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Dynamic Phosphine Fumigation Using Continuous Monitoring

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ABSTRACT

Phosphine gas is an essential means of controlling grain pests. However, for it to be effective, a certain gas concentration threshold must be held for a specific time period relative to grain temperature. It is therefore necessary to monitor the phosphine concentration throughout the fumigation process, as it can vary over time as a result of various phenomena like leakage, sorption, and chimney effect. Until the 1980s, colorimetric tubes were the only way to measure phosphine in the field. In 1986, the discovery that an electrochemical cell could measure phosphine made it possible to automate multi-point measurements and record and transmit data in real-time. After three decades of research and several prototypes, CaptSystemes created the PhosCapt®-MP, an automatic, connected multi-point device, designed to work in harsh conditions and offer high accuracy over a wide measurement range. The challenge for phosphine fumigations in a group of irregular-sized storages of variable sealing tightness is to achieve and maintain gas concentration uniformity at an effective level throughout the group. Thanks to multi-point monitoring with data transmission, concentrations can be precisely adjusted in any location using a variety of techniques, for example, by adapting the gas flow to different parts of the storage, or by re-dosing. In this way, the effectiveness of the techniques used can be verified. Four examples of dynamic fumigation using a PhosCapt-MP are highlighted in this paper: four 10,200 m^3 concrete silos without recirculation, eight 2,300 m^3 concrete silos with recirculation, a SIROFLO®-like system fumigation without tarpaulin in three 13,000 m^3 metal silos and another of 100,000 m^3 in two domed sheds. Continuous multi-point phosphine monitoring has proven to be an essential tool for guaranteeing fumigation efficiency, monitoring degassing, combatting the development of phosphine-resistant strains, and enhancing safety next to fumigated sites.

Keywords: Fumigation, Phosphine, Monitoring, Electrochemical cell, Efficiency, safety, PhosCapt, Phosphine resistance

INTRODUCTION

Today, grain pest control faces a number of new challenges. Alternatives to phosphine are disappearing. Contact insecticides are being phased out due to their residues. Anoxia is too complicated to implement on a large scale since it needs totally gastight sealing. The use of cold treatments is not cost-effective due to increasing energy costs. With global warming, insect infestations no longer stop in winter. Phosphine fumigations in large or non-gastight structures pose challenges in obtaining and maintaining a uniform gas concentration at an efficient level for a minimum amount of time defined by grain temperature. Yet, we cannot be sure whether the fumigation was successful without measuring the gas in key locations. The important advantage of continuous gas concentration measurements is the opportunity to adjust, in real-time, the amount of gas in all locations to guarantee a successful fumigation, even in the most complicated situations. "PhosCapt®" phosphine monitors (Fig. 1B), the result of more than 30 yr of research, have enabled the development of innovative dynamic fumigation techniques.

HISTORICAL BACKGROUND

For a long time, phosphine measurement methods were either too cumbersome, expensive, or difficult to implement in the field. Until the 1980s, the only measurement method in the field relied on Draeger® or Auer® colorimetric tubes. In 1986, for the first time, it was discovered that because phosphine is a reducing gas, an electrochemical cell could react to it (Ducom and Bourges, 1986). There were electronic devices measuring the reducing gas CO, and the manufacturer, Herrmann-Moritz, suggested that Ducom and Bourges (1986) modify a CO device to measure phosphine. This discovery opened the way for precise, easy-to-use, inexpensive measuring devices. It was finally possible to take a lot of measurements at a low cost. Thanks to the first microcomputers in the 1980s, it became possible to experiment with multi-point measurements, automation, data recording, and real-time data transmission. In 1987, the first automated prototype for taking multi-point phosphine measurements was developed at the LNDS laboratory in Bordeaux, France (Fig. 1A). Its data could be accessed remotely using a Minitel connection (the ancestor of the Internet in France). The PhosCapt®-MP phosphine monitor, commercialized since 2015, resulted from this research (Fig. 1B).

Fig. 1. A–Prototype in lab; B–PhosCapt®-MP first model in 2015; and C–AlP hydrolysis speed.

PhosCapt®-MP MONITORING SYSTEM

The system works autonomously and automatically to measure phosphine concentrations on twelve 4 mm (or ¼") ID lines of up to 200 m (650 ft) long several times a day on a user-defined periodicity (1, 3, 6, 8 h, or continuous). It was created to be easy to transport and deploy, to be accurate with a wide measurement range (0 to 15,000 ppm and a minimum detection of 0.02 ppm PH_3), and to transmit the results in real time via email to the fumigation operator and to a server for online concentration monitoring. A copy of the readings is recorded as a spreadsheet file in its non-volatile memory for traceability. It is made to resist harsh conditions like dust and large temperature amplitudes. In large-scale fumigations, multiple devices can be used together to increase the number of sampling points. When they are connected to an Ethernet network, one computer can configure and monitor them all locally. The configuration consists of identifying each line by assigning it a label and selecting its measurement mode from three different modes: *Efficacy (E), Clearance (C)* or *Security (S)*. Unused lines are deactivated, but they can be activated anytime. Then, the user selects the measurement series frequency and starts the measurement cycle. To receive email data, the user enters an email address. An optional alarm can be configured to trigger an email if a concentration threshold is reached. Depending on the settings and the line measuring mode, the device will trigger an alarm when the concentration falls under a low threshold (i.e., < 250 ppm) on an '*Efficacy (E)*' line or exceeds a high threshold on a '*Security (S)*' line (i.e., > 0.3 ppm).

To ensure maximum precision on a wide measurement range, two sensors are used. One sensor measures high concentrations in the 0 to 15,000 ppm PH_3 range with 1 ppm precision, and a second sensor measures low concentrations from 0 to 20 ppm PH_3 with 0.01 ppm precision. In lines configured in *Efficacy (E)* mode, only the high-concentration sensor is used. In lines configured in the other two modes (*Clearance (C)* and *Security (S)*), firstly, the high concentration sensor is used and then, if the concentration is lower than 20 ppm, a second sample is taken using the low concentration sensor with greater precision. The *Security (S)* mode is used in lines that check for leaks around the fumigation area. These lines are sampled first at each measurement cycle. The *Clearance (C)* mode is used in lines that monitor high concentrations for fumigation efficacy; when the concentration drops at the end of the fumigation, it automatically switches to the low concentration sensor to monitor degassing and to ensure that the area is safe for access. The *Efficacy (E)* mode is used in lines that only monitor high concentrations for efficacy.

Monitoring concentration ensures fumigation effectiveness and prevents having to re-fumigate too frequently. It enables a precise adjustment of the amount of gas used. It also allows for the fumigation of certain storage spaces that would be too expensive to seal.

For research use, the standard sampling settings can be adapted for special conditions like working with small bins or carrying out more frequent measurements. The PhosCapt®-MP is used in a wide variety of experiments in a laboratory or in the field as, for example, an AlP hydrolysis speed study (Fig. 1C), a PH_3 sorption study in wet wood, or in gas diffusion studies in containers or silos.

DYNAMIC FUMIGATION COMPONENTS

The principle of dynamic fumigation is that three components (storage sealing, gas delivery, and the circulation system) can be adjusted dynamically according to the real-time data from the gas monitoring system.

- Storage structures that are sealed using practical, affordable sealing methods of all major and most minor leak sources, so that fumigation gas leakage is minimal.

- A ground-level dosage generation delivery system, which safely delivers an efficient quantity of phosphine gas with the ability to re-dose easily (e.g., dry release cabinets as shown in Figure 2).
- An optional modular multi-storage unit gas circulation system using manifolds. This can be a closed-loop circuit like CLF (Noyes et al., 1998) or thermosiphon (Newman et al., 2012) or even an open SIROFLO®-like system. In large storage facilities, valves are used to enable a fine-tuning of gas routing and flow regulation in the different areas to adjust concentrations in all locations. Motorized gas circulation is an option.
- A reliable phosphine monitoring system, which allows fumigators to 'react in real time' by receiving continuous gas concentration measurements at key locations in all fumigated storage facilities and surrounding areas where leaks can occur. At the end of fumigations, monitoring helps determine when grain bins and work areas are safe for entry (Fig. 1B).

LARGE STORAGE STRUCTURE FUMIGATIONS IN FRANCE

In France, very few silos are sufficiently gastight to ensure good fumigation, i.e., to have uniform gas concentration and keep it in place. One exception is concrete silos that are generally sufficiently gastight if they are closed at the top. The silos can be inspected, and any leak sources such as manholes, extractors, vents, and grain inlets can be sealed. Traditionally, phosphine generators are placed at the top of the cell or sometimes at the bottom because, even though gas diffusion is slower, concentrations are more uniform (Ducom et al., 2021). Active recirculation can help, but might lead to more leakage, so it should be used with moderation. Metal silos are generally not made to be gastight, as they often have openings between the walls and the roof to allow dust and moisture to escape. There are also silos or flat storages, where cells are often impossible to keep gastight, even with tarping, which may also be too complex or expensive. In these conditions, it is necessary to implement a fumigation system that does not require sealing. A solution was proposed at CSIRO by Winks (1992) known as SIROFLO®. It is a continuous pressurized phosphine distribution system, which distributes gas upward throughout the grain. Winks (1992) showed that exposure time is far more critical than gas concentration. To control major grain-infesting species, it is essential to significantly prolong the usual exposure time of 5 d. In these conditions, high phosphine concentrations are not needed; in fact, the gas is more effective at lower than usual concentrations. Gas release must be continued long enough to overcome egg and pupal survival, so that sufficient gas is still available when the insects hatch. To avoid phosphine resistance, it is important to maintain a lethal concentration in all locations. In situations where sealing is possible but still not totally gastight, a recirculation system is often preferred, like CLF, which is one of the most advanced recirculation systems, as it combines multiple storage entities in one system.

GROUND-LEVEL DOSAGE GENERATION DELIVERY SYSTEM

Liquid phosphine in cylinders has not yet been certified for use in France. A technique has been developed which assists in the passing of a controlled flow of air into a dry release cabinet containing metal phosphide blankets (Fig. 2).

This enables gas to be injected with or without recirculation. The phosphine concentration leaving the cabinet varies depending on the air humidity, the fan flow rate, the quantity of AlP product loaded in the cabinet, and the use of recirculation or not.

Fig. 2. Two PH_3 dry release cabinets (MFD. Valérie Ducom).

CONTINUOUS MONITORING SYSTEM

To take advantage of these gas diffusion techniques, it is essential to have precise and continuous gas concentration monitoring in key locations: within the grain load at different levels, in the headspace, and near the openings (extractors, ventilation doors). Throughout the fumigation, gas concentration fluctuates due to leaks, sorption, thermal effects (Ducom et al., 2021), or other atmospheric events like pressure drops or wind. To maintain the minimum required concentrations in every location, real-time data is essential to dynamically adjust the different parameters: the fan flow rate, quantity of phosphine from the gas generator, recirculation system valve adjustment, and sealing—if needed and if possible. In this way, the effectiveness of the techniques used can be verified, which makes it possible to fumigate silos or warehouses that cannot be totally sealed. Outside the fumigated enclosure, monitoring helps detect possible leaks in critical areas like galleries that can be ventilated to protect the electrical installation from gas corrosion.

FOUR CASE STUDIES IN FRANCE

Fig. 3. Four treated storage systems located in France: 1–Baziège, concrete bins, durum wheat, no active diffusion or recirculation; 2–Roncenay, conical bottom concrete silos, peas, active gas diffusion with recirculation; 3–Pomacle, metal bins, wheat, active diffusion, no recirculation; and 4–Buchères, ground sheds, wheat, injected gas, no recirculation, and no tarping.

1–Baziège (Aug. 2019): 30,000 t of durum wheat in four 10,200 m^3 concrete bins.

Four silos were fumigated in passive mode, meaning that no active diffusion or recirculation was used, as shown in Figure 3(1). This fumigation was the subject of a study (Ducom et al., 2021) aimed at characterizing the differences in phosphine penetration and distribution into a grain mass using two types of applications—one from the top of a silo (Fig. 4A, 4B) and the other from the bottom (Fig. 4C, 4D). Ten PhosCapt®-MP monitors took a total of 30,000 measurements from 104 locations over 37 d. Data showed that gassing from the bottom gave total efficacy at all levels. On the other hand, gassing from the top gave no efficacy throughout the silo, even at double the dose. For the first time, it was possible to 'visualize' PH_3 distribution and its complexity.

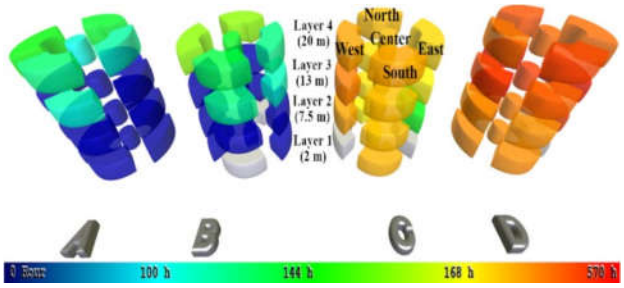

Fig. 4. 200 ppm PH_3 exposure time in 3D cartography.

2–Roncenay (Aug. 2023): Peas in eight 2,300 m^3 conical bottom concrete bins.

As shown back in Figure 3(2), active gas diffusion was used with four dry release cabinets and recirculation in eight silos with conical bottoms infested with pea weevils. Valves on the ventilation ducts were used to manually adjust the gas flow. One PhosCapt®-MP monitor with one line in the grain at the top of each cell and one line in the upper gallery to detect leaks took 1000 measurements at nine locations, eight times a day, for 14 d. The concentrations were relatively uniform after the first five days, except for cells C55 and C77, but all cells remained well above 200 ppm during the long gas exposure time, which exceeded 10 d (Fig. 5). Leakage in the gallery was very low, which is consistent with good results in the cells.

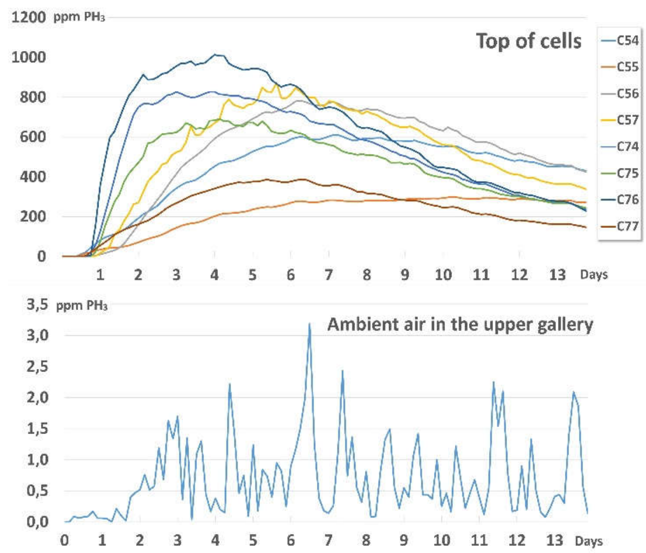

Fig. 5. PH_3 concentrations in Roncenay.

3–Pomacle (Aug. 2023): Wheat in three 13,000 m^3 non-gastight metal bins.

Three out of eight bins, as shown in Figure 3(3), were fumigated without roof sealing (as each bin had a roof–sidewall air gap) using active gas diffusion without recirculation, with one dry release cabinet per bin. The 16 ventilation ducts of each cell were connected to a manifold using flexible tubing from the dry release cabinet. Valves on the ventilation ducts were used to manually adjust gas flow. One PhosCapt®-MP monitor took a total of 1,000 measurements at six locations within the three bins (Fig. 6). One line was placed below the grain surface at the top of each cell, and one line was in each of the bottom galleries to detect leaks. The objective was to obtain as long of a continuous gas exposure time as possible (over 15 d in this case). The graphs in Figure 7 show that the gas concentrations were relatively uniform, remaining above 200 ppm in all three cells (CB2, CB3, and CB4) for more than 10 d. In the galleries, the PH_3 concentrations were quite high, especially at the start of the hydrolysis: 150 to 200 ppm. In fact, the sealing around the CB4 air entry doors was not tight enough. When the gallery doors were tightened, it took 2 d for the gas concentration in CB4 to reach the target level. After 5–6 d, concentrations in the galleries stabilized at around 40–60 ppm. After the fumigation, no live rice weevils or any other insects were found.

Fig. 6. A PhosCapt®-MP in a cabinet outside the bin.

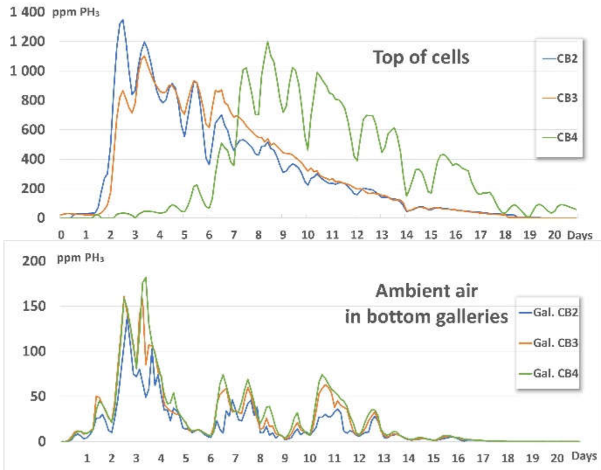

Fig. 7. PH_3 concentrations in Pomacle.

4–Buchères (Oct. 2022): 75,000 t of wheat in 150,000 m^3 in two ground sheds

Eight dry release cabinets connected to the ventilation system slowly injected gas inside 100,000 m^3 of grain without tarping or recirculation (as previously shown in Figure 3(4)). The ventilation flow was modulated based on air humidity and the PH_3 gas concentration measurements in each cell. In Cell 7, the concentration was maintained above 200 ppm for 10 d. Re-dosing on the 10th day prolonged this gas exposure to 20 d (Fig. 8).

In Cell 10, even after re-dosing, the gas concentration was still close to zero. It was necessary to adjust the ventilation duct valves to route enough gas to Cell 10 to reach the target value and maintain a good concentration for 8 d.

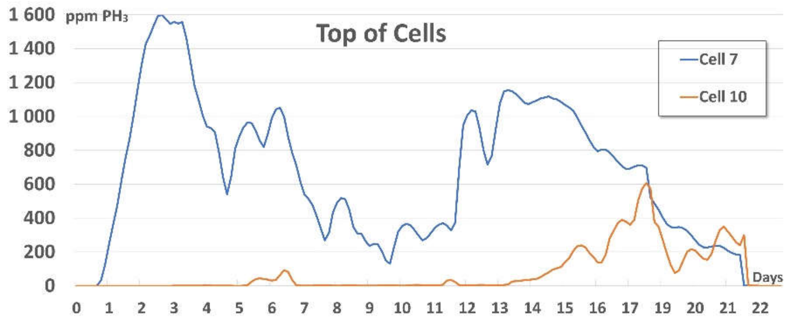

Fig. 8. PH_3 concentrations in Buchères.

Before the fumigation, there was a very significant rice weevil infestation in all the cells. After fumigation, sieving revealed no living insects. In the following 7 mo, no insects were found during quality checks. Three PhosCapt®-MP monitors took more than 5,000 gas concentration measurements at 29 locations over 25 d (Fig. 9).

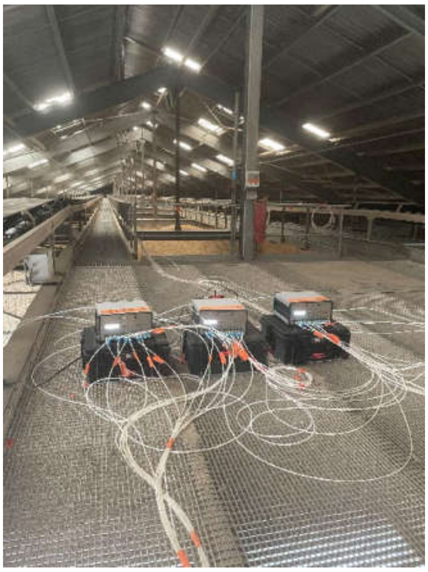

Fig. 9. Three PhosCapt®-MP monitoring 29 locations.

CONCLUSIONS

Phosphine fumigation remains almost the only economical and completely effective method for eliminating grain insects that does not produce residues. Continuous multi-point phosphine monitoring enables dynamic adaptation of the technique to each situation to guarantee an effective and safe fumigation. It introduces the precise control and maintenance of fumigation concentrations; thus, monitoring pays off through efficient dosage/concentration management, with much more predictable efficacy, and results in higher grain product quality and value. In the longer term, these techniques help prevent the emergence of phosphine-resistant insects since each fumigation eliminates all stages.

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