

Ducom V, Simioni F, Mercadal D, Busson D (2021) A comparative study of phosphine distribution using two application methods with 30,000 gas concentration measurements. Pp. 63-70. In: Jayas DS, Jian F (eds) Proceedings of the 11th International Conference on Controlled Atmosphere and Fumigation in Stored Products (CAF2020), CAF Permanent Committee Secretariat, Winnipeg, Canada.

A comparative study of phosphine distribution using two application methods with 30,000 gas concentration measurements

Valérie Ducom^{1*}, F. Simioni², D. Mercadal³, D. Busson³

¹Cérès Innovation, 6 rue Denis Diderot, 31400 Toulouse, France.

²Cérès AgroTech, 6 rue Denis Diderot, 31400 Toulouse, France.

³SCA Arterris, Loudes, 11400 Castelnaudary, France.

*Corresponding author's email: vducom@ceresinnovation.fr

Abstract

Uniform phosphine distribution inside a silo is key to an effective fumigation. To eliminate all insect life stages, and avoid phosphine resistance, gas concentration needs to be held above 200 ppm throughout the storage space during the exposure period. The silos used in this study were four identical, 10,200 m³ concrete cylinders each containing 8,000 tonnes (t) of durum wheat at a temperature between 27 and 30°C. The silos were partially sealed and did not have a recirculation system. Ten PhosCapt-MP phosphine monitors recorded and transmitted gas concentrations every 3 h from a total of 104 locations (26 points for each silo). The silos were divided into four 5 m vertical sections with 5 monitoring points located inside the grain of each section at East, West, North, South, and Center. Three additional points were located in the headspace and 3 others in the lower ventilation galleries. There were four treatments of two dosages (1.5 g and 3 g/m³) generated from Aluminum phosphide (AIP) bag blankets. One of each dosage was placed at the top of two of the silos, and one of each dosage at the bottom of the other two silos. The fumigation monitoring was conducted over 37 d, recording a total of 30,784 measurements. Gas from the blanket introduced at the top quickly penetrated to a depth of 10 m from the top out of a total depth of 22 m of grain and reached 200 ppm in the first 12 h of fumigation, but not long enough to be effective. Then, its progression became very non-uniform for both gas dosages. In the bottom half of the silos, the concentrations never reached 200 ppm. From the blanket placed at the bottom, the gas propagation, regardless of the dosage, was slower and more uniform. It took 7 d for the gas to reach 200 ppm at 10 m from the silo bottoms and 10 d to obtain a complete admixture throughout the whole depth of the silo that was maintained for more than a week above 200 ppm. To conclude, introduction of fumigant at the bottom worked very well. The PH₃ convection inside the silo was also analyzed.

Keywords: Phosphine, PH₃, Fumigation, Gas distribution, Phosphine monitoring, Silo

Introduction

Uniform phosphine distribution inside a silo is key to an effective fumigation. To eliminate all insect life stages, and avoid phosphine resistance, gas concentration needs to be held above 200 ppm throughout the storage space during the exposure period. In large deep silos, it is difficult to attain uniform concentration. The goal of our study was to characterize the differences in phosphine penetration and distribution into a grain mass under real conditions using four silos each holding 8000 t of durum wheat, using two types of applications, one from the top of the silo and the other from the bottom. Two doses were tested.

Materials and methods

This study was conducted in Baziège, France in August 2019. The ambient air temperature was 22 – 29°C (26°C average) at the beginning and 18 – 25°C (22°C average) at the end. The tests were carried out at the Arterris cooperative site in four concrete silos (each silo was 24.5 m diameter, 19.8 m high and 5.5 m high cone-shaped metal roofs thus with a volume of 10,200 m³ and held 7,600 to 8,000 t of recently harvested durum wheat). The grain conditions at the beginning were fairly homogeneous: temperatures 27 – 30°C, 11.5 – 13.7% moisture content, 810 – 820 kg/m³ density, and 13 – 13.4% protein. The roofs were gas-proof, but not perfect. All four silos were equipped at the bottom with 24 ventilation pipes. The gassing was carried out using Aluminum phosphide generators Detia-Degesch Bag Blankets (BB) and mini-Bag Blankets (mBB). Each 3.4 kg BB released 1.1 kg of PH₃ and each 680 g mBB released 226 g of PH₃. The mBB were used for the bottom short-length aeration system. Silos A and C were fumigated with a dose of 1.5 g/m³ PH₃, using 14 BB, and Silos B and D were fumigated with a dose of 3 g/m³ using 17 BB and 50 mBB. Silos A and B had BBs placed at the top, and silos C and D had BBs and mBBs placed at the bottom.

The concentrations were measured every 3 h by 10 dual-sensor PhosCapt-MPs with email reporting (Fig. 1) from 26 locations in each silo (Fig. 2). Each device monitored twelve 4 mm ID PE lines up to 200 m length, with automatic sensor selection between high concentrations (up to 15,000 ppm, 1 ppm precision) and low concentrations (0.1 ppm to 20 ppm, 0.01 ppm precision). All the sensors were calibrated with the same gases at 940 ppm and 5 ppm.



Fig. 1. PhosCapt®-MP: 12 lines Phosphine monitor. CaptSystemes, France. (phoscapt.com)

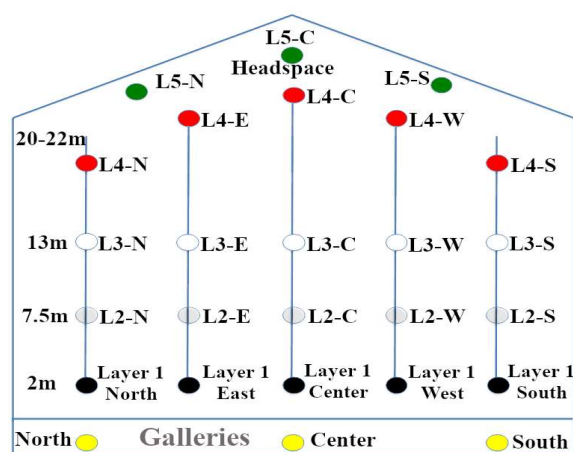


Fig. 2. Phosphine measurement locations in a silo.

The non-centered measurement lines were attached to the temperature sensor cables located halfway between the center and the wall (5.5 m from the wall). The four silos were fumigated in passive mode, meaning that no recirculation was used during the fumigation. The gassing operations were carried out simultaneously. One team gassed Silo A, while another team gassed Silo C. The same for Silos B and D. For silos gassed from the top: the closed BB were deposited in the center of the silo. Two operators opened the BB and arranged them in a star pattern on top of the grain. For silos gassed from the bottom: the closed BB were arranged in front of each ventilation pipe. Two operators began the gassing from the first pipe to be gassed, then went on to the next one. The BB were opened and were inserted into the pipes. The mini-BB were deposited at the pipe entrances. Efficacy was assessed by the gas measurements. The target was to maintain ≥ 200 ppm (Noyes and Philips, 2004) during the fumigation based on the temperature. In our case, temperature was at 27 – 30°C. Therefore, the minimum exposure time at 200 ppm was 144-168 h (Ducom, 2005).

Results and discussion

With 104 measurement locations in four silos and a 3 h measurement interval over 37 d, we had a total of 30,784 measurement data. Phosphine released from the top (Silos A and B) penetrated rapidly into the first few meters at the top of the silos, reaching 2,000 to 4,000 ppm (Fig. 3). We then observed the low phosphine concentration at lower layers of the grain mass which was below 100 ppm. The same trend was found in Silo B with the double dosage. These results differ from those found by Williams et al. (1996) for 2500-t silos gassed from the top with blankets. In their trials, the overall concentration was efficient at all levels, including the bottom, due to the very good sealing of the silos.

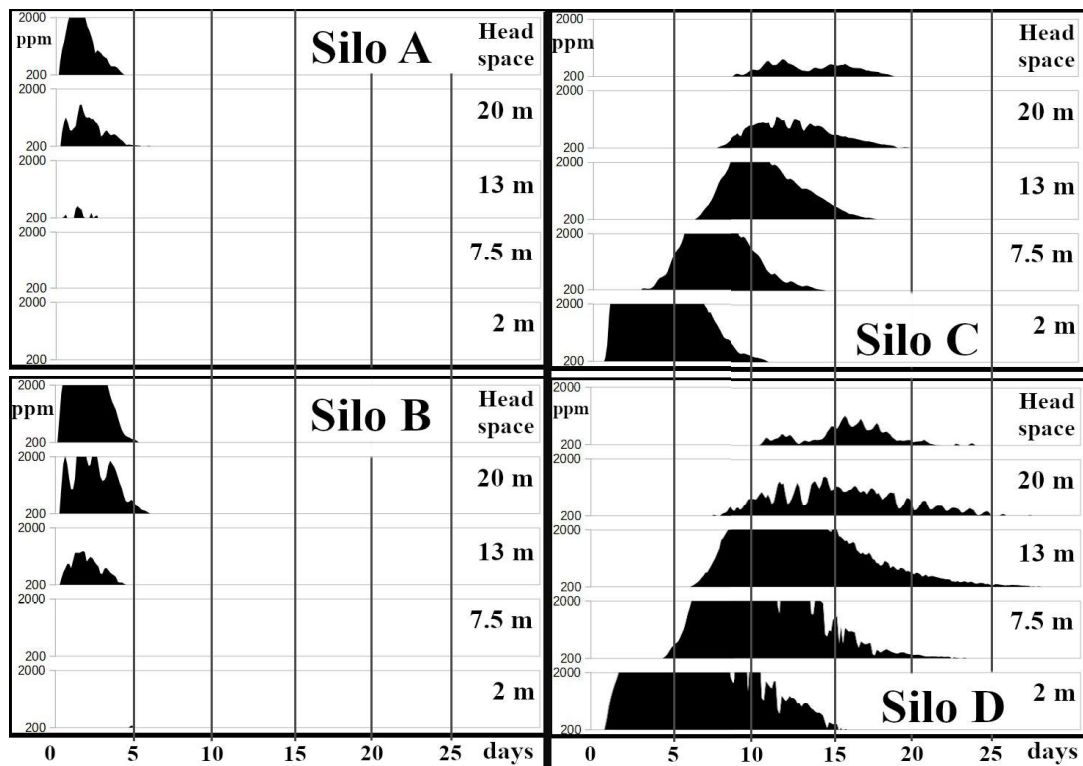


Fig. 3. Average concentration in the four silos (range: 200 to 2000 ppm)

The concentration time (Ct) products in each layer were calculated, not for the efficacy evaluation, but to calculate the quantity of gas. We noticed a huge difference in the Ct of PH₃ between gas releasing at the top and at the bottom (Table 1, Fig. 4). We also noted in Silo D (with a double dose at the bottom of the silo), a doubling in the Ct values for the bottom three layers, compared to Silo C (with a single dose). The differences in Ct products in the upper layers of Silos C and D were lower. This could be explained by a possible gas leakage at the top of the silos, even though the silo roofs were sealed.

Table 1. Concentration time product above 200 ppm in different layers (kppmh: kilo ppm × hour).

Layers	Silo A	Silo B	Silo C	Silo D
L5 Headspace	122	269	112	156
L4 20 m	90	188	191	308
L3 13 m	15	77	343	694
L2 7.5m	0	0	410	812
L1 2 m	0	0	652	1174

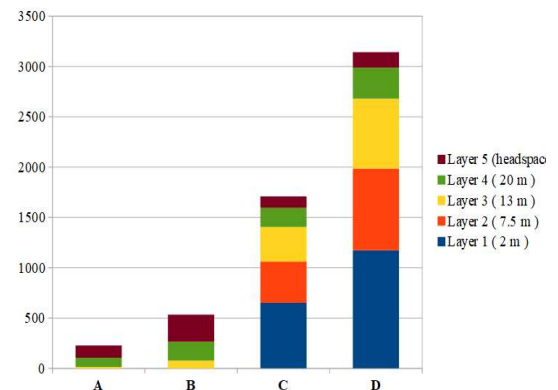


Fig. 4. Concentration time product above 200 ppm in different layers (kppmh).

During gas releasing, concentrations increase until the end of hydrolysis is at a peak and then start to decrease. The decrease is due to gas diffusion, sorption and leakage. In silos gassed from the top, the PH₃ peaks in the highest layers of the grain occurred between 30 and 51 h. In the lower layers, the peaks never reached 50 ppm (Fig. 5).

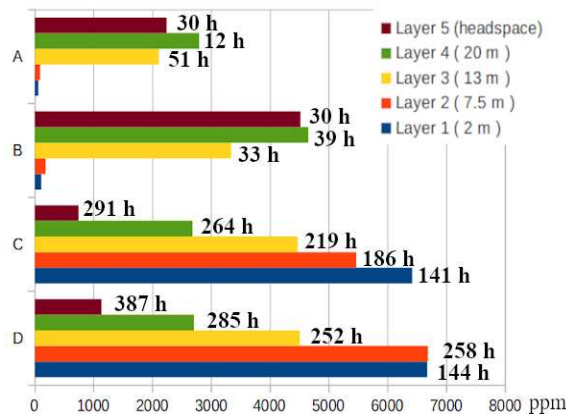


Fig. 5. Silo layer concentration peak times and values

Gassing from the bottom looked very different. In Silo C, where the PH₃ generators were placed in the ventilation ducts, the concentrations stayed above 11,000 ppm for about 100 h with a peak at 12,400 ppm. In Silo D (double dose), the ventilation duct concentration values were the same as for Silo C (single dose).

Gassing from the bottom showed a very slow gas penetration rate. Peaks at 1 m from the top of the surface (Layer 4) were obtained in 264-285 h (11 d). The peaks in the headspace were obtained in 12 to 16 d (Fig. 5). However, concentrations were high at all layers, including the highest layer where they reached nearly 400 ppm. Thus, there was a slow but remarkable rise in concentrations.

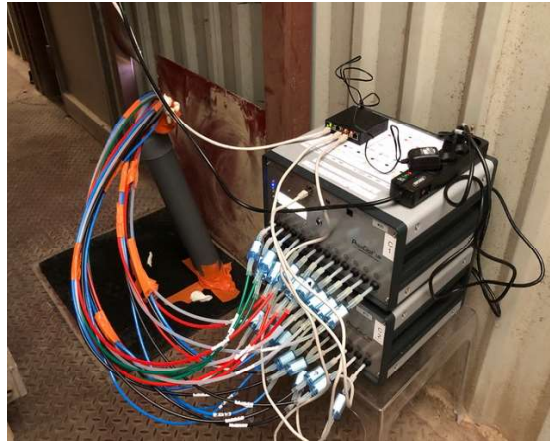


Fig. 6. Two PhosCapt-MPs placed in Silo C, monitoring 23 lines

The PhosCapt-MP (Fig. 6) is capable of measuring concentrations of up to 15,000 ppm (Fig. 5). Preliminary gassing tests in the bottoms of different silos showed that the concentrations never reached more than 12,000 ppm for application doses of 3 g/m³ PH₃. This could have been due to a lack of water vapor that naturally limited the AIP hydrolysis speed and, as a result, the instantaneous quantity of PH₃ produced. We were thus well below the 17,900-ppm value, the flammability zone of phosphine (Green et al., 1983).

The fumigation insecticidal efficacy reference is the tandem ‘200 ppm for 144 h’. Thanks to the very large number of measurements taken, it was possible to precisely determine the ranges where the duo ≥ 200 ppm for > 144 h was obtained. In Silos A and B, (application from the top of the silos) did not allow us to obtain this tandem in all the layers. Fumigation was not effective. However, in Silos C and D (application from the bottom), efficacy was obtained in all the layers for the two application doses (1.5 and 3 g/m³) (Table 2, Fig. 7).

Table 2: Exposure time (h), per layer, based on the concentrations above 200 ppm

Layers	Silo A	Silo B	Silo C	Silo D
L4 20 m	135	135	294	444
L3 13 m	51	99	279	534
L2 7.5m	0	0	282	459
L1 2 m	0	0	252	369

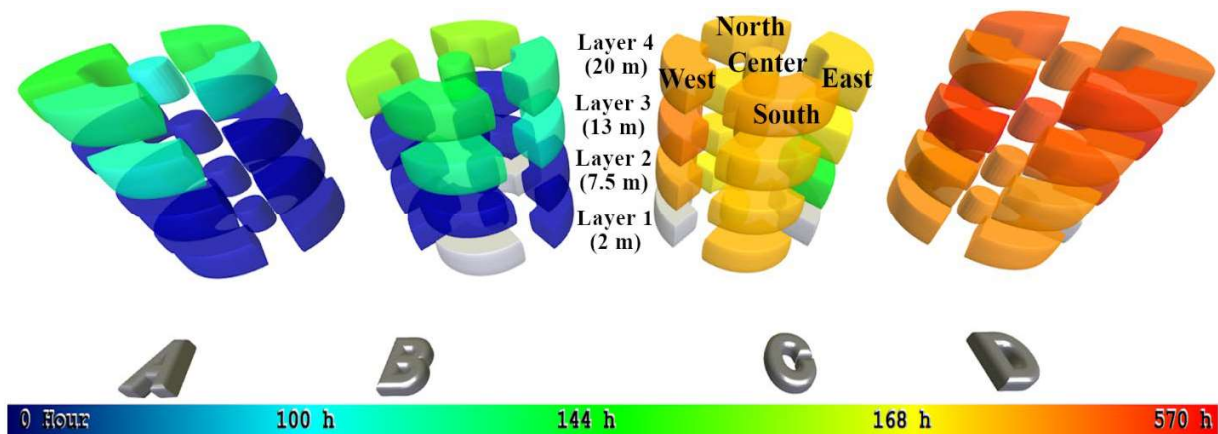


Fig. 7. 200ppm exposure time 3D cartography (Grey = data unavailable).

Phosphine concentrations in the grain were extremely variable in time and space. Constant gas movements were observed despite very stable general climatic conditions. The raw values given by the measuring devices showed very large fluctuations mainly in the center axis as shown in Figs. 8 to 11.

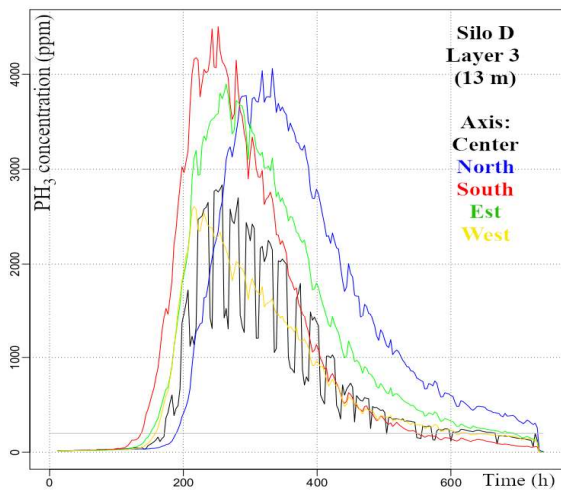


Fig. 8. Evolution of PH₃ concentration near the middle of Silo D, Layer 3 (13 m)

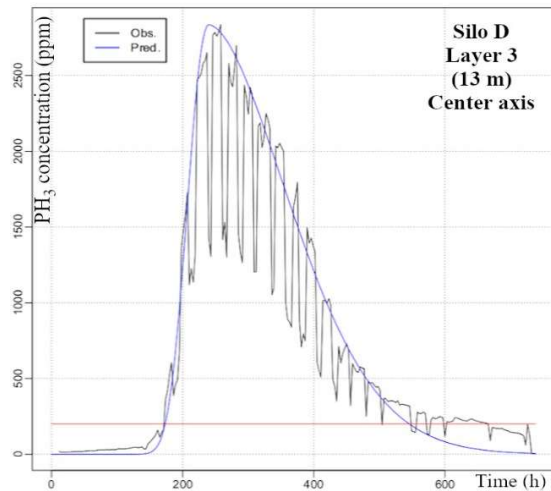


Fig. 9. Daily oscillations at the center axis

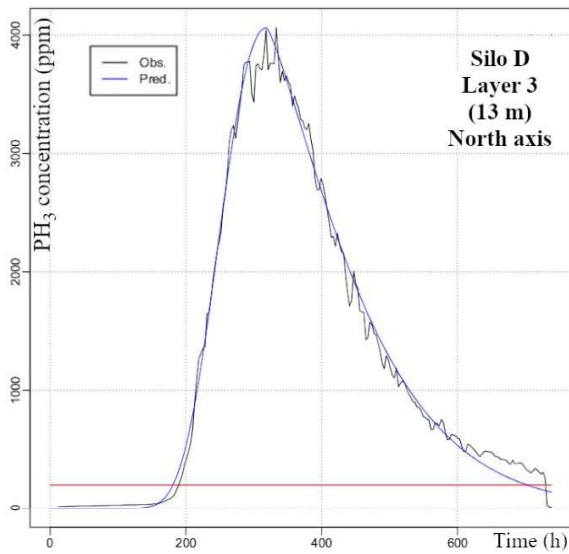


Fig. 10. Smaller oscillations in the north axis

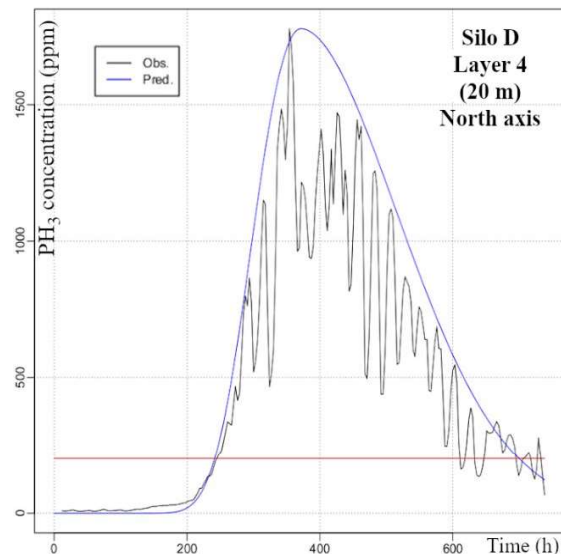


Fig. 11. Oscillations near the surface level

All the results for each line and each silo were subjected to a parametric smoothing to check the consistency of the measured values. This consisted in three steps: an apogee coordinate estimation, an ascending branch adjustment by a function inspired by the log-normal distribution probability density, and a descending branch adjustment by a function inspired by the Weibull distribution survival function. The curves were thus much more readable and showed the general trend (Figs. 9-11) despite the regular daily concentration oscillations.

The continuous measurements allowed us to observe remarkable daily oscillations for the first time in 8,000-t silos (Figs. 8-11). For the central lines, we noticed a regular daily evolution with a high amplitude: the concentration was the lowest in the morning, and the highest in the evening (Figs. 8-9). The Silo D center axis values showed a 1500 ppm variation for a 2800 ppm concentration. However, the oscillations of the non-centered lines (North, South, East and West) were much less accentuated. Their amplitude remained under 300 ppm as shown in Fig 10. Near the surface level (20 m), the PH_3 oscillations in the grain fluctuated in the morning and evening on all lines, but with a stronger and more irregular intensity. These oscillations were even accentuated on the central line. The "chimney effect" is clearly observed in Fig. 11.

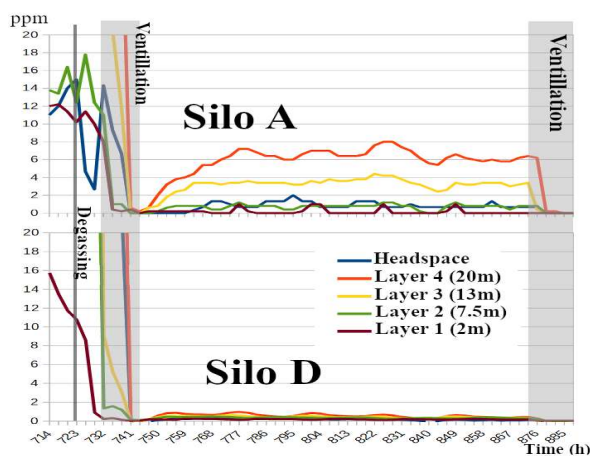


Fig. 12. Degassing in Silos A and D

The degassing started after 30 d (723 h) under gas. Ventilation ran for 12 h starting at hour 732. There was still between 30 and 50 ppm of gas in the silos gassed from the top. As we can see in Fig. 12, the fall in the concentrations was very rapid, reaching zero ppm in about 10 h.

When ventilation stopped, we then witnessed a slow rise in concentrations of 1 to 5 ppm in Layers 4 and 5 in Silo A, and less in the other layers. These values were quite stable for 5 d. The passive degassing was very slow. Ventilation was restarted 5 d later and the gas was completely evacuated in a few hours. For the silos gassed from the bottom, the concentrations measured in the grain were 50 to 160 ppm. After the first 12-hour ventilation, the concentrations dropped to zero ppm and rose again between 0.2 and 1 ppm. We noted that under the test conditions, the degassing was very rapid, thanks to the ventilation. After 7 d of degassing, the sorbed PH₃ was totally evacuated at hour 888 after the second ventilation cycle.

Conclusions

This full-scale trial was carried out in four 8,000-t silos of durum wheat. Measured concentrations from 104 locations during 37 days gave PH₃ concentration values at a 3-h interval. Our data showed that gassing from the bottom gave a total efficiency at all levels, estimated by the threshold of 200 ppm for 6-7 days. On the other hand, gassing from the top gave no efficacy throughout the silo, even at double the dose. This trial showed a large difference in gas distribution when gas was introduced from the bottom or from the top of a silo. Phosphine application is still in development in France, where silos were not built for fumigant use and are rarely gas-tight. The empirical data from our several million tonnes of treatment to date has taught us that everything is fumigable if we develop new fumigation techniques using multi-point monitoring. Our goal is to be efficient and not create PH₃ resistance, even when fumigating non-sealed silos.

For the first time, thanks to the 30,000+ measurements, we were able to visualize PH₃ distribution in all of its complexity. As our friend Jan Van Graver used to say, "If you are not monitoring, you are not fumigating." We can add today, "Monitor to better understand, monitor to innovate, monitor to succeed."

Acknowledgements

We would like to thank Patrick Ducom for his advice and always pertinent analysis; Thierry Ducom (CaptSystemes, France) for the data collection and Yves Le Gat (INRAE, France) for the statistical analysis. Thanks also to the Arterris cooperative for letting us use their installations with 32,000 t of durum wheat.

References

- Noyes RT, Phillips TW (2004) A model for selecting tablet vs. pellet dosages in storages with closed loop fumigation (CLF) systems. Pp. 393-401 In: Proc 7th Intern Conf Controlled Atm Fumi Stored Prod, Brisbane, Australia.
- Ducom P (2005) The issue of phosphine fumigation. Pp. 60-61. Proc Annual Intern Res Conf on Methyl Bromide Alternative and Emissions Reductions, October 30-November 1, San Diego, California.
- Williams P, Nickson PJ, Braby MF, Henderson AP (1996) Phosphine fumigations of wheat in 2500 m³ steel bins without recirculation. J Stored Prod Res **32**: 153–162.
- Green AR, Sheldon S, Banks HJ (1983) The flammability limit of pure phosphine-air mixtures at atmospheric pressure. Pp. 433-449. In: Ripp BE, Banks HJ, Calverley DJ, Jay EG, Navarro S (eds) Proc Intern Symp Practical Aspects of Controlled Atm and Fumi in Grain Storages, Amsterdam, Holland.