after a warehouse is opened. This is when concentrations downwind from the warehouse will be the greatest, and regulatory compliance will be the most difficult. This peak concentration outside can be minimized by a more gradual release of phosphine. The model often used to assess regulatory compliance ("SCREEN", Version1.1) (Brode 1988), and similar models, directly and linearly correlate gas concentration at a given distance from a warehouse to the mass of gas released from the warehouse per unit time (=phosphine emission rate).

The maximum allowable phosphine emission rate per warehouse will vary from one storage complex to another. Different complexes differ in their number of warehouses and total volume. Individual warehouses differ in tightness, and therefore have different phosphine concentrations when aeration starts. Property boundaries may be very close or very far from the nearest fumigated warehouse. All this means that fumigators need the ability to control phosphine emission rates according to local conditions.

One way to do this is to exhaust phosphine with a control apparatus such as the fan/stack exhaust system which we used. The warehouse remains otherwise sealed. By controlling the exhaust rate (in this case the fan speed) the fumigator can control the rate of aeration and reduce the peak emission rate of phosphine.

The applicator can also use the control apparatus to take advantage of the constant lowering of warehouse concentrations due to aeration. The maximum allowable exhaust rate (volume air and phosphine exhausted per unit time) at the start of aeration is dictated by the maximum allowable phosphine emission rate. (The latter is determined by the aforementioned regulatory models.) However, as phosphine concentrations decline during aeration, the applicator can increase exhaust rates without exceeding the allowable emission rate. By adjusting exhaust rates frequently, the applicator minimizes aeration time while complying with emission standards.

We have developed a model to describe such controlled aeration. The model can be used by both the applicator to comply with standards and the regulator to assess such compliance. It describes phosphine emission rates from the warehouse, concentrations inside, and exhaust rates to achieve desired emission rates under specific site conditions. It also calculates the periodic increases in the exhaust rate that are allowable as the warehouse concentration declines. The model is designed to be sufficiently comprehensive, but simple enough to be used by an applicator at the fumigation site.

Model Development

Background. The model considers three sites where phosphine may be or may move to: (1) the void space within the tobacco packages stored in the warehouse (=product), (2) the space within the warehouse not occupied by the packages (=freespace), and (3) the outside of the warehouse. Examples of tobacco packages are cases and hogsheads of tobacco. Within the package, phosphine is assumed to be only in the volume not occupied by tobacco. This void space within the package of tobacco is approximately 70% of the volume of most commercially packed cases and ≥ 70% of most other commercial packages (unpubl. data). Too little is known about phosphine sorption on and desorption from tobacco to make assumptions, except that sorption and desorption have little impact on the model.

Phosphine is assumed to be uniformly distributed throughout the freespace. Phosphine (PH_3) has about the same specific density (=1.18 at 25°C) as normal air (=1) and disperses readily in all directions. If uniform distributions becomes doubtful and crucial to model behavior, a simple solution is to ensure that the exhaust system removes phosphine from a number of sites within the warehouse. For example, this can be done with porous or branching uptake hoses dispersed within the warehouse.

Phosphine in the product must move to the freespace before it can be exhausted to the outside. It does this by diffusion, the rate of which depends on the concentration difference between the product and the freespace. Because the freespace volume is always greater than the product volume, phosphine moving from product to freespace quickly becomes diluted. At the start of aeration the two concentrations are usually about equal. In very leaky warehouses, the concentration in the product tends to be greater than in the freespace.

Model development and field validation were based on a fan/stack system to exhaust phosphine. Validation was done during several commercial fumigation/aerations on different dates in different warehouses. A hose (30-cm diam.) placed inside the otherwise sealed warehouses collected air from the center of the 14,300-m^3 warehouses and directed it to the fan and stack outside. The fan had a maximum speed of approximately 600 m/sec and the stack was 30 cm in diameter.

In using such an exhaust system, air must enter the structure to displace the air being removed. A small opening or perhaps even normal porosity of the structure (e.g., minute openings in seams of the structure) should provide sufficient intake of air. In our validation tests, displacement air was provided through a slightly opened vent on the wall opposite the exhaust stack. The vent provided an opening of approximately 200 cm^2.

Time consideration. We considered the variable, time, in two ways. One, the smaller time frame, deals with each period when changes in phosphine emission rates and warehouse concentrations follow an exponential decay (Fig. 1). The exhaust rate is fixed. For development of equations, each period was broken down into N time subunits of length, Δ. Therefore, the length of each period = $N \bullet \Delta$. The larger time frame covers the entire aeration period, in practice about three days (Fig. 1). This time frame is denoted by the variable, T, where $T = 0, \tau$ and the

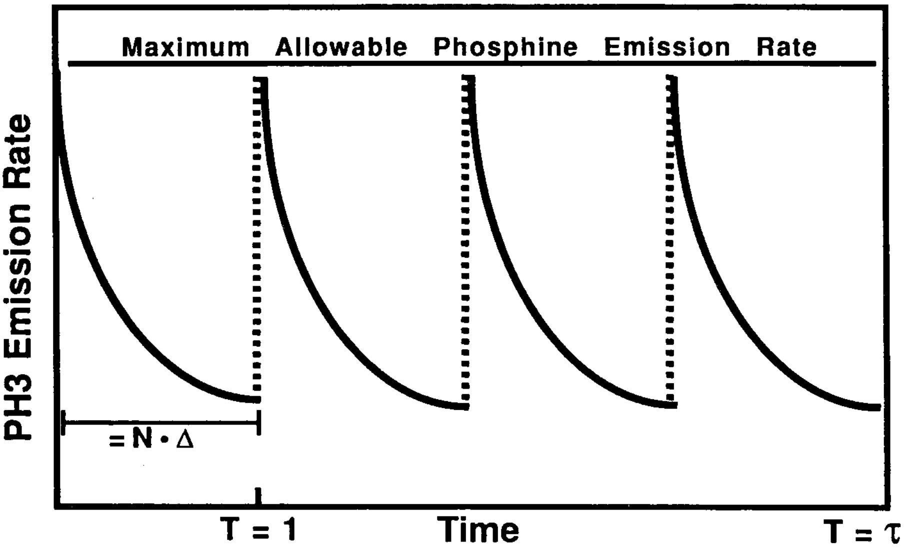

Fig. 1. Diagrammatic representation of how the variable, time, is addressed in the model. Dashed vertical lines represent the restoring of the initial phosphine emission rate through the increasing of gas exit velocity. (T) = number of larger time units, each of which corresponds to one exponential decay curve, (N) = number of time subunits per exponential decay curve, and (Δ) = length of each time subunit.

length of the total aeration period = $\tau \bullet (N \bullet \Delta)$. During this time frame, exhaust rates can be increased on a regular interval to produce the series of exponential decay curves (Fig. 1).

Equation development, smaller time frames, exponential decays. During each of these periods of length, $N \bullet \Delta$, the exhaust rate (or fan speed) is fixed. The overall phosphine concentration in the warehouse at the start of aeration = C_w,0 where

$$C_{w,0} = (V_f \bullet C_{f,0} + V_p \bullet C_{p,0}) / V_w$$

where V_w = total warehouse volume, V_f and V_p = volumes of the freespace and product, respectively, and C_f,0 and $C_{p,0}$ = initial concentrations (ppm) of the freespace and produce, respectively.

During one time increment of aeration, Δ, the proportion of the warehouse volume exhausted = λ_0, the subscript denoting T=0 (first exponential decay curve), and

$$\lambda_0 = (A \bullet S_0 \bullet \Delta) / Vw$$

where A=area of the exit opening of the exhaust system and S_0 = exit velocity for T = 0. The product, A • S_0, is the volume of air moved per unit time, Δ.

At the end of this time period (T = 0 → 1), the new warehouse concentration = C_{w},1. Developing equations to calculate this concentration can be approached in at least two ways. A simple approach is to ignore diffusion from the product to the freespace. In this case,

$$C_{w,1} = C_{w,0} \bullet (1 - \lambda_0)^N \qquad \text{(Eq. 1)}$$

The second approach, considering diffusion, is much more complex. The complexity is due to (1) the exhaust rate is a constant while the effective diffusion varies with the concentration difference between the freespace and product, and (2) phosphine moving into the freespace is diluted so the ratio of freespace concentration to product concentration is not constant. The changes in freespace and product concentrations per time increment, Δ, are expressed by

$$C_{f,(k+1)\bullet\Delta} = C_{f,k\bullet\Delta} \bullet [1 - (A \bullet S_0 \bullet \Delta/V_f)] + (C_{p,k\bullet\Delta} - C_{f,k\bullet\Delta}) \bullet r_d \bullet (V_p/V_f)$$

$$\text{and } C_{p,(k+1)\bullet\Delta} = C_{p,k\bullet\Delta} - (C_{p,k\bullet\Delta} - C_{f,k\bullet\Delta}) \bullet r_d$$

where r_d = the proportion of the concentration gradient that diffuses in time, Δ. The value V_p/V_f, accounts for dilution of phosphine moving into the freespace from the product, and (A • S_0 • Δ/V_f is the proportion of the freespace exhausted.

Using the diffusion approach, no simple, practical solution was found for calculating the value, $C_{w,1}$. So, the importance of diffusion in the rate of aeration from tobacco warehouses was questioned. Using spreadsheet software (Microsoft Excel®) to calculate results, the two approaches were compared for a typical tobacco warehouse under such controlled aeration (Fig. 2). Results of the two methods differed very little with a maximum difference of 7 ppm at time = 16 hr. Beyond that time the differences steadily decreased.

The diffusion coefficient of 0.22/hr was determined in a laboratory study of diffusion from cases of tobacco (unpubl. data). Given the size of tobacco warehouses (14,000 to 50,000 m^3) and the capacity of most commercial fans, the value of 0.08 for λ is reasonable. In practice, it may be somewhat less. The difference of 25 ppm between the freespace and product concentrations in this example is equal to or greater than the differences usually found. An analysis showed that differences in results of the two approaches are directly proportional to the product, $\lambda \bullet (C_{p,0} - C_{f,0})$.

Given the characteristics of the tobacco warehouse aeration, diffusion may not have a great impact on the rate of overall warehouse aeration. The calculation of $C_{w,k}$ using the simpler approach appears to be reasonably accurate. Therefore,

$$C_{w,1} = C_{w,0} \bullet (1 - \lambda_0)^N$$

$$\text{and } C_{w,k+1} = C_{w,k} \bullet (1 - \lambda_k)^N \qquad \text{(Eq. 2)}$$

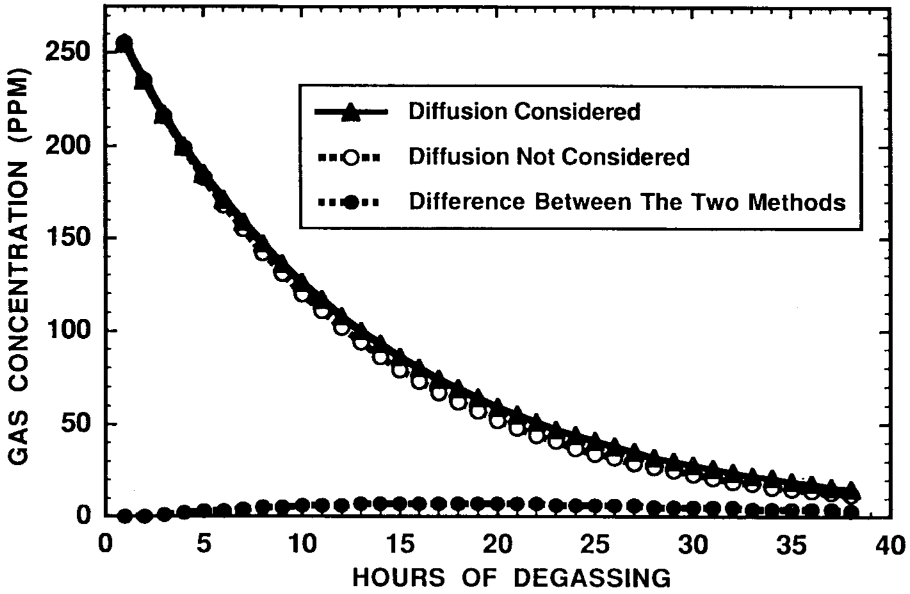

Fig. 2. Comparison of two methods of describing diminishing warehouse phosphine concentrations due to aeration at a fixed exhaust rate. Conditions were $\lambda = 0.08$, $r_d = 0.22$, $C_{p,0} = 275$, $C_{f,0} = 250$, $V_f = 0.8 \bullet V_w$, and $V_p = 0.2 \bullet V_w$.

Equation development, larger time frame, linkage of exponential decay sequences. At the end of each exponential decay sequence, the value of $C_{w,k}$ must be updated. This value can be calculated for any point in time from,

$$C_{w,1} = C_{w,0} \bullet (1 - \lambda_0)^N$$

$$C_{w,2} = C_{w,1} \bullet (1 - \lambda_1)^N = C_{w,0} \bullet (1 - \lambda_0)^{N} \bullet (1 - \lambda_1)^N$$

$$\therefore \quad C_{w,k} = C_{w,0} \bullet \prod_{i=0}^{k-1} (1 - \lambda_i)^N \qquad \text{(Eq. 3)}$$

If needed, the warehouse concentration within an exponential decay period can be calculated by

$$C_{w,k[+j \bullet \Delta]} = C_{w,0} \bullet (1 - \lambda_k)^{j \bullet \Delta} \bullet \prod_{i=0}^{k-1} (1 - \lambda_i)^N \qquad \text{(Eq. 4)}$$

At the start of each new exponential decay period, the exhaust rate is adjusted upward to increase the phosphine emission rate to the maximum allowable rate and to minimize the time needed to aerate the warehouse. The size of the exit opening of the exhaust system is unchanged. So, the fumigator increases the exhaust rate by increasing exit velocity, S_k. The phosphine emission rates at the beginning of each exponential decay period are equal if $S_k \bullet C_{w,k} = S_{k-1} \bullet C_{w,k-1} = ... = S_0 \bullet C_{w,0}$. The value of S_k can be calculated using Eq. 3.

$$S_k = S_0 \bullet (C_{w,0}/C_{w,k}) = S_0 \bullet (C_{w,0})/(C_{w,0} \bullet \prod_{i=0}^{k-1}(1 - \lambda_i)^N)$$

$$\therefore \quad S_k = S_0 \bullet \prod_{i=0}^{k-1}(1 - \lambda_i)^{-N} \qquad \text{(Eq. 5)}$$

Procedure for using the method. A computer program using the above equations was written in Microsoft® QuickBasic, and is available from the senior author (D. W. Keever). The program describes how a controlled aeration system can be operated to maximize the rate of aeration while staying in compliance with regulatory standards on phosphine emissions. The program is designed to be easily used, even by those not very familiar with computers. Before using the model, an air dispersion regulatory model, such as "SCREEN" (Brode 1988), must be run to determine the allowable phosphine emission rate for a site based on many factors (e.g., distance to the property boundaries, height at which phosphine will be released into the air, and local meteorology). This process will be required by regulators, and must be handled by someone skilled in computer programming. The allowable emission rate will be used to determine the allowable exit velocity (=AEV) of the exhaust system at that site. This AEV will be based on some standard, such as for one warehouse with a phosphine concentration of 100 ppm. These steps need to be done only once per site unless physical characteristics of the site change.

The next step is for the fumigator to put our model to use. The AEV is adjusted, usually downward, based on the number of warehouses to be aerated and their mean phosphine concentration. This can easily be done on a simple calculator. The only data the fumigator must put into the model are the initial phosphine concentration in the warehouse, the initial exit velocity of the exhaust system, and the time interval at which exit velocity (fan speed) is to be increased. If so desired, the exit velocity need not be changed. All the data that would not normally change, such as physical characteristics of the warehouse, will already have been put into the model. The model will supply the fumigator a listing, for all times during the aeration, of what exit velocity adjustments should be made, phosphine emission rates, and the concentration of phosphine remaining the warehouse.

Model validation. Fig. 3 shows results of two tests of the model's ability to describe the exponential decay in phosphine concentrations. Both tests used our

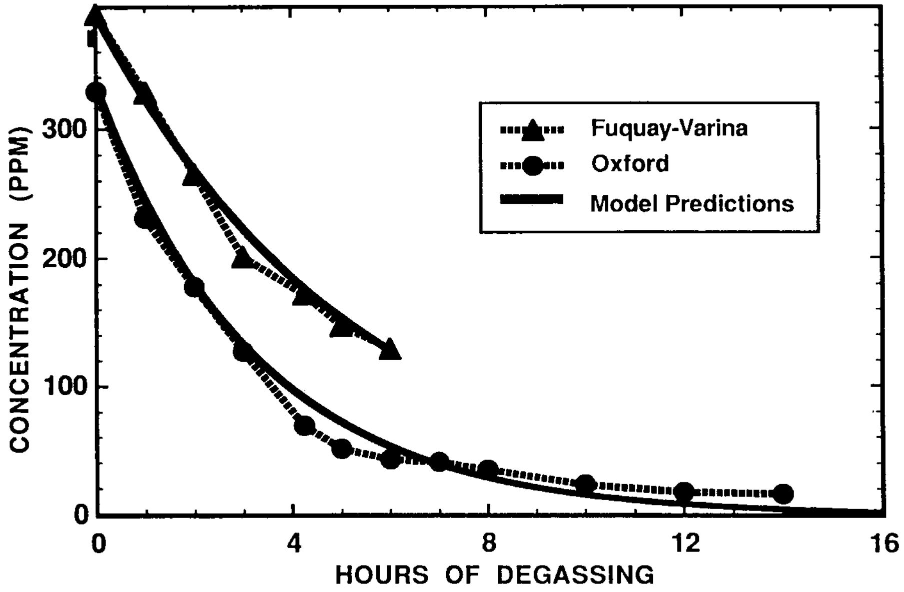

Fig. 3. Results of two tests used to validate the model's ability to describe the exponential decay in phosphine concentrations. Both tests used as fan/stack system at a fixed fan speed to aerate 14,300 m^3 commercial tobacco storages.

fan/stack system to aerate 14,300 m^3 commercial tobacco storages, and both were done in conjunction with the aeration of the entire respective warehouse complexes. The two tests were conducted at different sites and several weeks apart. During validation tests, warehouse concentrations were sampled with polyethylene sampling lines that ran from multiple sites within the warehouse to the outside where concentrations were measured with Drager® tubes. Sampling sites in the warehouses were at both 1.8 and 4.9 m above the warehouse floor.

In the Fuquay-Varina test, the model accurately predicted the declining concentrations, but we were able to collect data for only 6 hours of aeration. This warehouse had an unusually high concentration prior to aeration, and still had approximately 130 ppm when we stopped monitoring it. In the Oxford test, we monitored concentrations for 14 hours of aeration when the concentration was down to approximately 20 ppm. Again, the model very accurately predicted what declining concentrations would be based on the initial warehouse concentration and fixed speed of our fan.

The model appeared to provide an accurate description of declining phosphine concentrations during a controlled aeration. The model is most accurate in the earlier and middle portion of the aeration. It lacks the precision to consistently predict when warehouse concentrations toward the end of aeration will be low enough (< 0.3 ppm) to permit re-entry by personnel. With slight modification, the model may be useful in describing the controlled release of gases from other commodity storages. This is probably true if the diffusion rate between the freespace and product is high relative to the maximum aeration rate of the control apparatus. If the diffusion rate of these gases is relatively low, results during the earlier period of aeration may still be applicable. The model's usefulness to the fumigator has been stressed here, but it may be helpful to anyone interested in phosphine emission rates and/or rapidity of aeration during controlled aerations.

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