A Comparative Study Of Phosphine Distribution Using Two Application Methods With 30,000 Gas Concentration Measurements

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Abstract: Homogeneous phosphine distribution to all locations inside a silo cell 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 silo cells used in this study are four identical, 10,200 m^3 concrete cylinders each containing 8000 tons of durum wheat at a temperature between 27 and 30°C. The cells were partially sealed and did not have recirculation fitted. 10 PhosCapt-MP phosphine monitors recorded and transmitted gas concentrations every 3 hours on a total of 104 points. The cells were divided into four 5 m vertical sections with 5 monitoring points placed inside the grain at East, West, North, South and Center. An additional 3 points were placed in the headspace and 3 others in the lower ventilation galleries. There were 4 treatments of two dosages (1.5g and 3g.m^{-3}) generated from Aluminium Phosphide (AlP) bag blankets. One of each dosage was placed in the top of two of the cells, and one of each dosage at the bottom of the other two cells. The fumigation monitoring was conducted over 37 days, recording a total of 30,784 measurements. Gas introduced at the top quickly penetrated the first 10 m (of the 22 meters) and reached 200 ppm in the first 12 hours of fumigation, but not long enough to be effective. Then, its progression became very heterogeneous for both gas dosages. In the bottom half of the cells, the concentrations never reached 200 ppm. When gas was introduced at the bottom, the gas propagation, regardless of the dosage, was slower and more uniform. It took 7 days for the gas to reach 200 ppm at 10 m from the cell bottoms and 10 days 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, bottom fumigation works very well. The PH_3 convection inside the silo cell is also analyzed.

Keywords: Phosphine, PH_3, Fumigation, Gas Distribution, Phosphine monitoring, Silo, Bin, Cell

Introduction

The goal of our study was to characterize the differences in phosphine penetration and distribution into a grain mass in real conditions. This was conducted on four 8000-ton cells of durum wheat using two types of generator applications, one from the top of the cell and the other from the bottom. Two doses were tested: 1.5 g.m^{-3} et 3 g.m^{-3}. 10 Phosphine monitoring devices (PhosCapt-MP) followed the evolution of the gas concentrations at 104 measuring points 8 times a day.

Materials And Methods

This study was conducted in Baziège (France) in August 2019 with clement weather conditions. At the beginning of the test period, the outside air temperature was 22 – 29°C (26°C average) and 18 – 25°C (22°C average) at the end. The tests were carried out at the Arterris cooperative site in four 24.5 m diameter, 19.8 m high round cement cells with 5.5 m high cone-shaped metal roofs, a 10,200 m^3 volume and real tonnage from 7600 to 8000 of recently harvested durum wheat. The grain characteristics at the beginning were fairly homogeneous: temperatures 27 – 30°C, 11.5 – 13.7% moisture content, 81.1 – 82.6 specific gravity and 13 – 13.4 % protein. The roofs were gas-proof, but not perfectly so, as we will see. All 4 cells 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 releases 1.1

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Kg of PH_3 and each 680 g mBB releases 226 g of PH_3. The mBB were used for the bottom short-length aeration system. Cells A and C were gassed with a dose of 1.5 $g.m^{-3}$ PH_3, using 14 BB and Cells B and D were gassed with a dose of 3 $g.m^{-3}$ using 17 BB and 50 mBB.

The concentration measurements were carried out every 3 hours by 10 dual-sensor PhosCapt-MP with email reporting (Figures 6 and 13). Each device can monitor 12 4mm ID PE lines of up to 200 m, with automatic sensor selection between high concentrations (up to 15,000 ppm, 1ppm precision) and very 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. The non-centered measurement lines were attached to the temperature sensor cables situated halfway between the center and the wall (5.5 m from the wall). Measurement points were arranged in the following manner:

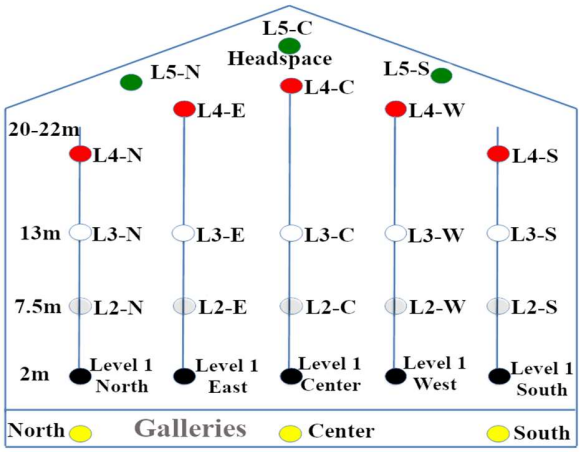

Figure 1: Measurement points map

The 4 cells were gassed in passive mode, meaning that no recirculation was used during the fumigation time. The gassing operations were carried out simultaneously. One team gassed Cell A, while another team gassed Cell C. The same for the gassing of Cells B and D. For cells gassed from the top: The closed BB were deposited in the center of the cell. Two operators opened the BB and arranged them in a star pattern on top of the grain. For cells 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 in front of each pipe and were placed on a 3m cable routing. The mini BB were deposited at the pipe entrances.

Efficacy was assessed by the gas measurements. The target is to maintain ≥ 200 ppm (Noyes and Philips, 2004)[1] during the exposure time defined by the temperature. In our case, temperature being at 27 – 30°C, our standard for minimum exposure time at 200 ppm was 144-168h (Ducom, 2005) [2].

Figure 2: 8,000 T cells at Arterris site

Results And Discussion

With 104 measurement points in 4 silos and a 3-hour measurement interval over 37 days, we have an unprecedented total of 30,784 measurement data.

Gassing from the top (Cells A and B) led to a significant and very rapid increase in concentrations in the first few meters at the top of the cells, reaching values from 2,000 to 4,000 ppm. We then observed the inability of PH_3 to penetrate into the lower layers of the grain mass where we found very low and

erratic values below 100 ppm. The same trend was found in Cell B with the double dosage. These results differ from those found by Williams et al, (1996) [3] for 2500-ton silos gassed from the top with Blankets. In these trials, the overall concentration was efficient at all levels, including the bottom, due to the very good sealing of the cells.

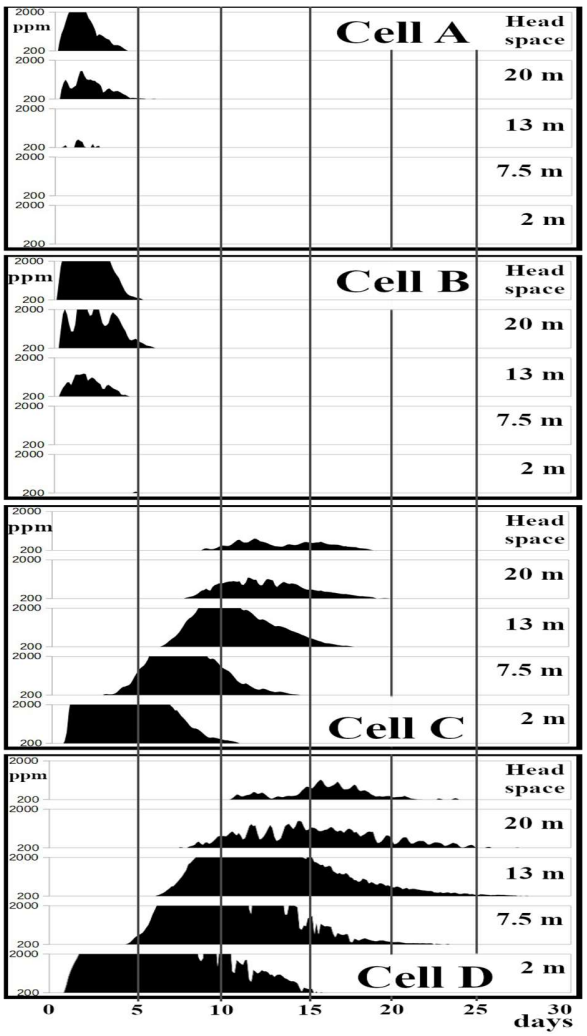

Figure 3: Per level concentration averages in each cell (range: 200 to 2000 ppm).

In order to accurately measure the presence of gas in the different cells, the CTP of the average PH_3 concentrations per level were calculated. This was a detour from the notion of CTP usually used to assess the efficacy of a fumigation with fumigants other than phosphine (MeBr, SF, HCN, etc).

Table 1: Per level Concentration Time Product of concentrations above 200 ppm. (in Kppmh)

Levels		Cell **A**	Cell **B**	Cell **C**	Cell **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**

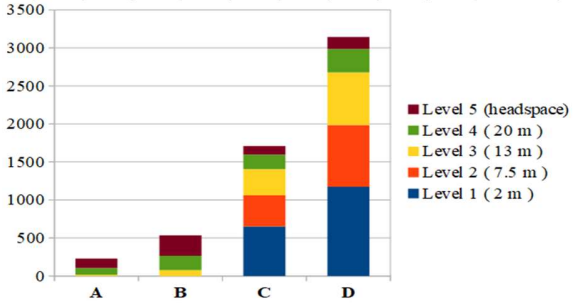

Figure 4: CTP calculated from the per level averages of PH_3 concentrations above 200 ppm (in Kppmh).

We noticed a huge difference in the presence of PH_3 between a gassing performed by placing the generator at the top of the cells and one with the generator at the bottom. We also noted in Cell D (with a double dose at the bottom of the cell), a doubling in the CTP values for the bottom three levels, compared to Cell C (with a single dose). The differences in CTP in the upper layers of Cells C and D were lower. This could be explained by a probable gas leakage at the top of the cells, even though the cell roofs were sealed.

During gas production by generator, concentrations increase until the end of hydrolysis at a peak and then start to decrease. The decrease is due to gas diffusion, sorption and leakage.

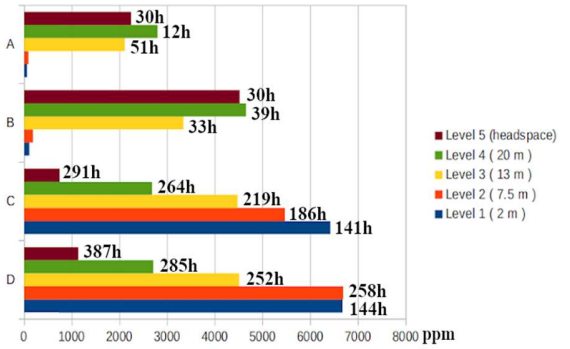

Figure 5: Cell level concentration peak times and values

In cells gassed from the top, the PH_3 peaks in the first few meters of the grain occurred between 30 and 51 hours. In the lower levels, the peaks never reached 50 ppm. Gassing from the bottom looked very different. In Cell C, where the PH_3 generators were placed in the ventilation ducts, the concentrations stayed above 11,000 ppm for about 100 hours with a peak at 12,400 ppm. In Cell D (double dose), the ventilation duct concentration values were the same as for Cell C (single dose). The PhosCapt-MP is capable of measuring concentrations of up to 15,000 ppm. Preliminary gassing tests in the bottoms of different cells showed that the concentrations never reached more than 12,000 ppm for application doses of 3 $g.m^{-3}$ PH_3. This could have been due to a lack of water vapor that naturally limited the AlP hydrolysis speed and, as a result, the instantaneous quantity of PH_3 produced. We are thus well below the 17,900 ppm value, the flammability zone of phosphine (Green et al, 1983) [4].

Gassing from the bottom showed a very slow gas penetration rate. Peaks at 1 meter from the top of the pile (Level 4) were obtained in 264-285 hours (11 days). The peaks in the headspace were obtained in 12 to 16 days. However, concentrations were high at all levels, including the highest level where they reached nearly 400 ppm. Thus, there was a slow but remarkable rise in concentrations.

Figure 6: 2 PhosCapt-MP placed in Cell C, monitoring 23 lines with Ethernet remote control

The fumigation insecticidal efficacy reference is the tandem '200 ppm for 144 h' minimum previously indicated. Thanks to the very large number of measurements taken, it was possible to precisely determine the ranges where the duo ≥ 200 ppm for > 144-168 hours was obtained. In Cells A and B, the generator application from the top of the cells did not allow us to obtain this tandem at all levels. Fumigation was not effective. However, in Cells C and D where fumigation was done from the bottom, efficacy was obtained at all levels for the 2 application doses (1.5 and 3 $g.m^{-3}$). See Table 2 and Figure 7 below:

Table 2: Exposure time, per level, based on the concentrations above 200 ppm averages (in hours)

Levels		Cell **A**	Cell **B**	Cell **C**	Cell **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**

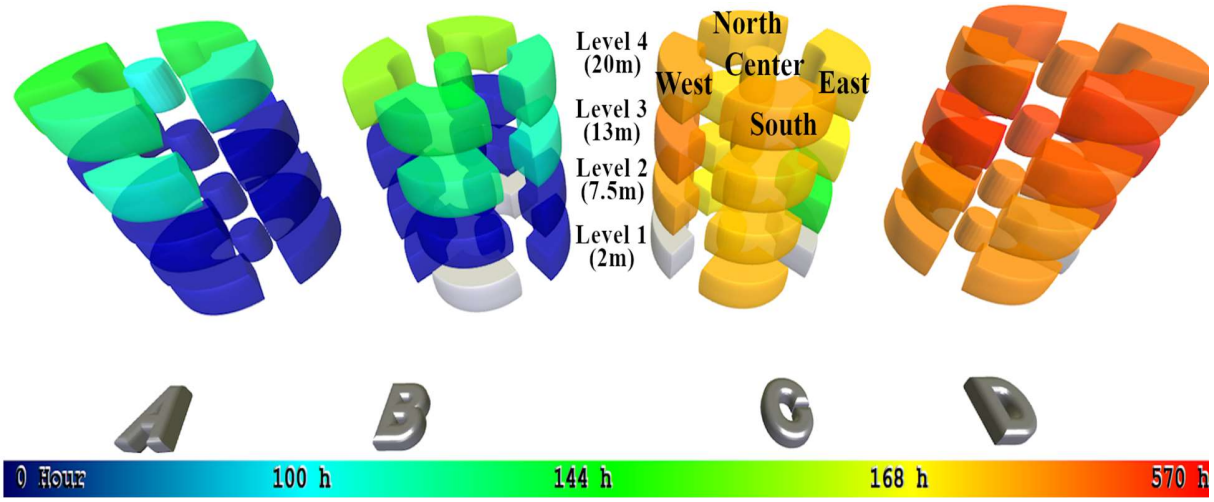

Figure 7: 200 ppm exposure time 3D cartography (Grey = data unavailable).

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 Figures 8 to 11.

All the results for each line and each cell 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 (see Figures 9 to 11) despite the regular daily concentration oscillations. The continuous measurements allowed us to observe

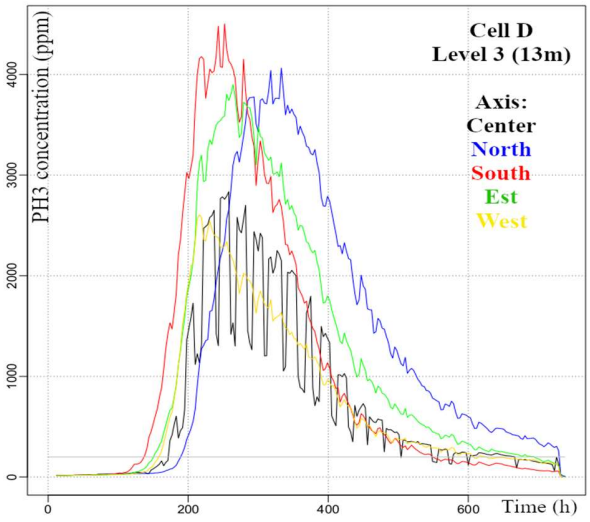

Figure 8: Evolution of PH_3 concentration near the middle of Cell D at Level 3 (13m)

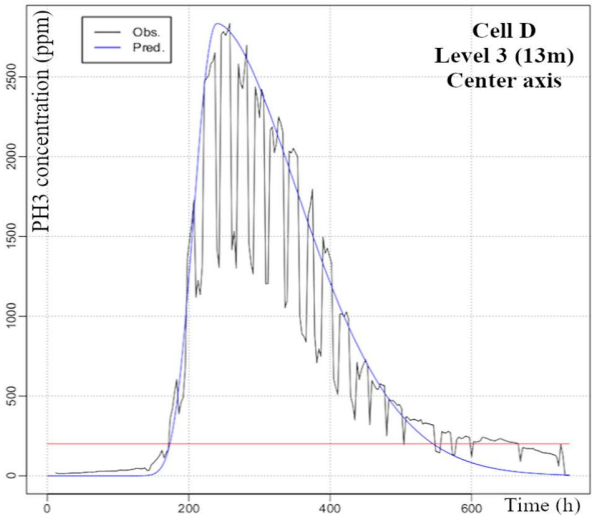

Figure 9: Daily oscillations in the center axis

remarkable daily oscillations for the first time in 8000-ton cells (see Figures 8 to 11). For the central lines, we noticed a regular daily evolution with a high amplitude: the concentration was lowest in the morning, and highest in the evening. The Cell D center axis values show 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 below on Figure 10:

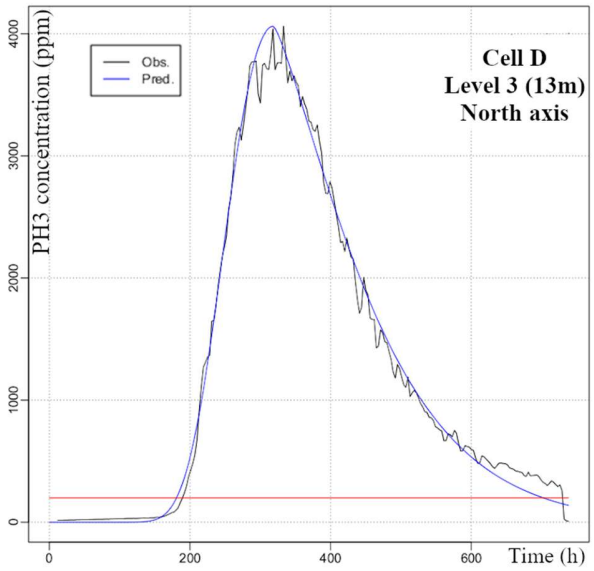

Figure 10: Smaller oscillations in the north

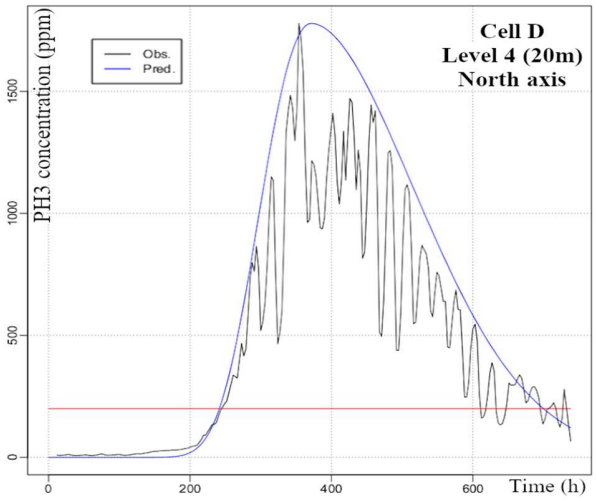

Figure 11: Oscillations near the surface level

Near the surface level (20m), 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 Figure 11.

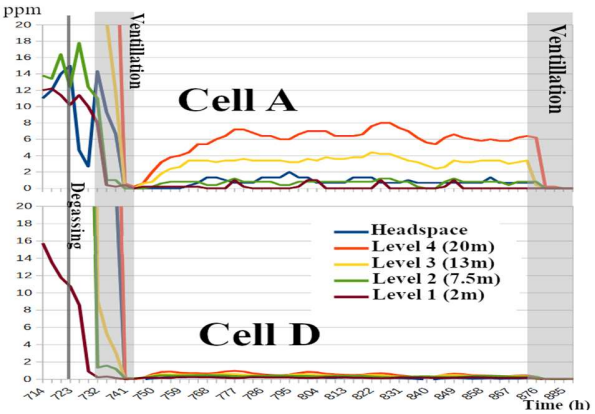

Figure 12: Degassing in Cells A and D

The degassing started after 30 days (723 h) under gas. Ventilation ran for 12 hours starting at hour 732. There was still between 30 and 50 ppm of gas in the cells gassed from the top. As we can see in Figure 12, the fall in the concentrations was very rapid, reaching zero ppm in about ten hours. When ventilation stopped, we then witnessed a slow rise in concentrations of 1 to 5 ppm on Levels 4 and 5 in Cell A, and less on the other levels. These values were quite stable for 5 days. The passive degassing was very slow. Ventilation was restarted 5 days later and the gas was completely evacuated in a few hours. For the cells 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 days of degassing, the sorbed PH_3 was totally evacuated at hour 888 after the second ventilation cycle.

Conclusion

This full-scale trial was carried out in four 8000-ton cells of durum wheat. 104 measuring points during 37 days gave PH_3 concentration values at a 3-hour 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 cell. PH_3 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 tons 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 PH_3 resistance, even when fumigating non-sealed silos.

For the first time, thanks to the 30,000+ measurements, we were able to visualize PH_3 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."

Figure 13: PhosCapt®-MP: Phosphine monitoring of 12 lines with dual-sensor and email reporting. CaptSystemes, France. (phoscapt.com)

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 tons of durum wheat.

References

[1] Noyes RT, Phillips TW (2004) A model for selecting tablet vs. pellet dosages in storages with closed loop fumigation (CLF) systems. International Conference of Controlled Atmosphere and Fumigation in Stored Products, 393-401. FTIC Ltd. Publishing, Israel.

[2] Ducom P (2005) The issue of phosphine fumigation. Proc. Annual International Research Conference on Methyl Bromide Alternative and Emissions Reductions, October 30-November 1, San Diego, California, 60-1.

[3] Williams P, Nickson PJ, Braby MF, Henderson AP (1996) Phosphine fumigations of wheat in 2500 m3 steel bins without recirculation. Journal of Stored Products. Res., 32, 153–162.

[4] Green AR, Sheldon S, Banks HJ (1983) The flammability limit of pure phosphine-air mixtures at atmospheric pressure. Proc. Int. Symp. Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages, Perth, Australia. Ed. Ripp E et al.:433-449.