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INVESTIGATION OF THERMOSIPHON PIPES TO DISTRIBUTE PHOSPHINE GAS THROUGH GRAIN SILOS FROM A GROUND LEVEL INTRODUCTION POINT

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ABSTRACT

A system of recirculating phosphine gas by a thermosiphon pipe and applying aluminium phosphide at ground level was tested on twelve 1472 m³ silos. The Ground Level Application System (GLAS) introduces aluminium phosphide (AIP) tablets or blankets into a reaction chamber duct at the base of a sealed silo which is connected by a thermosiphon pipe to the headspace of the silo. The experiment demonstrated the effect created by ambient conditions on movement of phosphine gas through the silos. Air in the pipe expanding under passive heat exchange from the sun becomes less dense and moves up the pipe, during the day. This air movement lifts the phosphine gas as it is released from the AIP in the reaction chamber, into the grain profile via the headspace. After sunset the air cooled and move down the pipe into the reaction chamber. Thermosiphons work due to differences in temperature between internal and external silo environments. In any 24 hr period there will be parity in temperatures at least twice when the air in the pipe does not move. During these periods, the released phosphine gas must diffuse from the reaction chamber directly upward into the grain bulk through perforated duct covers. This prevents potentially explosive concentrations developing in the reaction chamber. This system has implications for improved worker safety and reduced selection for phosphine resistance in the resident stored product insects.

Key words: Thermosiphon, grain storage, phosphine, aluminium phosphide, recirculation, sealed silo.

INTRODUCTION

Thermosiphoning is passive heat exchange which circulate liquid or air without a mechanical pump. In grain storage it consists of a pipe connected to the headspace and base openings of the structure. As air in the pipe expands under passive heat exchange from the sun, it becomes less dense and buoyant and moves the gas/air mixture upwards in the pipe drawing air into the pipe from ducts at the base of the silo. The process is continual provided there is a temperature differential between ambient and the stored commodity, which sets up a circulation of the internal grain void space air mixed with the gas introduced into the system.

Previous work on the use of thermosiphon pipes to enhance circulation of phosphine gas:

- Boland (1983)¹ gas distribution in a 22 metre high concrete cell
- South Australia Cooperative Bulk Handling $(2000)^2$ trial on a horizontal grain store
- Newman (2006)³ trial in 75 t sealed silo circulating phosphine from a GLAS point
- Ball (2003 Personal communication) Thermosiphon distributed fumigation, 1200t silo, South Australia. (Data published in this paper)

The standard technique to fumigate grain silos is to load Aluminium phosphide (AIP) into the headspace where the phosphine gas evolves and is then conducted throughout the silo by diffusion and internal thermal convection air currents. Without a recirculation system it can take many days to reach threshold concentrations throughout large well sealed silos >200t.

In large grain silos, complete gas distribution can be achieved by powered recirculation but this is not commonly fitted in Australia when the silo is constructed on farms. Powered recirculation needs continuous energy for approximately four days for the fan to distribute the phosphine throughout the grain bulk as it is liberated from the AlP formulation.

Initial thermosiphon fumigation Balaklava, South Australia

An investigative thermosiphon trial on one 1200 t silo in 2008 was undertaken by Australian Fumigation, South Australia (Fig. 1). The existing 100mm PVC headspace pressure relief pipe fitted on the south side was utilised as the thermosiphon, bypassing the pressure relief valve at ground level and connecting it to the aeration intake seal plate with a 90mm id flexible tube. Blanket formulation AIP was loaded into the headspace of the silo at a rate of 1.4g/m³. Phosphine gas reached a concentration of 200 ppm at all 8 monitored points in the silo approximately 66 h after application of the AIP into the headspace and remained above this level for the 15 days of the monitored period. It was observed the headspace the gas was conducted into the grain bulk by air currents caused by the thermosiphon pipe soon after liberation from the blankets. The results of this trial indicated a further investigation of the process.

MATERIALS AND METHOD

Two sites were selected to provide a range of climatic and commodity types for adequate testing of the thermosiphon system. Site 1, Arthur River in Western Australia has four 1200t aerated silos 'sealed in construction' arranged in a group. Site 2, Balaklava in South Australia has four 1200t 'retro sealed' aerated silos arranged on an east-west line. The GLAS tested in this project introduces AlP at the base of a sealed silo into a reaction chamber which is connected to a thermosiphon pipe attached to the headspace. The reaction chamber is also the aeration duct or plenum formed in the concrete base of the silo to enable effective distribution of air across the silo floor but is of sufficient volume to accommodate the blankets of AlP and allow a safe headspace in which the phosphine will generate. The plenum consists of two channels 0.6m×0.2m in profile and 10.3m in length providing a volume of 1.24 m³ each. The perforated steel plates that cover the channel and support the grain allow diffusion of the gas into the grain when air movement stops in the thermosiphon pipes. The two channels are cast in a 'V' formation so a fumigation door on each side of the transition section enables the blankets of AlP to be probed into the opposite channel (Fig. 2).

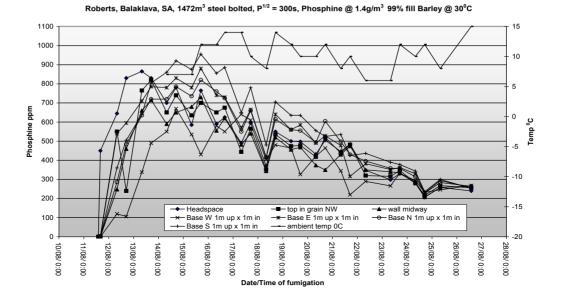


Fig.1- Initial thermosiphon fumigation in 1200t bolted steel silo

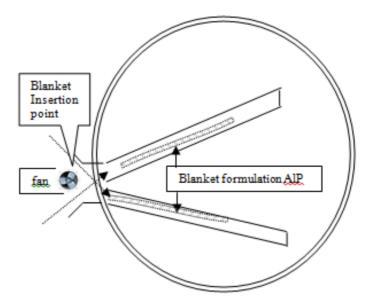


Fig. 2- Plan of aeration ducts/phosphine reaction chambers in silo base.

Site 1 Arthur River, Western Australia

At the Arthur River site the silos are located in a group of four which causes strong shading during the day. To avoid structural changes to the silo wall, entry into the silos was limited to the aeration transition section with the consequent reduced effect on the amount of sun falling on the pipes of the two western silos. Two parallel thermosiphon pipes were installed as a rigid fixing (Fig. 3) on three of the silos, the fourth silo was left as constructed in order to conduct a standard top loaded fumigation as a control. The pipes complete with pressure relief valves were fitted at the SSW of Silo 1, ESE of Silo 2 and SSW of Silo 3. Ground level phosphine introduction points were created in the aeration transition duct by manufacturing a small door sealed with rubber strips and locked with bolts and wing nuts.

One black pipe and one white pipe of 100mm diameter were fitted to compare the relative efficiency of black versus white to move the air from the bottom to the top of the pipes under diurnal sun conditions. Black PVC pipes are not manufactured in Australia so the alternative is to paint a white pipe with the attendant problems of maintenance at height as the paint weathers. The aim of this installation was to discover if it was possible to use white pipes only to conduct the air.

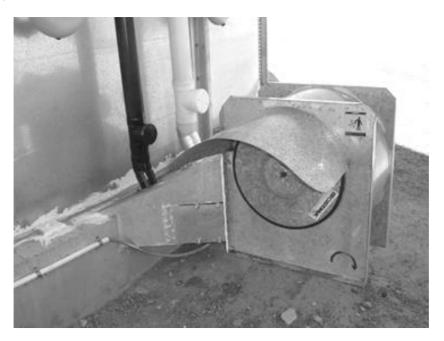


Fig. 3- Thermosiphon pipes fitted into aeration transition

Gas monitoring tubing of 1mm i.d. was attached to a steel cable with cable ties and installed centrally in the silo with an eye bolt through the roof near the peak and tensioned with a turnbuckle to the internal unloading auger motor housing. Monitoring points were located above the silo floor at 1, 4, 8, 12, 14 m and in the headspace. The six monitoring tubes were drawn through a PVC fitting in the neck of the top inspection hatch and conducted to ground level within a 25 mm i.d. UV stable PVC black irrigation pipe to provide long term protection from weather and parrots.

After one year of operation it was found that the drag on the lines by the outloading grain had stripped them from the cable. A new set of internal lines were assembled, covered

with heat shrink tubing and refitted which has proved successful in preventing further damage.

A monitoring tube was inserted into the left branch of the plenum and one tube into each of the thermosiphon pipes and stainless steel tubing of 1mm i.d. was inserted at four points around the base of the silos 0.5 m above silo floors and probed 0.3 m into the grain

Site 2 Balaklava South Australia

At the Balaklava site an additional 100mm black painted PVC pipe was added to the north side of each of the four 1200t silos to increase the period of sun exposure and air recirculation in the silo. The pipes enter near the peak of the roof and connect into the outloading auger inspection plate with flexible 90mm pipes to complete the air circuit across the silo. The transition section of the aeration system was modified to fit a sealable fumigation door on each side (Fig. 4) to provide access to the aeration plenums.

Prior to grain loading, monitoring points were installed on a central tethered cable. The monitoring line consisted of five lengths of 1mm id nylon tubing bundled with a 3mm stranded support cable encased in heat shrink tube. The tubing lines were spaced on the cable at 1 m, 3 m, 8 m and 10 m above floor height and in the headspace, and were passed through a PVC fitting in the apex of the silo and terminated outside the silo at ground level. The cable was attached by an eye bolt through the roof structure near the apex, then was tethered and tensioned to the gearbox of the outloading sweep auger at the base. When the outload sweep is used the operator releases the turnbuckle to avoid twisting the monitoring lines. Stainless steel tubing of 1mm i.d. was inserted at four points around the base of the silos one metre above silo floors and probed 0.3 m into the grain. Nylon tubing monitoring lines were inserted into each branch of the plenum.



Fig. 4- South thermosiphon pipe enters via the aeration fan seal plate. Fumigant access door cut into aeration transition duct with probing channel in place.

RESULTS

Fumigations Autumn 2010, Site 1 Arthur River Western Australia

The fumigation conducted in May 2010 provided the opportunity to study ground level thermosiphon (GLAS) fumigation under cool conditions. The silo contained approximately 300 t of grain giving it a 75% headspace reducing monitoring to three points on the centre line at 8.1 m (headspace) 4 m and 1 m above floor level. A complication was that the black thermosiphon pipe had fractured at the wall to roof joint and had to be capped for a fumigation to proceed leaving one 100mm white PVC pipe to conduct the gas from the plenum.

Silo 3 Fumigation (1200t / 1472m³)

Two thousand grams of blanket formulation of AIP were probed into the plenum/phosphine reaction chamber and monitoring commenced 40 minutes later. This silo has the thermosiphon pipe located on the SSW side so in winter sun exposure is limited to approximately 2 hrs per day in cool conditions. There was limited movement of gas into the headspace due to the absence of a long period of sun on the thermosiphon pipe so it took 5 d for phosphine to reach 200 ppm at all monitored points in the silo. Gas values stayed above 200 ppm for the remaining 5 d of the monitored period; most gas readings were trending upward at the final reading.

The gas slowly diffused upwards into the grain with limited effect from the thermosiphon pipe. The ambient temperatures were low but the sun acting on the north side of the silo caused air to rise, drawing phosphine gas from the plenum at high concentrations past the north monitoring point which was located 0.5 m from the silo floor and 0.3 m into the grain.

The experience and data from this fumigation demonstrated the critical requirement of positioning the thermosiphon pipe on the north wall of the silo for maximum sun exposure. To augment air movement in silos 1 and 3, black painted 100 mm PVC pipes were fitted on the NNE and connected to the inside of the silo through the outloading auger inspection plate with a 90 mm flexible pipe. The fumigation also demonstrated that the evolving phosphine gas, with limited assistance from the thermosiphon pipe, diffused upwards into the grain above the plenum grating without reaching dangerous concentrations.

Silo 3 Tests of plenum concentrations

The white pipe warms more slowly than black which reduced the time available for the air gas mixture to be drawn from the plenum. To discover what effect this would have on the development and distribution of the evolving gas and enable field testing of the high concentrations in the plenum, a dilution technique was used.

A Canary Co 'SiloChek' has a range 0-2000ppm. To measure high values a peristaltic electric diaphragm pump was used to draw the phosphine/air mixture from the reaction chamber into a Tedlar® gas tight bag. Two hundred ml of this gas was drawn into a 1000ml laboratory grade syringe and then a further 500ml of air was drawn in before being injected into another Tedlar® bag. The diluted Tedlar® bag was attached to a Canary monitor and the final displayed concentration multiplied by 3.5. This technique shows that the concentrations did not exceed 5000 ppm.

The gas remaining in three of the Tedlar® bags was transported to the DAFWA phosphine resistance laboratory and tested to obtain a cross reference using a gas chromatograh. The results are shown in Table 1. From this limited test it is suggested the concentrations in the reaction chamber as indicated by the Canary monitor in the field could

be elevated by approximately 1600 ppm making the highest recorded concentration 6220 ppm, compared to 17,900 ppm at the phosphine explosive limit.

Site 2 Balaklava South Australia Winter 2010

Silo 2 Fumigation (1200t / 1472m³) top loaded

The silo was 65% filled with wheat at 8.9% mc. The silo pressure test exhibited a halving pressure (P'_2) of 120 seconds. To compare GLAS and top loaded fumigations 2000g of AlP were added to the headspace of this silo providing 1.35g of phosphine/m³. Monitoring commenced 18 hrs later using a combination of a Spectros non dispersible infra red automatic data logging unit and a hand held Canary Company 'SiloChek' electronic cell. The Spectros monitor had four operating monitoring points which were attached to the plenums and to the North thermosiphon pipe on silos 2 and 4. All other points were monitored using the 'SiloChek'. For these experiments a gas value of 200ppm was adopted as the threshold at which the fumigation period commenced.

Table 1. Comparison of electronic monitor field readings with gas chromatograph analysis

Canary (ppm)	GC (ppm)	GC/Canary
2600	3950	1.52
3031	4880	1.61
2450	4090	1.67
2694	4307	1.60
		0.08
		4.73
	2600 3031 2450	3031 4880 2450 4090

Phosphine gas reached 200ppm at all monitored points in the silo within 26 hrs after application of the AlP to the headspace (Fig. 5). All points recorded concentrations between 200 and 1400 ppm for the remaining 10 days of the monitored period.

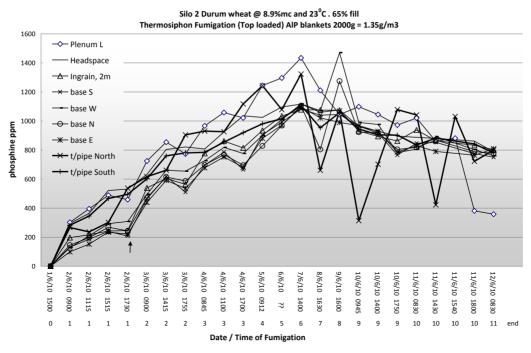


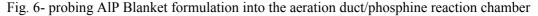
Fig. 5- Top loaded Thermosiphon fumigation.

Phosphine concentrations show a co-related rise and decay at all points in the grain bulk as the gas is drawn into the grain bulk soon after release from the AlP. This is in comparison to a non recirculated silo where there is an immediate high concentration of phosphine gas at the AlP insertion point and a slower rise at all other points at the gas diffuses though the grain bulk with some assistance from internal air currents. The graph also shows large oscillations of concentrations in the thermosiphon pipes due to the diurnal and nocturnal variations of temperatures.

Silo 4 (1200t / 1472m³) Ground level application

The silo was filled to 95% with wheat at 9.5% mc. The silo pressure test showed a halving pressure ($P_{2}^{1/2}$) of 180 seconds. The dosage of 2000g of AlP were probed into the aeration plenums of this silo providing 1.35g of phosphine /m³ (Fig 6).





Monitoring commenced 18 hrs later and the threshold concentration of 200ppm was reached in 48 hrs. Concentrations were recorded between 200 and 800 ppm for the remaining nine days of the monitored period (Fig. 7). The concentrations followed a similar path of correlated rise and decay as in silo 4 and large oscillations of phosphine concentrations in the thermosiphon pipes. The slower time to threshold at all points was most likely due to the ground level application technique.

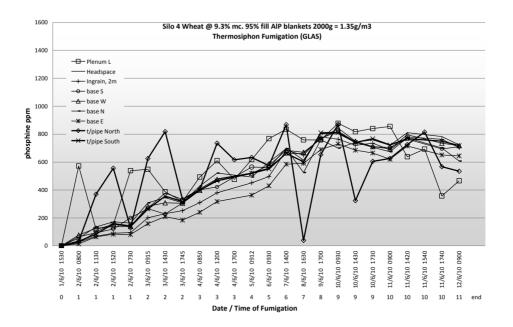


Fig. 7- Winter GLAS Thermosiphon fumigation Fumigations Autumn 2011

Site 2 Balaklava South Australia

Fumigations commenced on all four 1200t silos in March with warm days and cool nights. The fumigations were recorded with hand held Drager electronic gas monitors with a maximum reading of 2000 ppm. Aluminium phosphide blankets containing 1000 g of phosphine were probed into each plenum branch of each silo (2000g total dosage) and monitoring commenced the following morning.

Rapid peaks of concentration were observed which were caused by diurnal movement of phosphine in the thermosiphon pipes and plenum. After sunset the air in the thermosiphon pipes ceased to move and phosphine generated from the AlP blankets diffused into the grain above the perforated duct cover plates. At sunrise the thermosiphon pipes warmed and concentrations escalated rapidly as the gas generated overnight was drawn out in the first hour. Sunrise occurred at approximately 07:00 and due to low overnight ambient temperatures of ~5°C it took a further 15 minutes for the south thermosiphon pipe to warm and cause air to rise. From repeat monitoring, the concentrations was observed to rise after 07:20 from zero through to ~600ppm in 45 minutes. High concentrations of phosphine were observed moving up the south thermosiphon pipe 20–24 h after application of the AlP but time to reach 200 ppm of phosphine at all monitored points varied between 60 and 144 h.

As an example of a fumigation in the four silos the record of Silo1 is presented in Fig. 8. Low levels of phosphine were recorded across the base approximately 24 hrs after application of the AIP and in the headspace and all other points after 32 hrs. This shows the mixing of the internal air by the current emanating from the thermosiphon pipes. The fumigation period commenced 111 hrs (4.6 d) after application when all points in the silo reached 200 ppm and remained above this concentration for a further 6 days when monitoring was terminated. The concentration of phosphine throughout out the grain bulk remained between 200 and 500ppm at all points in this period.

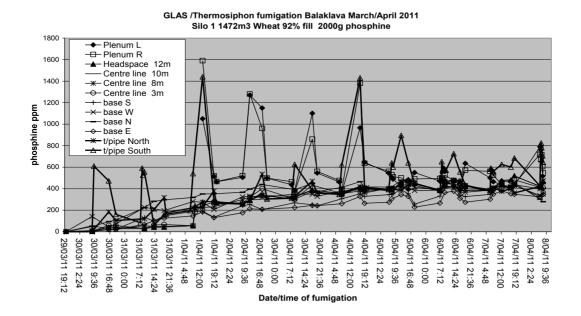


Fig. 8- Example of autumn GLAS thermosiphon fumigations

Fumigations Summer 2012

Fumigations commenced in February 2012 under generally warm ambient conditions. Gas concentrations were taken with a Drager X am 5000 electronic phosphine monitor with an upper limit of 2000 ppm. Some points in silos at Balaklava were recorded using a Spectros non-dispersible infra red monitor. Drager phosphine indicator tubes (500 - 10000 ppm) were used on some silos soon after application of the AlP to record the concentrations developing that were beyond the range of the X am 5000.

Site 1 Arthur River Western Australia

All silos on this site had been subjected to aeration after grain loading creating a stable temperature throughout the silos and reducing the internal thermal air currents. An on site temperature logger provided precise data which shows the influence of the sun on movement of gas in the thermosiphon pipes. From two fumigations on this site it was observed there is an approximate correlation between rising ambient temperatures and rising phosphine gas values as the released gas is drawn from the reaction chamber via the thermosiphon pipes and into the headspace (Fig. 9). It was also observed that the peak concentrations in the plenum occur when there is a reversal of air in the thermosiphon pipe and the gas that has liberated into the grain bulk is drawn down into the plenum or is drawn down from the headspace through the thermosiphon pipe into the plenum.

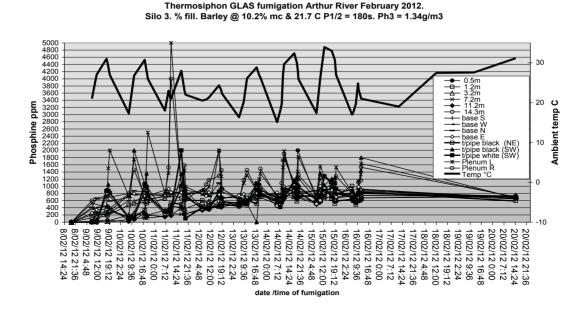


Fig. 9- Example of summer fumigation GLAS

The addition of a black painted 100 mm thermosiphon pipe at the approximate NNE point was effective with gas shown to move up these pipes into the headspace within a day after loading of the AlP. For the gas to be drawn up this pipe it needs first to emanate from the reaction chamber and move across the silo floor before penetrating into the auger channel, seeping around the closed grain control slide plates. Thermosiphon pipes are attached to

unloading augers on six of the seven silos tested in this experiment and it is recorded that although they do not exhibit the dramatic peaks and falls of the unimpeded pipes, they are a significant contributor to the circulation of phosphine in the silo

The phosphine gas in this silo reached 200 ppm at all monitored points 63 hrs after application of the AIP into the ground level reaction chamber and remained above this level for the remaining nine days of the fumigation. Drager phosphine indicator tubes (500–10000 ppm) were used to record gas concentrations in the plenums when the Drager X am electronic monitor was observed to reach maximum concentration rapidly after connection. The highest recorded concentration was 5000 ppm 63 hrs after application of the AIP.

Non recirculated fumigation

As a direct comparison to thermosiphon gas distribution, silo 4 with no thermosiphon pipes fitted, was top loaded with 2000 g of AlP. From experience a silo top loaded with AlP, the slowest point to reach the required concentration is the base of that silo. Monitoring points of stainless steel tubing 1mm i.d. was inserted at four points around the base of the silo one metre above ground level and probed 0.3 m into the grain. The silo contained a 50% load of Canola at 7.8% m.c. and achieved a $P\frac{1}{2}$ of 180 s. Phosphine gas readings started to appear on the Drager monitor after 4 days and reached 100 ppm after nine days. The gas did not reach 200 ppm at all points before monitoring ceased at 12 days.

Site 2 Balaklava South Australia

Blanket formulation AIP was probed into the reaction chamber at the base of three silos and gas concentrations were recorded at all monitored points 24 - 36 h after application. The threshold concentration of 200 ppm was reached between 90 - 108 h and remained above this level for the monitored period.

A Spectros phosphine monitor was attached to four points on silos 1 and 2 including the plenum to record the concentrations that develop at the critical times as phosphine gas is generating and the airflow changes direction. A large difference was recorded in the concentrations between the two plenums; this may be due to the monitor tube placement in proximity to the AIP.

After probing blanket formulation of AlP into the reaction chamber of silo 2 it was found that one monitor tube was blocked and a new line was probed. This tube appears to have lodged in the blanket formulations presenting high readings for most of the monitored period. The Spectros monitor records automatically at three hour intervals and is able to analyse concentrations ~10,000 ppm. The placement of the monitoring tube provided an opportunity to observe the gas release in relation to safety of the GLAS system. The highest phosphine concentration observed was 10,690 ppm (Fig. 10).

CONCLUSIONS

The results from 10 experiments on large silos under a range of climatic conditions from warm to cool showed that thermosiphon pipes attached to GLAS are successful in delivering the evolving phosphine gas from ground level reaction chambers into the headspace and creating a recirculating current within the grain bulk to achieve even distribution. Thermosiphon fumigations do not typically display the high peaks in the headspace after application of the AlP and the tailing off concentrations at all other points in the silo. Lower co-related phosphine concentrations were noted throughout the grain bulk whether the AlP was top loaded or applied at ground level.

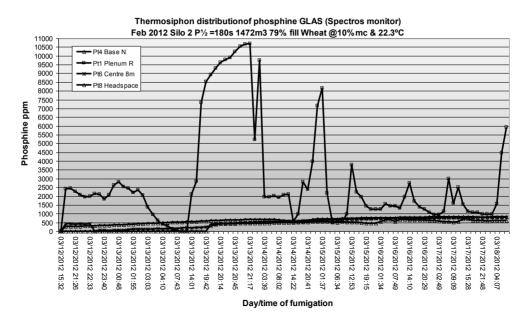


Fig. 10- Analysis of concentrations of Ph3 in reaction chamber, GLAS fumigation

A sealed silo exhibiting a minimum $P\frac{1}{2}$ =180s is essential to ensure the required concentration × time (Ct) product is achieved to control all life stages of the target species. The concentration of phosphine gas and time needed varies according the susceptibility of the resident population of insects. The threshold concentration chosen for these experiments is 200 ppm but the time factor will depend on the resistance of the endemic insect population to phosphine.

The test on a non thermosiphon (check) silo showed the concentrations did not reach 200 ppm 12 d after application of the AIP. This has implications for time of outturn and may contribute to development of phosphine resistance if there are surviving insects in this zone.

The top loaded fumigations reached the threshold concentration more quickly than a ground level fumigation which can affect outturn timing and can be critical to meet shipping schedules. GLAS fumigations have significant safety advantages for the application of large quantities of AlP but the slower time to minimum concentration must be taken into account when determining an outloading date.

The thermosiphon process works when there is a difference in temperature between the internal and external silo environment. In any 24 hr period there will be parity in the temperatures at least twice when the air in the pipe will cease to move. It is necessary to ensure that during these periods released phosphine gas can diffuse from the reaction chamber into the grain to prevent potentially explosive high concentrations developing in the reaction chamber.

There is an observable correlation between rising ambient temperatures and the increase in gas concentrations moving up the pipes after sunrise. In particular as sunlight warms the thermosiphon pipes the gas concentration can be observed climbing rapidly in the first 60 minutes, accounting for the spikes seen on the graphs, before settling to a lower level during the day. It is also observed that the gas concentrations in the plenum will increase around sunset as the air in the thermosiphon pipe stalls and then reverses pushing phosphine into the reaction chamber and through the grating into the grain bulk at the base.

Safety in the use of phosphine is critical; part of these experiments was to ensure that concentrations would not build to the lower flammability limit. Intensive sampling of the concentrations emanating from two phosphine reaction chambers found maxima between 6220 and 10,690 ppm which remains well below the lower flammability limit of 17,900 ppm. It is necessary to ensure that the circulation of air in the thermosiphon system is not impeded and annual checking of the pipe work must be undertaken prior to loading AIP. If using a grated or perforated plenum as the phosphine reaction chamber, it is essential to ensure this perforated flooring is not blocked with fines or dust from previous crops. When using aeration to cool grain prior to fumigation it is essential to ensure the incoming air humidity will not cause moulding of the grain adjacent to the plenum grating which could create a resistance to airflow. It is likely that phosphine will penetrate the moulds but any air restriction will impede the development of the Ct in the grain bulk.

Shading or poor positioning of the pipe which reduces exposure to the sun has a direct impact on the speed of gas delivery and admixture. A pipe oriented to approximately north is more likely to be successful but a south facing pipe will have some positive benefit on gas delivery. To avoid making structural changes when retrofitting a thermosiphon pipe to an established silo the best entry point will be through the outloading machinery and aeration in point which may not be the best position. When constructing a new silo it is possible to take this into account and orient the silo aeration or unload systems to enable favourable positioning of the thermosiphon pipe.

Retro fitting ground level application points to large silos fitted with aeration and a plenum is possible but the fitting of the thermosiphon pipe to the peak of the roof presents the risk of working at heights and should be undertaken by a professional team using an elevated work platform or industrial rope access techniques.

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