Fumigation of non gas-tight buildings and horizontal structures using continuous phosphine injection

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Abstract
Sealing of structures for fumigation could require intensive use of capital, time and resources. Some old mills, buildings and horizontal warehouses were not conceived to hold gas throughout a fumigation process. Some of these structures are only fumigated occasionally, thus it is difficult to justify the investment in permanent sealing. These poor sealing conditions can be overcome with a continuous phosphine injection. Continuous phosphine injection using pure phosphine and the Horn Diluphos System technology is an alternative to carry out a successful fumigation of non gas-tight structures, being able to overcome the natural leakage of the structure, controlling the phosphine concentration during extended periods of time, controlling the insects and reducing corrosion problems as compared with traditional metal phosphide fumigations. During the fumigation period or exposure time, a Horn Diluphos System (HDS) equipment was set to inject an air-phosphine mixture with a concentration close to the target concentration, depending on the natural leakage rate of the structure being fumigated. As pure cylindered phosphine is free from corrosive ammonia, present as a by-product on traditional metal phosphide formulations, less corrosion problems occur when using pure cylinderized phosphine in comparison to fumigations made using metal phosphides. Even more, in corrosion sensitive facilities or non gas-tight buildings, the Horn Diluphos System offers the option to interconnect the HDS equipment to an electronic phosphine CertiPh3os® monitor which is able to control the concentration in between a narrow range, being able to control the insects with the lowest effective concentration, minimizing the amount of phosphine used and also minimizing the corrosion problems, independent from changing environmental conditions, as strong winds. On practical experience, phosphine concentration in the surrounding areas was monitored throughout the fumigation process using electronic detectors and no dangerous phosphine concentrations, over 0.3 ppm, were detected in the surrounding areas.

Keywords: phosphine, continuous injection, mill fumigation, HDS, corrosion

1. Introduction
The worldwide food industry is facing a lack of chemical, cost effective and practical methods to control insects in stored products and food processing facilities. Today, fumigant alternatives are reduced basically to phosphine, methyl bromide and sulfuryl fluoride. Although methyl bromide has excellent fumigant properties, it has been identified as an ozone depleting substance by the Montreal protocol, and thus its use has been limited worldwide for quarantine and critical uses in which there has not been identified fumigation alternatives.

Sulfuryl fluoride used as fumigant for food products has been questioned worldwide due to the fluoride residues present in fumigated products after aeration and its association with dental issues, which is limiting its use on different countries. On the environmental side, it has been described that sulfuryl fluoride has a strong global warming effect, 4.800 times
compared with carbon dioxide and it persist in the atmosphere for around 36 years (Papadimitriou, 2008). Regarding the fumigant properties, sulfuryl fluoride has a poor ovicidal effect and its global efficacy is very sensitive to temperature (Athanassiou, 2012).

Phosphine has been in the global market for more than 80 years, and it is today the most widely used fumigant for the control of pests in stored products worldwide. Phosphine has been proved to be effective to control insects in all life stages at a reasonable cost. Before 2001, the only way to obtain phosphine was through the hydrolysis of metal phosphides such as aluminum phosphide or magnesium phosphide. As this application relies on a chemical reaction, it has been difficult to accurately control the application, which has lead to poor fumigation results, inadequate concentration during exposure time, and fires due to the pyrophoric nature of phosphine.

The optimization of the use and the application of the actual fumigants available in the market is required by the food industry in order to keep them functional and effective for the future. In 2001, the Chilean company Fosfoquim developed a method to dilute pure cylinderized phosphine directly with air through an automated equipment known as Horn Diluphos System. This technology has been successfully adopted by several industries such as grain, dried fruit, fresh fruit, seeds, forestry, and others, for either domestic and export processes, in different countries including USA, Australia, Argentina, Chile, Uruguay, Paraguay, New Zealand, Philippines and others.

![Horn Diluphos System equipment. Model HDS 200 for fumigation using pure cylinderized phosphine.](image)

The basic premise for fumigation is the need of a gas tight facility capable to hold the fumigant gas, for enough time, in order to control the insects. Sealing of structures for fumigation could require intensive use of capital, time and resources. Old mills, buildings and horizontal warehouses were not conceived to hold gas throughout a fumigation process. Some of these structures are fumigated just occasionally, on years with large harvests, thus it is difficult to justify the investment in permanent sealing. In the case of mills, the time available for the fumigation becomes into a limitation when selecting the appropriate fumigation method. The traditional method of application of phosphine using metal phosphides requires some time in order to achieve lethal concentrations on the facilities to be fumigated, this time depends on ambient conditions such as temperature and moisture.

Corrosion in metals such as copper, silver and gold has been identified as a limitation for the application of phosphine in mills and food processing facilities. The incidence of corrosion
depends on various factors, such as phosphine concentration, ammonia presence, temperature and others.

In the case of the traditional phosphine formulations, they contain ammonium carbamate which generates ammonia together with phosphine in the hydrolysis reaction. Similar to phosphine, ammonia is a corrosive gas for metals such as copper. Through the use of technology such as the Horn Diluphos System together with pure cylinderized phosphine, it is possible to optimize the application of phosphine, overcoming most of the typical disadvantages of the application of traditional aluminum or magnesium phosphide formulations.

2. Materials and Methods

Two practical applications of the Horn Diluphos System technology in non gas tight and corrosion sensitive facilities are presented.

2.1. Non gas-tight horizontal warehouse with continuous phosphine injection

2.1.1. Description of the facility

The fumigation was carried out on a lyophilization plant, also known as freeze-drying, located in Buin, 50 km south from Santiago, Chile. The fumigated facility corresponds to the end-product warehouse.

Figure 2  Lyophilization plant. Buin, Chile.

The warehouse dimensions were 8 m width, 21 m long, 7.5 m height metal sheet warehouse with concrete floor, having two loading docks and two man doors. The construction has been designed to hold freeze-dried products protected from ambient conditions. The facility has never been fumigated and has not been sealed for fumigation purposes. Inside the warehouse, lyophilized products were present in various types of packaging material, including cardboard and plastic bags. The products were organized on racks, with product at different heights in the facility.
Figure 3  Warehouse with end product in different packaging.

2.1.2. Preparation for fumigation

In preparation for fumigation, all access doors were sealed using polyethylene sheeting. Through one of the man doors, the phosphine injection hose was installed in order to introduce the gas throughout the fumigation time. Major cracks and openings found on the facility were sealed using polyethylene sheeting, PVC tape, or polyurethane expansion foam.

Figure 4  Sealing of doors using PVC tape and polyethylene sheeting.

In order to monitor the fumigation treatment, one electronic real time phosphine monitor, model CertiPh3os, was used. Three 4 mm inner diameter monitoring lines were installed in the warehouse covering the different areas.
An exclusion zone of 10 meters was established around the building in order to avoid any non-target phosphine exposures. Warning signs were installed throughout the building and the exclusion zone to inform people about the fumigation process.

2.1.3. Fumigant injection

The fumigant injection could be separated in two stages, initial injection and continuous top up. For the initial injection, and Horn Diluphos System equipment, model HDS 200 was connected to the warehouse. This equipment was programmed to perform the initial injection process of 500 ppm in a short period of time. The initial injection took approximately 18 minutes. At the end of the initial injection process, lethal phosphine concentrations were measured in all three monitoring zones. After the initial injection, one Horn Diluphos System, model HDS 30, was connected to the warehouse. The purpose of this equipment was to maintain the phosphine concentrations throughout the exposure time by adding a continuous flow of phosphine mixed with air at a concentration close to the target concentration defined for the fumigation of 200 ppm.

Figure 5 CertiPH3os phosphine monitor with GSM modem.

Figure 6 Horn Diluphos System, Model HDS 30 used for continuous phosphine injection.
This condition was maintained during the entire exposure time. After 72 hours, the continuous injection of phosphine ceased.

2.1.4. Fumigation control

During the fumigation process, the HDS 30 was set to inject continuously with a phosphine flow rate of 3 grams per minute. This initial setup was made according to the judgement of the fumigators in charge of evaluating the site for the fumigation. Periodic visits to the fumigation site were programmed during the exposure time to verify phosphine concentrations in the facility and the surrounding areas, and to modify the phosphine flow rate of the HDS 30 if required. Throughout the fumigation time, there was windy and warm periods, which affected the leakage rate of the warehouse, affecting the concentrations. Adjustments to the phosphine flow rate on the HDS 30 were perfumed according to conditions and readings observed during site visits.

2.1.5. Aeration

After the 72 hour exposure period, the facility was aerated using forced air extraction. The extraction was maintained until the concentration in the entire facility was verified below legal limit of 0.3 ppm.

2.2. Flour mill automated fumigation

2.2.1. Description of the facility

The fumigation was carried out on a flour mill constructed in 1965, located in San Bernardo, 20 km south from Santiago, Chile. The building has seven floors and a volume of 12,500 cubic meters. The building was not designed to be able to hold gas throughout a fumigation process. The front of the building is a glass wall, conceived to allow natural light to enter into the building. This building has been fumigated under regular intervals, three times a year, for the last 15 years.

Figure 7 Flour mill, San Bernardo, Chile.

The building has electric and electronic equipment inside, and thus corrosion is a major concern regarding fumigation.
2.2.2. Preparation for fumigation

The sealing of the building was done by permanent and non-permanent sealing. Regarding the permanent sealing, this was made using elastomeric paints and geotextile fabrics, which offers durability over the years even exposed to weather conditions. This kind of sealing was used mainly on structural and fixed structures around the building. In terms of non-permanent sealing, this was made using craft paper stripes and wall-paper glue, polyethylene sheeting, polyurethane foaming and duct taping. This type of sealing was used on structures in the building subject to movement such as doors, windows, some equipment, venting, and exhaust systems, among others. This type of sealing can be easily removed after aeration.

Some corrosion sensitive equipment such as PLC’s, computers and analytical equipment were removed from the building. There was a lot of equipment that remained in the building, which were not possible to remove in a practical way. The electronic equipment that remained in the building were sealed using non-permanent sealing. Electronic cabinets, control rooms, and some electronic equipment remaining in the building was sealed and pressurized using compressed air in order to maintain a positive pressure which will prevent phosphine to enter in those areas.

Figures 8 Protection of electronic cabinets (left) and equipment (right) using polyethylene sheeting and compressed fresh air injection during fumigation.

In order to monitor the fumigation four electronic, real time phosphine monitors, model CertiPh3os, was used. Twelve monitoring lines were distributed throughout the building in order to gather data about the process. As a way to improve the distribution of the gas in the mill, and in order to speed up the aeration process, a 11,000 cubic meter fan was installed on the first floor of the mill, blowing into a ventilation shaft that goes up to the seventh floor. An exclusion zone of 10 meters was established around the building in order to avoid any non target phosphine exposures. Warning signs were installed throughout the building and the exclusion zone to inform people about the fumigation process.

2.2.3. Fumigant injection

For the phosphine injection, in order to achieve an even and fast distribution of the gas inside the building, a permanent distribution system was fitted in the building. The distribution
system consist in a net of PVC pipes that direct and release the phosphine gas in the different areas of the building on all seven floors. As the time is a constraint for this type of fumigations, an initial injection using two Horn Diluphos System equipments, model HDS 200, was performed, being able to achieve lethal phosphine concentrations all over the mill in a short time, of about one hour. As a way to maintain the phosphine concentrations during the exposure time, a Horn Diluphos System, model HDS 30 was used.

This HDS 30 was connected to a phosphine monitor, model CertiPH3os, which was measuring the phosphine concentration in a representative area on the building. Phosphine concentration limits were set on the CertiPH3os monitor, in order to maintain the concentration in the building close to 200 ppm during the whole exposure time. Every time the phosphine concentration in the building goes below 200 ppm, the CertiPH3os monitor sends a signal to the HDS 30 equipment to start phosphine injection, until concentration reaches the established level. In addition the fan installed inside the mill was also set to turn on only while the HDS 30 was injecting phosphine in order to improve the distribution.

**Figures 9** HDS CF (left) used for continuous injection, controlled by CertiPH3os electronic phosphine monitors (right).

### 2.2.4. Fumigation control

During the fumigation period, the HDS 30 was adjusted to inject about 5 grams per minute of phosphine, when receiving the fumigation signal from the CertiPH3os monitor. This initial setup was made according to the judgement of the fumigators in charge of evaluating the site for the fumigation and previous fumigation data from the mill. Periodic visits to the fumigation site were programmed during the exposure time to verify phosphine concentrations in the facility and the surrounding areas, and to make adjustments to the HDS 30 if required. The concentration was maintained according to the fumigation strategy during the fumigation period.

### 2.2.5. Aeration

After the 72 hour exposure period, the facility was aerated using a mix of natural diffusion and forced air ventilation. In order to initiate the aeration, a crew of fumigators, using SCBA equipment entered the building in order to open doors and windows in different levels. The fan installed inside the mill was turned on in order to help speeding up the aeration process. This condition was maintained until the concentration in the whole facility was verified below
legal limit of 0.3 ppm. At this stage the fumigators went into the facility to remove non-permanent sealing materials.

3. Results and Discussion

3.1. Phosphine concentration

3.1.1. Non gas-tight horizontal warehouse with continuous phosphine injection

Phosphine concentrations were established throughout the facility shortly after initiating the gas injection in all monitored zones. The continuous phosphine injection using the HDS 30 was able to overcome the leakage rate of the structure during most of the exposure time. There was a 6 hour period, during the first day of fumigation, in which strong winds were recorded in the fumigation area, causing the phosphine concentration to fall below the target concentration of 200 ppm. This situation was advised during one of the visits to the fumigation site, and the phosphine injection rate on the HDS 30 was increased from 3 gr/min to 4.5 gr/min.

![Phosphine concentration record obtained from the non gas-tight warehouse fumigated using continuous phosphine injection.](image)

After increasing the phosphine injection rate, the concentrations in the warehouse was maintained above the target concentration until the end of the fumigation time. By using this approach of continuous injection of phosphine during the exposure time, it is possible to overcome the structural leakage of the structure under certain conditions as temperature or wind in the surrounding areas. This approach requires the fumigator to go to the fumigation site at least twice a day to verify the conditions of the fumigation and perform adjustments to the fumigation equipment if required.

3.1.2. Flour mill automated fumigation

Lethal phosphine concentrations were established throughout the mill shortly after initiating the fumigation using two HDS 200 equipments, reaching about 350 ppm during the first hour of fumigation and getting stabilized at about 250 ppm during the first 4 hours of fumigation. After this initial phosphine injection, the HDS 30 equipment and the CertiPH3os monitor
were setup to control the concentration in the mill. The phosphine concentration was maintained above the target concentration during the entire exposure time.

![Flour mill fumigated using automated phosphine injection](image)

**Figure 11** Phosphine concentration record obtained from the flour mill fumigated using automated phosphine injection.

As corrosion was a concern due to presence of electric and electronic equipment inside the mill, one of the goals of the fumigation was to maintain the lowest possible phosphine concentration in the building able to kill the pests, reducing the corrosion issues. This goal was achieved by using the approach of automated injection, being able to maintain the concentration in between 200 and 250 ppm during the entire fumigation time. By using this approach for the fumigation, changing weather conditions can be compensated by the HDS 30 and the CertiPH3os equipments, injecting more or less phosphate if the leakage rate of the building is modified by external factors. The use of the CertiPH3os monitors, which transmit the data through a GSM modem to a website in real time, allows the fumigator to remotely monitor the fumigation conditions, being able to identify potential problems even without the need of going into the fumigation site. Text messages and e-mails alarm messages can be configured on the CertiPH3os website to alert the fumigator when the concentration goes below adjustable limits or if there is an alarm on the monitor.

### 3.2. Safety, Ambient concentrations

Considering that the fumigated facilities were located under a large structure, shared with other processing facilities and offices, or close to other production areas, the fumigations were programmed during a weekend to avoid workers to be close to the fumigation site. During the exposure time phosphine was monitored in the exclusion zone surrounding fumigated facilities using low concentration electronic detectors. In both cases, the phosphine concentration in the surrounding areas was below 0, 3 ppm during the exposure time.
Figure 12  Ambient concentration around the fumigated warehouse during exposure time.

During the aeration process, the concentration was monitored and found to be below 1 ppm in all monitored zones. The aeration conditions, exclusion zones, and access restrictions were maintained until the phosphine concentration in all areas of the facility were below 0.3 ppm.

4. Conclusions

By using the Horn Diluphos System technology it is possible to perform successful fumigations of non gas-tight buildings and structures without the need of investing large amounts of capital and resources in permanent sealing of the structures. Continuous phosphine injection during the exposure time allows mitigation of the natural leakage of the fumigated structures, being able to maintain the phosphine concentrations. Weather conditions, such as wind or temperature can affect the leakage rate of the structure, affecting the concentrations during the exposure time. The integration of the Horn Diluphos System technology with the CertiPH3os electronic monitor allows to create a dynamic injection
scenario, in which external factors affecting the leakage rate can be compensated by injecting more or less phosphine into the facility, maintaining the phosphine concentration in between a narrow range, allowing effective control of the insects, reducing the corrosion problems, and optimizing the amount of phosphine utilized for the fumigation. In terms of safety of the fumigation, in both cases, no dangerous phosphine concentrations were recorded in the exclusion zones or surrounding areas during the exposure time.

References