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An approach for developing a phosphine dosage procedure and calculator for silo bags

R BARTOSIK[1,2*], L CARDOSO[1], D DE LA TORRE[1], B ABADÍA[1], M IGARTUA[3]

[1]*National Institute of Agricultural Technology (INTA), Balcarce, Argentina*

ABSTRACT

The aim of this study was to integrate the available information and develop a PH_3 dosage procedure and calculator for silo bags. An automatic pressure decay test (APDT) device was developed, consisting of a portable plastic suitcase, including an electrical fan, connecting hoses, pressure gauge, valves and a controller. The controller had Bluetooth connectivity, so all the parameters recorded by the APDT were automatically transmitted to a cell phone. Based on literature data, correlations were developed to estimate PH_3 losses according to PDT results in silo bags. A PH_3 concentration prediction model that takes into account PH_3 liberation from aluminum phosphide, PH_3 losses, void spaces and PH_3 sorption by the grain was proposed and compared with experimental results. It was observed that losses were over estimated when the silo bag had a PDT close to 60 s and an enhanced model was proposed and validated with literature data. The need of better correlations for estimating PH_3 losses in silo bags and PH_3 release were discussed. A procedure for calculating the dosage for a successful PH_3 fumigation was proposed, which combines the use of the APDT device and the PH_3 concentration model (programmed in Excel).

Key words: Air tightness, Fumigation, Fumigant losses, Hermetic storage, Model, Pest control

Silo bag technology has been extensively implemented in Argentina for storing grains, (e.g. wheat (*Triticum aestivum* L.), corn (*Zea mays* L.) barley (*Hordeum vulgare* L.), sunflower (*Helianthus annuus* L.) and soybean [*Glycine max* (L.) Merr.] among others) since the mid-1990s (Bartosik, 2012). Silo bags can achieve a high air tightness level which could benefit pest control treatments with PH_3 or modified atmospheres. Phosphine (PH_3) is the main fumigant and one of the most used chemical insecticides worldwide for stored-product pests. For achieving an effective pest control with PH_3, a minimum concentration has to be maintained during a minimum exposure time (ct-product, e.g. 200 ppm during 120 h). However, PH_3 concentration evolution in time is difficult to predict, since it depends on the initial fumigant dose, the fumigant losses during the treatment, and the fumigant sorption by the product, among others. Although critical information for a successful fumigation is available, the information on target concentration and exposure time required for different species and stages (Bell, 2000), procedures for evaluating air tightness of storage structures (Navarro, 1998), expected fumigant losses for different hermeticity levels (Navarro and Zettler, 2000), empty space of grain bulk (ASAE, 2013), phosphine sorption effects (Reddy et al., 2007) is not clearly integrated or easily available for farmers and grain elevator managers for practical fumigation recommendations.

Hence the aim of this study was to integrate the available information and develop a PH_3 dosage procedure and calculator for silo bags.

MATERIALS AND METHODS

To determine the air tightness of storage structure, Navarro (1998) proposed to implement a pressure decay test (PDT). The equipment required for

[2]CONICET, Argentina.

[3]Agronomy College, Mar del Plata National University, Argentina.

[*]Corresponding author e-mail: *bartosik.ricardo@inta.gob.ar*

performing a PDT includes a vacuum device (usually a fan), a connection between the fan and the fumigation chamber, a valve to avoid pressure losses once the fan is turned off after reaching the desired pressure, a pressure gauge for measuring the internal pressure of the chamber, a timer for timing the pressure losses and a notepad for recording the data. The equipment is quite simple, but if a large number of tests have to be performed and different operators are involved, results might not be comparable because of the operational errors. Also, the labour involved in the setting up of the test discourages its implementation.

An automatic pressure decay test (APDT) device was developed to overcome these limitations (Fig. 1). The APDT is an integrated system, portable in a standard plastic suitcase, including an electrical fan, connecting hoses, pressure gauge, valves and a controller. The controller has Bluetooth connectivity, so all the parameters recorded by the APDT are automatically transmitted to the cell phone. Additionally, all the configuration of the APDT is made through the cell phone application. The operator inserts the probe in the silo bag, seals the edge against the plastic cover, and connects it to the APDT with a hose. The APDT automatically starts the fan until the initial negative pressure is reached (e.g. –250 Pa); closes the valve and periodically measures the pressure inside the storage structure until the negative pressure recovers half the initial value (–125 Pa). According to Navarro (1998), a structure of less than 500 t, 95% full, could be suitable for fumigant treatment if the PDT is greater than 90 s. Thus, based on this time threshold, the pressure test is rated as ‘failed’ or ‘succeeded’. With the APDT the errors in determining the PDT are minimized and the test itself is simplified (the entire operation for performing an APDT in a silo bag takes less than 5 min). The APDT was developed by the National Institute of Agricultural Technology (INTA), Balcarce, Argentina.

Navarro and Zettler (2000) measured the daily losses of PH_3 (with an initial PH_3 concentration of 1500 ppm) in an empty fumigation chamber of 7.5 m^3 with predetermined orifices (from 1.6 mm to 6.4 mm diameter). Based on this data, a correlation was developed to predict normalized losses according to the PDT (Eq. 1).

$$L\left(\frac{ppm}{day}\right) = PH_3\ (ppm) \times [-0.0011 \times PDT^3 + 0.0104 \times PDT^2 - 0.0428 \times PDT + 0.183] \qquad \text{(Eq. 1)}$$

where L are the daily PH_3 losses (ppm/d); PH_3 is the fumigant concentration in a given day; PDT is the pressure decay test (min).

A model to predict PH_3 concentration in silo bag was developed (Eq. 2), taking into account the

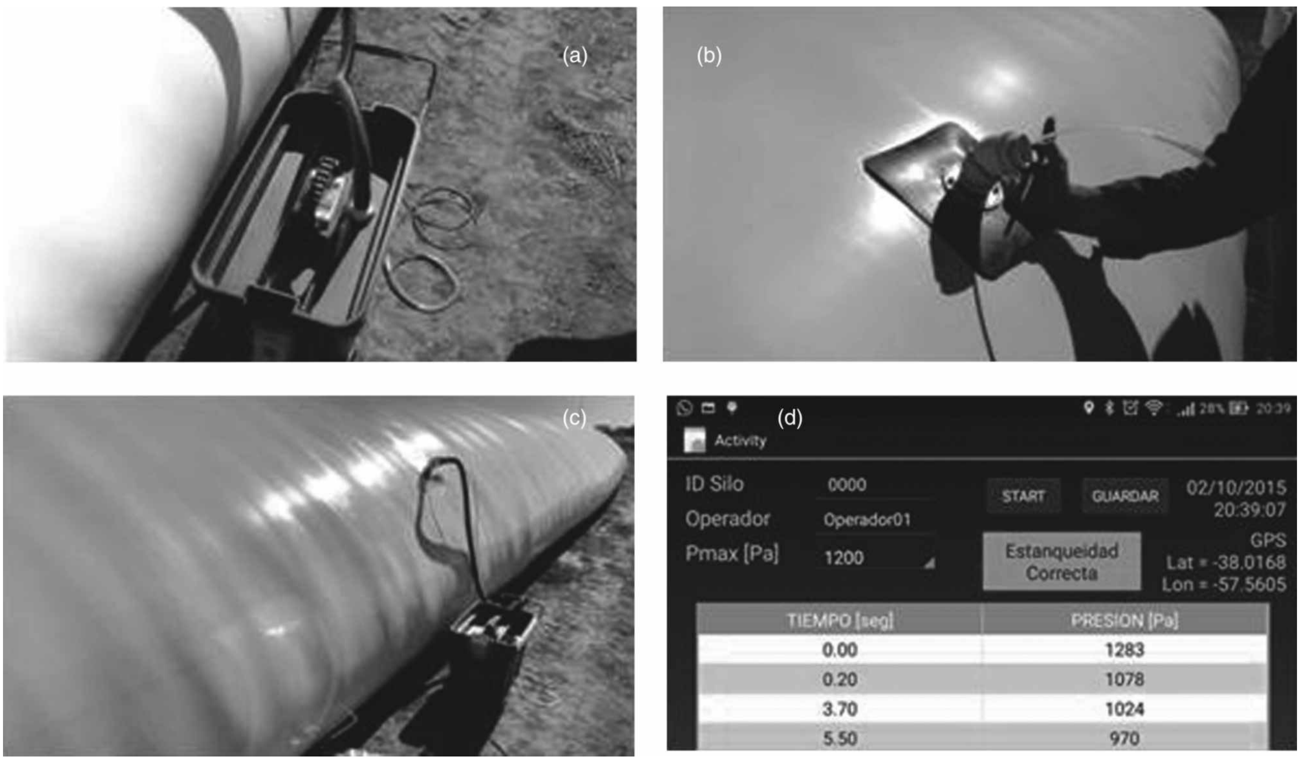

Fig. 1. Automatic pressure decay test (APDT) device. (a) APDT portable box, (b) APDT probe inserted into the silo bag, (c) APDT connected to the silo bag, (d) cell phone app showing the result of the PDT

following inputs: Desired PH_3 minimum concentration (ppm); Days at the desired minimum concentration (d); Grain bulk (t); Grain density (t/m^3) (ASAE, 2013); Initial PH_3 dosage (g PH_3/m^3); Void space (ASAE, 2013); PH_3 sorption (%) (Reddy et al., 2007); PH_3 losses (ppm/day) (Navarro and Zettler, 2000).Model assumption: 1 g/m^3 of PH_3 generates 718 ppm; the complete liberation of PH_3 from aluminum phosphide occurs during 4 days, at 25% per day (Navarro and Zettler, 2000).

$$[PH_3]\ (\text{ppm}) = \frac{D\left(\frac{g}{t}\right) \times BD\left(\frac{t}{m^3}\right)}{P} \times 718 \left(\frac{ppm}{g}\right) \times (1 - S) - [L \left(\frac{ppm}{day}\right) \times T\ (\text{days})] \quad \text{(Eq. 2)}$$

where $[PH_3]$ is the current fumigant concentration (ppm), D is the initial dosage of PH_3 (g/t); BD is bulk density (t/m^3); P is grain porosity (decimal); 718 is the PH_3 concentration with a dosage of 1 g of PH_3 in 1 m^3 of empty space (ppm/g); S is the PH_3 capture by the grain due to sorption (decimal); L are the daily losses of PH_3 (ppm/d); T is the time elapsed since beginning of fumigation (d).

RESULTS AND DISCUSSION

Fumigation data presented by Carpaneto et al., (2016) were used for validating the prediction of the model. Fig. 2a shows the measured PH_3 concentration in a wheat silo bag which was not sealed at the end and with noticeable perforations in the plastic cover. The PDT was not performed in this silo bag, but based on PDT performed in several silo bag with similar air tightness conditions (Cardoso et al., 2012), PDT of this bag was estimated to be <15 s. When the silo bag was not sealed and the PDT trended to 0, the actual losses were significantly greater than the predicted ones. The maximum concentration measured were from 250 and 430 ppm (depending on measuring point), while the predicted maximum concentration was 700 ppm. It is possible that when the bag has large perforations and PDT trends to 0, the gas leakage increased exponentially and cannot be predicted by extrapolating data from Navarro and Zettler (2000) (the lowest PDT that they considered was of 1 min). Thus, Eq. 2 was not able to accurately predict PH_3 concentration in silo bag when PDT was close to 0. Other observation from Fig. 2a was that when the PDT was less than 15 s, there was a great variability in the concentration measured in different sections of the silo bag. This could be caused by the greater losses

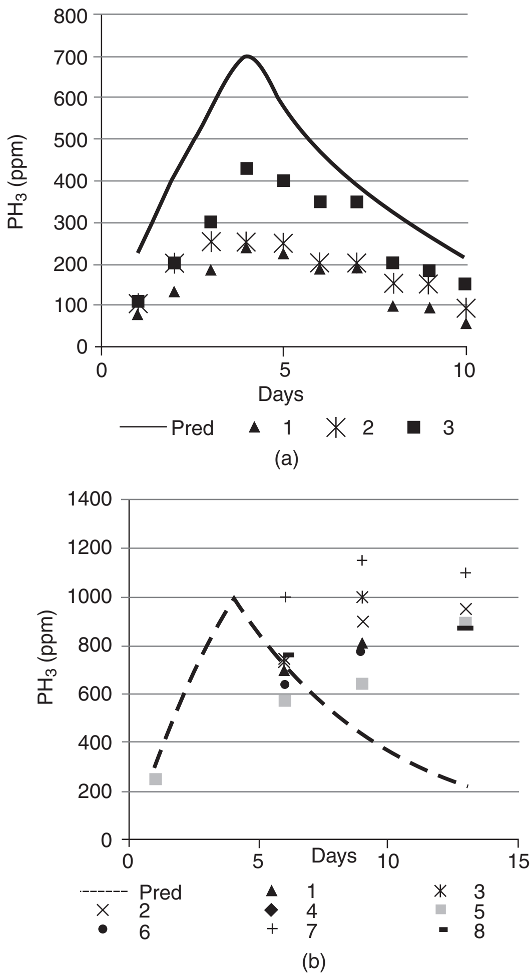

Fig. 2. Predicted and measured PH_3 concentrations (in different locations) in wheat silo bags with initial dosage of 1 g/t and PDT of less than 0.25 min (*a*) and initial dosage of 1.4 g/t and PDT of 1 min (*b*). References: Pred is predicted concentration; numbers 1-8: measuring fumigant concentration points in silo bags. Measured data from Carpaneto et al. (2016)

of fumigant concentration produced in those locations that are close to the openings. For this reason, even if the model was able to predict with greater accuracy the average condition of the bag, this information would not be useful for targeting an appropriate fumigant dosage, because the locations close to the openings would result with significantly greater losses and failed fumigation treatments.

Fig. 2b shows the observed and predicted data for a wheat silo bag with a PDT close to 1 min. In this case, the losses model (Eq. 1) overestimated the observed losses. Two possible hypotheses could be offered to explain the discrepancy between the observed and predicted losses. The first one would imply that the PDT conducted was not representative of the true level of air tightness of the bag, which is not likely since the PDT is a simple procedure and when the test is replicated the results are highly similar. The second would imply that the losses model generated with data from Navarro and Zettler (2000) might not be appropriate for silo bags, since the study was performed in an empty fumigation chamber and the condition in the silo bag is substantially different (full of grain). On one hand, in this kind of storage system there is no headspace and, theoretically, no leakage of gas occurs as result of pressure release. On the other hand, fumigant diffusion inside a silo bag full of grain should be lower than in an empty space, so leakage must also be lower. Additionally, the pick on PH_3 concentration in the measured data occurs after 4 days, indicating that liberation of PH_3 in field fumigation treatments is slower that that reported by Navarro and Zettler (2000) (they reported that complete liberation was achieved in 4 days, but the aluminum phosphide pellets were wet twice a day). These observations indicated that additional test should be carried out to better estimate the fumigant losses based on the PDT for silo bags and fumigant liberation under real fumigation conditions.

Based on the data presented in Fig. 2b, the PH_3 liberation rate was modeled and the daily losses adjusted to fit the observed data. The PH_3 liberation rate was obtained from a correlation as follows:

$$R\left(\frac{ppm}{day}\right) = -0.0005T^3 + 0.0141T^2 - 0.1306\mathrm{T} + 0.4303 \qquad \text{(Eq. 3)}$$

where R is the PH_3 liberation rate (% per day); and T is day from beginning of fumigation (starting at 1).

Daily PH_3 losses were adjusted in order to match the observed data of Fig. 2b, finding that a daily loss of 4.2% of concentration (corresponding to a PDT of about 6.5 min estimated by Eq. 1) was able to predict the average variation in concentration for the different measurements points during 13 days of the experimental fumigation trial. Thus, a multiplier of 6.5 is proposed to adjust the prediction of losses in silo bag, and the enhanced model for predicting daily losses is:

$$LM\left(\frac{ppm}{day}\right) = \mathrm{PH_3}\,(ppm) \times [-0.0011 \times (PDT \times M)^3 + 0.0104 \times (PDT \times M)^2 - 0.0428 \times (PDT \times M) + 0.183] \qquad \text{(Eq. 4)}$$

where LM is the daily PH_3 losses affected by a multiplier (ppm/d); PH_3 is the current concentration of fumigant (ppm); PDT is the pressure decay test (min); and M is the multiplier to adjust predicted losses to silo bag (6.5).

A general enhanced model (Pred – EM) for predicting PH_3concentration in silo bags is proposed as:

$$[PH_3](ppm) = \int_n^1 \left[\frac{D\left(\frac{g}{t}\right) \times R \times BD\left(\frac{t}{m^3}\right)}{P} \times 718\left(\frac{ppp}{g}\right) \times (1-S) \right] - LM\left(\frac{ppp}{day}\right) \qquad \text{(Eq. 5)}$$

where $[PH_3]$ is the current fumigant concentration (ppm), D is the initial dosage of PH_3 (g/t); R is the daily release of PH_3, BD is bulk density (t/m^3); P is grain porosity (decimal); 718 is the PH_3 concentration with a dosage of 1 g of PH_3 in 1 m^3 of empty space (ppm/g); S is the PH_3 capture by the grain due to sorption (decimal); LM are the daily losses of PH_3 (ppm/d); and 1 to n is the integration time since fumigation started (d).

The Eq. 5 integrates on a daily basis the generation of PH_3 and the losses. Fig. 3a exhibits the observed and predicted data with the enhanced model (the initial dosage was the same as reported for Fig. 2b, all the other parameters used in Eq. 2 were not modified). Overall, the enhanced model improved the prediction of the maximum concentration achieved and the evolution of fumigant concentration during 13 days of the fumigation treatment.

Other set of data from the literature (Ridley et al., 2011) was used for validating the enhanced model (Eq. 5). These data were generated in a silo bag of wheat (*Triticum aestivum* L.) fumigated with an initial PH_3 dosage of 1.6 g/m^3 (equivalent to 2.1 g/t). The PDT of this bag was estimated to be close to 1 min (Carpaneto et al., 2016). Fig. 3b shows the predicted PH_3 concentration with the enhanced model and the measured data, showing that the model overestimated the maximum concentration achieved (1750 ppm predictive vs 1450 measured), but overall the shape of the concentration curve and the fumigant concentration at the end of the fumigation trial (17 days) were close enough to use the model for targeting an effective initial dosage (1300 predicted vs 1250 measured).

Though a preliminary validation of the model was performed, it is clear that stronger correlations should be developed for relating daily PH_3 losses according to PDT for silo bags (no headspace condition). Better models for PH_3 release from aluminum phosphide pellets or tablets would also improve the prediction of fumigant concentration, especially during the first days of the treatments. In this study, a sorption effect of wheat of 19% was considered according to Reddy et al. (2007). These authors reported sorption values from

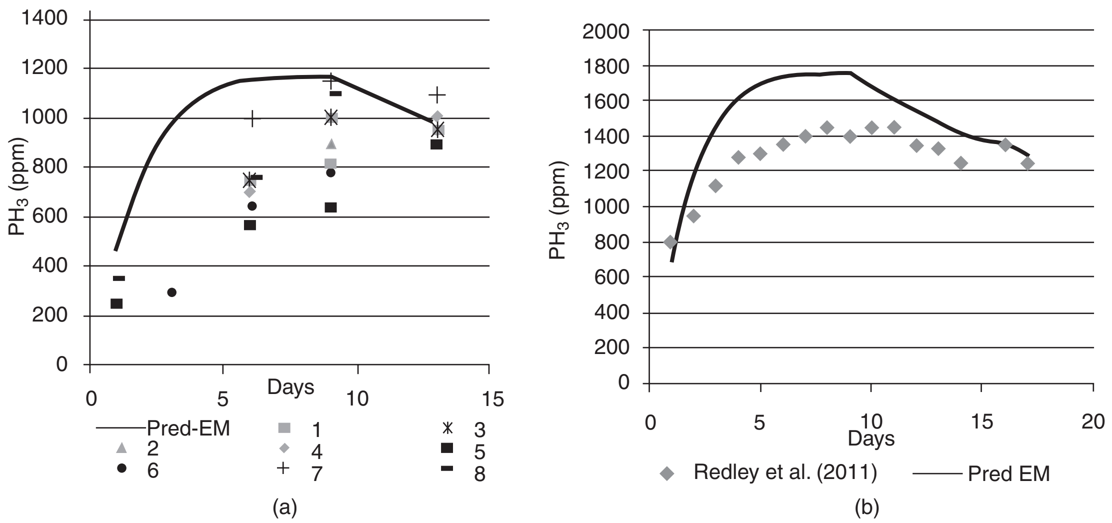

Fig. 3. (*a*), Predicted and measured PH_3 concentrations in wheat silo bags with initial dosage of 1 g/t and PDT of 1 min. References: Pred-EM is predicted concentration using the enhanced model (Eq. 5); numbers 1-8: measuring fumigant concentration points in silo bags. Measured data from Carpaneto et al. (2016). (*b*), PH_3 predicted concentration with the enhanced model and measured PH_3concentration from Ridley et al. (2011)

18 to 30% for most cereal grains, which seems to be in agreement with observed and predicted fumigation data. However, these authors also reported extremely high sorption values for other seeds such as sunflower *Helainthus annuus* L. (92%), in-shell peanuts (*Arachis hypogala* L.) (95.5%), and paddy rice (*Oryza sativa* L.) (72%) among others. Such sorption values would substantially affect the prediction of concentration during PH_3 fumigation, beyond what is observed in practice.

CONCLUSION

Based on these results, it is proposed to use the phosphine dosage procedure and calculator for achieving a successful fumigation according to the hermeticity of the bag and the requirement of fumigant concentration and exposure time. Following this procedure, the operator connects the APDT device to the silo bag and performs the test directly in the field. The result of the PDT test (s) is entered in the Excel spreadsheet with the enhanced prediction model (Eq. 5), along with the other critical information: type of grain, amount of grain and fumigation target (i.e. required PH_3 concentration and exposure time). Once these parameters are entered, a recommendation of dosage is made (grams of phosphide per t or m^3) to achieve the prescribed concentration during the entire fumigation period. Additionally, total amount of aluminum phosphide pellets required and fumigation cost (total cost and cost per t) are also calculated.

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