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Developing and verifying a fumigant loss model for bulk stored grain to predict phosphine concentrations by taking into account fumigant leakage and sorption

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ABSTRACT

To ensure fumigation effectiveness and address phosphine resistance concerns, fumigant concentrations and movement in a grain storage silo need to be understood. A mathematically accurate fumigation model was developed that is capable of predicting fumigant concentration and movement throughout a grain storage silo that takes into account fumigant loss from leakage and sorption, and was verified with experimental fumigation data. Equations estimating fumigant leakage and sorption were developed based on literature values and added to an existing finite element model. Fumigation data was used from a fumigation conducted on an Australian made silo filled with 45.5 tonnes of maize in Manhattan, Kansas. Two verifications were conducted based on phosphine concentration release times of 24 h and 30 h, with both verifications demonstrating accurate prediction of phosphine fumigant values and trends. The two verifications resulted in concentration-time products that were within 0.9% and 4.3% of the experimental values, respectively. The fumigation model is most accurate during the times of highest phosphine concentration. However, the model under predicted phosphine concentrations during the first 12 h of fumigation and over predicted phosphine concentrations beyond the first six days of fumigation. This fumigation model was found to be sufficiently accurate to allow for future experimentation on predicting fumigant concentrations as a function of environmental conditions and operational variable.

1. Introduction

A successful fumigation relies on exposing each insect within a grain mass to the specific concentration of fumigant for a specified amount of time needed to kill all insects present at all life stages. There is a significant amount of literature available on the bio-efficacy of fumigants such as phosphine against a range of stored product pests at multiple life stages (Chaudhry, 2000; Price and Mills, 1988), however, information on the fumigant activity within the commodity during a fumigation is very limited. Therefore, modeling the behavior of gas fumigants in the interstitial air volume of the stored grain mass is helpful in determining what factors may cause fumigation failures, and how those factors can be affected by environmental conditions. A previous attempt at developing such a fumigation model was made by Isa et al. (2016) using the program Fluent instead of an independent computer code. They also simulated vertical gas flow in a silo using Fluent and Comsol (Isa et al., 2011). While using any of the available fluid dynamics software packages has several advantages, such as ease of use and ease of visualizing results, it has disadvantages as well. Their fumigation model simulates both sorption and leakage losses, but the leakage losses are not influenced by weather condition or operational variables. Since the boundary conditions are set inside Fluent, loss was implemented with point losses only. The amount of loss was then controlled only by pressure half loss time. This strategy may be insufficient not only for fumigant loss that is affected by weather, but also in its inability to consider the combined effect of many small leaks over the entire external surface of the silo.

The M-L 3D finite element ecosystem model was previously developed to investigate stored grain environments and has the

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capacity to monitor chemical concentrations throughout the grain mass (Lawrence, 2010; Lawrence and Maier, 2011). In order for this model to accurately predict fumigant concentrations the model had to be improved with the added capacity to account for fumigant loss. The primary sources of fumigant loss are fumigant leakage from the silo and fumigant sorption into the grain.

Sorption of gas by grain was listed as one of the factors most likely to cause inadequate fumigation conditions in Australia (Darby, 2011). Wheat at higher temperature sorbed a greater amount of phosphine than lower temperature wheat. After 96 h in a container with initially 1 mg/L phosphine, the fumigant concentration in the interstitial airspace of stored wheat at 35 °C was below 0.1 mg/L, whereas in wheat at 15 °C it was around 0.5 mg/L (Darby, 2011). That result was supported by Reed and Pan (2000), Sato and Suwanai (1974) and Dumas (1980) who reported phosphine sorption increased with higher grain temperature and moisture content. An increase of temperature also caused faster rates of sorption of phosphine in wheat independently from moisture content. An increase from 24 °C to 35 °C caused the sorption rate constant to increase from 0.0064 to 0.186 (Banks, 1986; Berck, 1968). Increased adsorption of phosphine to the surface of cereal grains with increasing temperature was also shown in Sato and Suwanai (1974).

In addition to fumigant sorption, it is also important to understand how much fumigant is being lost from the grain storage structure into the environment. In a mathematical examination of fumigant loss, the most important environmental factor causing leakage from an enclosure is wind effect, followed by chimney effect, headspace temperature variation, barometric pressure variation, temperature variation in the grain bulk, and diffusion (Banks, 1990). Quantitatively, for a medium sized leak (estimated equivalent area of leak at 650 mm^2), wind was calculated to have a fumigant loss rate of 6.3% per day, and chimney effects of about 4% per day (Banks and Annis, 1984).

The chimney effect can be caused both by temperature differences between the grain silo and the outside environment, and by differences in concentration between the grain silo and the environment. The chimney effect on fumigant loss is higher for the concentration differences than it is for temperature differences (Banks and Annis, 1984). This is also supported by Noyes and Phillips (2007) that state that higher concentrations will lead to greater amounts of leakage from the storage structure. The amount of fumigant lost is a function of the sealing efficacy for both chimney and wind effect losses. The temperatures and pressures inside the grain silo, however, are not heavily affected by the degree of silo seal (Banks and Annis, 1984).

Wind effect is the more important of the two convective fumigant loss factors (Banks, 1990). Fumigant leakage rate was analyzed for methyl bromide and sulfuryl-fluoride fumigations in grain processing building structures (Chayaprasert et al., 2012). They showed that wind speed is the only environmental factor that affected fumigant leakage rate. This finding might be extended to phosphine as wind-driven convection loss of fumigants is not significantly affected by the kind of fumigant used (Cryer, 2008). In a separate experiment, phosphine leakage was reported to increase with an increase in grain temperature and moisture content (Reed and Pan, 2000).

How well a silo is sealed is an important factor, but it has not been investigated to the same degree as the other parameters of fumigant loss. An attempt to model fumigant loss using the pressure decay time was made by Mann et al. (1999) who calculated an equivalent area of leakage. This technique, however, was not successful as it had errors in its area of leakage estimations ranging from −17.5% to 23.1%. Ultimately they concluded that the observed gas loss was inconsistent with the predicted values. A similar technique was used by Chayaprasert et al. (2010) to predict methyl bromide and sulfuryl-fluoride pressure decay half-life times. The model was mostly able to predict half-life times within one hour of the actual value.

The objectives of this research were to build a model that is capable of accurately predicting fumigant concentration and movement throughout a grain storage silo that takes into account fumigant loss from leakage and sorption, and to verify this model with experimental fumigation data. In this study, we used phosphine as the primary fumigant due to its current dominant role as a disinfestant of stored products across the globe.

2. Materials and methods

2.1. Effect of sorption

To estimate sorption loss, an equation for concentration as a function of time was obtained from Daglish and Pavic (2008). The equation is valid at a 1 mg/L application, and 0.75 fill ratio, resulting in an R^2 value of 0.96 at 25 °C and 55% relative humidity. The equation presented in the literature was adjusted to fit the time step and units in the code, an hourly time step and units of kg/m^3. Additionally, to calculate the amount of phosphine lost due to sorption, equation was modified by taking the derivative with respect to time. The resulting baseline sorption equation was [1]:

$$C = 0.0000026e^{-0.0017t} \tag{1}$$

Fumigant sorption also varies due to other factors that are important variables in our experiment, such as temperature and moisture content of grain. To account for these variables, Eq [1] was multiplied by factors dependent on temperature and moisture content. The effect of temperature on phosphine sorption was studied by Darby (2011) who determined sorption losses at 35 °C were about five times as large as losses at 15 °C, at a constant equilibrium relative humidity of 65%. Therefore, this result can be modeled with an exponential equation dependent on temperature, where the value at 35 °C is five times the value at 15 °C. The value for this expression is set to equal one when the temperature is at 25 °C, because that is the temperature of the baseline equation from Daglish and Pavic (2008). This means that when the temperature equals that of the baseline equation, the overall equation should be unchanged. The effect of moisture content on the sorption of phosphine was studied by Reed and Pan (2000). They determined fumigant loss for several temperatures at two values of wheat moisture content, i.e., 11% and 13.5%. The sorption at the higher moisture content was 1.8 times greater than the sorption at the lower moisture content at 25 °C. This was modeled with an exponential equation which was set to 11.5%, the equilibrium moisture content of the wheat from the baseline Daglish and Pavic (2008) equation. The resulting equation for fumigant loss due to sorption into the grain mass when modified to account for changing temperatures and moisture contents is therefore:

$$C = 0.0000026e^{-0.0017t} * 0.13365e^{0.0805T} * 0.067e^{0.235M} \tag{2}$$

Where,

C = fumigant concentration lost [kg/m^3]
t = time [h]
T = temperature [^oC]
M = moisture content [%], wet basis

Implementation this equation into the computer code required that the fumigant concentration lost due to sorption is subtracted