Donahaye, E.J., Navarro, S. and Leesch J.G. [Eds.] (2001) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Stored Products, Fresno, CA. 29 Oct. - 3 Nov. 2000, Executive Printing Services, Clovis, CA, U.S.A. pp. 379-389

HIGH DOSE PHOSPHINE FUMIGATION USING ON-SITE MIXING

B. BRIDGEMAN,[1]* R. RYAN,[2] D. GOCK [3] AND P. COLLINS[4]

[1]*Grainco Australia, 619 Ruthven Street, Toowoomba, 4352, QLD, Australia*
*[*e-mail: barry.bridgeman@grainco.com.au]*
[2]*BOC Gases, Sydney, NSW, Australia*
[3]*CYTEC Australia Ltd, Sydney, NSW, Australia*
[4]*Dept of Primary Ind. Qld, 80 Meiers Road, Indooroopilly, QLD 4068, Australia*

ABSTRACT

Methyl bromide (MB) is relied on to maintain insect free grain exports from Queensland Australia. The eminent demise of this fumigant has been the catalyst for the trials conducted at the Globex International Gladstone Port Terminal using high doses of phosphine (PH_3) at 1 mg/L, 2 mg/L and 3 mg/L. The trials compared on-site mixing of ECO_2FUME and Phosphine/air mix to existing conventional technologies. Modifications to the existing MB fumigation system were minimal and although procedures to carry out this work had to be compiled during the trials, the fumigations were successful. The efficacies of the trial fumigations were assessed using bioassays of mixed age cultures of several species of target insects with typical levels of PH_3 resistance.

Results indicated that at 25-27°C, fumigation with PH_3 at 750 ppm for 5 d was successful in controlling all stages of target pests tested. The mobile stages were totally controlled within 3 d, while control of eggs and pupae required a further 1.5 to 2 d. The trials indicated that although the fumigation time could not be reduced to below 5 d, at 25°C, the cost of fumigant was substantially reduced when compared to MB. The cost of using liquefied forms of PH_3 compared well to all other formulations and the fumigation duration could be reduced by 2 days without compromising efficacy. The other significant advantages of the systems under trial, were that complete dosing and distribution of the fumigant into the bin took 60 - 80 min and clearance of the fumigant to below detectable levels was reduced to less than 6 h. The systems using liquefied PH_3 do not require disposal of spent residues.

Grainco Australia has begun implementation of a high dose PH_3 capability at all Globex Ports and further research and development of PH_3/air mixing is a priority.

INTRODUCTION

Globex is a wholly owned subsidiary of Grainco Australia, operating a series of Port facilities on the eastern seaboard of Australia. These strategically located facilities are designed with minimal infrastructure. They are primarily places to unload a commodity from trucks and trains and load it on to ships very quickly. Commodities are usually stored on site for a maximum of one to two weeks. While some consignments are kept for a month or longer there are also significant volumes loaded directly onto ship from rail. This process relies very heavily on MB to comply with the phyto-sanitary requirements of importing countries and the 'Export Control Act'. The 'Export Control Act' prohibits the presence of live insects in commodities being loaded for export. In transit, ship-board fumigations are not permitted in Australia. The MB fumigations at Globex take about 12 h from start to complete post-fumigation gas clearance. This includes time for sealing and cell pressure testing. This flexibility has been designed into the system. Each of these ports has only enough storage capacity to load a couple of average size ships. All storages, which are predominantly concrete vertical bins, are gas tight (pressure decay from 150 mm to 75 mm Hg in 15 min), and all are manifolded to a recirculation system. The handling operation relies on logistics to enable the product to arrive at the port in a timely fashion, and this process has been very successful. A period of fifteen years has now past since a client last detected insects in commodities originating from a discharge port of Grainco Australia. With the impending demise of MB this mode of operation is now under review.

There are numerous chemicals being investigated at present in an attempt to put in place alternatives, prior to 2005 (Desmarchelier 1998). Dependence on the development of future research potential requires a solid contingency plan. At present the only other fumigant, ready and registered for disinfestation of grain, is PH_3. Consequently, PH_3 is the logical immediate replacement. The primary concern in using PH_3 fumigation as a MB replacement is the increase in fumigation duration required to attain comparable standards of insect control. The secondary issue is the need for it to be cost effective in achieving the required standard. An issue, which is inherent with use of PH_3 is the dangerous possibility of exceeding the explosive limit. In this context, the fumigation procedures that were subjected to trial here were also examined to evaluate the relative safety inherent in the use of liquid formulations.

This series of trials investigated the feasibility of replacing MB with PH_3 at port fumigations. Phosphine is currently registered for the purpose of grain fumigation and is widely accepted for disinfestation purposes. This series of trials examined two application methods requiring the use of Vaporphos; the first using on-site mixing of "Ecofume" (ECO_2FUME - 2% PH_3 98% CO_2), the second introducing "Vaporphos" ($VAPORPH_3OS$ - 100% PH_3) directly into the air-stream within the recirculation ducting. The objective of these trials using liquid formulations was to enable reduction of purge time (time required to introduce the gas and reach even concentration throughout the bulk) and clearance times (time to expel the gas from the bulk at the end of fumigation) for PH_3 as well as reduction in exposure time from that displayed on the label (7 d) as being the time required to achieve complete kill of all life stages of the target pests. Within the scope of these trials was an examination of the relative costs involved with the various application methods. The data generated from this series of trials could be used to support a change in label specifications, should such a change be justified.

MATERIALS AND METHODS

Available Formulations

The most common application method for PH_3 fumigation is by the use of solid formulations such as aluminium phosphide. The major benefit of solid formulations is that they are very cost effective. However, their drawback is that they require a significant time-period for gas to evolve before the required concentration is attained, and effective fumigation begins. The solid formulations also require removal and subsequent disposal of the spent residues after fumigation. The use of liquid formulations has the advantage of being able to deliver the required dosage during the initial gas purge, in much the same way as in a MB fumigation. This involves a potential saving of two days. The liquid formulations also benefit from not requiring removal of residues. Therefore, fumigations using liquid formulations should be easier to apply and safer to clear. It is possible that the fumigant will also be able to be cleared more quickly in fumigations using liquid formulations since recirculation systems are a pre-requisite for this technology.

Costs

The cost comparison was based on the cost of fumigant alone, whereas the costs of fumigant application, monitoring and clearance were taken to be constant. The cost of fumigant varies significantly between suppliers, location and user. The costs outlined here are indicative of recommended retail prices in Queensland Australia as obtained from the major supplier.

Fumigation exposure times

The fumigation exposure times on the label were used as an estimate of how long the fumigation duration should be. In the 2 g/m^3 and the 3 g/m^3 dosage trials the estimates were based solely on indications from laboratory trials as the label does not stipulate a time duration for these doses. A data matrix was developed for each concentration to allow estimation of fumigation duration required to obtain population extinction ($LD_{99.9}$) (Collins *et al.* 2000).

Data Matrix

The laboratory data was collected at the Farming Systems Institute by assessing mixed age cultures of target species using flow-through technology (Winks and Hyne 1994). The process is described in another paper presented at this conference (Collins *et al.* 2001). The collected data was constructed into a matrix, which delineates the time required for a particular Ct product to achieve efficacy to the 99.9% mortality level (Bridgeman *et al.* 2001). From this matrix an accurate estimate of the necessary duration for each concentration could be calculated. The bioassays using mixed age cultures were selected from field strains of resistant insects from each of the target species. This process has become standard operating procedure in Grainco Australia fumigation practice (Bridgeman and Collins 1994; Bridgeman 1999; Bridgeman *et al.* 2001).

Trial Protocol.

Trial 1: The on-site mixing trial was conducted at the Globex, port facility in Gladstone. The process involved mixing pure liquefied PH_3 "Vaporphos", with CO_2 as required. The process could be achieved using cylinderised "Ecofume"; however the logistics of handling large numbers of heavy cylinders (12 per bin) was a significant operational concern. The CO_2 was delivered from a 12 tonne bulk tank via a vaporiser. The phosphine as "Vaporphos" was supplied in G size cylinders. The concentrated gases were delivered to the mixer through particularly sized orifice plates, which ensured that the correct mix (2% PH_3 and 98% CO_2) was maintained in the flow. The mixer was controlled to immediately shut off flow from both cylinders if either of the flows could not be maintained. The mixer was constructed by Gas Apps, the Vaporphos was supplied by Cytec Australia, and the CO_2 delivery system supplied and installed by BOC Gases. Once mixed, the 2% PH_3 mixture was delivered via 50 mm PVC pipes to the bin recirculation system.

Trial 2 and 3: The 'phosphine and air mix' fumigation was conducted at the Globex installation, Fisherman Island. The process involved feeding the 100% PH_3 "Vaporphos" directly into the MB recirculation system. Trial 2 was conducted at a dosage of 2 mg/L and Trial 3 at 3 mg/L. The fumigant that was introduced through ducting into the closed recirculation system was regulated directly by manual operation of the cylinder valve. The fans on these recirculation systems are designed to deliver a complete air change to the silo in 20 min. The airflow is delivered upward through the grain into the headspace were it is forced into the return ducting and back down to the fan. High-speed fans such as these are generally not suitable for PH_3 fumigation due to the negative pressure generated at the fan tips causing a significant reduction in the minimum flammability limit of PH_3. To negate the effect of this negative pressure, the fumigant was ducted into the positive pressure side of the fan and the concentration of fumigant was kept below 3,000 ppm at all times during the fumigation, with particular care being taken during the initial purge. With careful management, this maximum concentration could be avoided throughout the process, in all areas except in the small section of the ducting immediately after the induction point. This site was monitored by direct observation of the process through a viewing window provided for the purpose.

The recirculation system

The recirculation systems used at both sites were designed to carry out fumigant distribution and post-fumigation gas clearance quickly. They achieve a minimum standard of a complete air change in 20 min and are tested periodically for seal integrity.

The silos

The storages in both trials were concrete vertical bins of 10,000 m^3 capacity. All were conical based and sealed to a high degree of gas tightness. All bins exceed the GA minimum standard pressure decay of from 150 mm Hg to 75 mm Hg in 15 min, by a considerable margin.

Fumigant 'induction' and distribution

To achieve the desired concentration in each trial, the airflow from the fan, and the gas release from the mixing sites were synchronised. The time required to attain even distribution was estimated from the measured flow inside the ducting. The addition of fumigant mixture was maintained until the calculated dose was delivered, and air flow was then continued until an even distribution was obtained; namely, when the top and bottom in-grain PH_3 concentration readings differed by no more than 50 ppm. If further fumigant was required to achieve the desired concentration, recirculation would be continued while the required fumigant was added, until an even distribution was attained. Daily recirculation of the fumigant remaining in the bin was carried out to ensure adequate and even distribution.

Field assessment of fumigation efficacy

Gas concentrations were monitored during the fumigation process and the accumulated Ct products were recorded. Bioassays using mixed age cultures of the lesser grain borer *Rhyzopertha dominica,* the rice weevil *Sitophilus oryzae* and other target insects were carried out to monitor fumigant efficacy (Bridgeman *et al.* 2001; Collins *et al.* 2001). Vials of the test insects were removed three days prior to, and on the day after, the 99.9% control time, as predicted by the data matrix. These vials were returned to the Farming Systems Institute for analysis. The measured Ct products and the data from the bioassays were then combined to establish the validity of the laboratory data matrix.

RESULTS

Bioassays

The results from the bioassays closely followed those predicted in the laboratory trials. This data confirmed that, when the grain temperature was about 25ºC, the 99.9% control of all the major insect pests of stored grain could be achieved within 5 d in concentrations of above 1 mg/L. The data also indicated that there was little advantage in increasing concentrations above 1.5 mg/L.

The data represented in Figs. 1 and 2 show the $LD_{99.9}$ for *R.dominica* (resistant strain QRD569) (Fig. 1) and $LD_{99.9}$ for *S. oryzae* (resistant strain QSO335) (Fig. 2). The lines indicate the effect of the fumigation at the 1 mg/L concentration over time. The reduction in population was calculated when compared with a control culture. There was little difference in the 2 mg/L and 3 mg/L dose rate trials. Although other species were also tested, these two species are considered the most important for establishing the required dose rate.

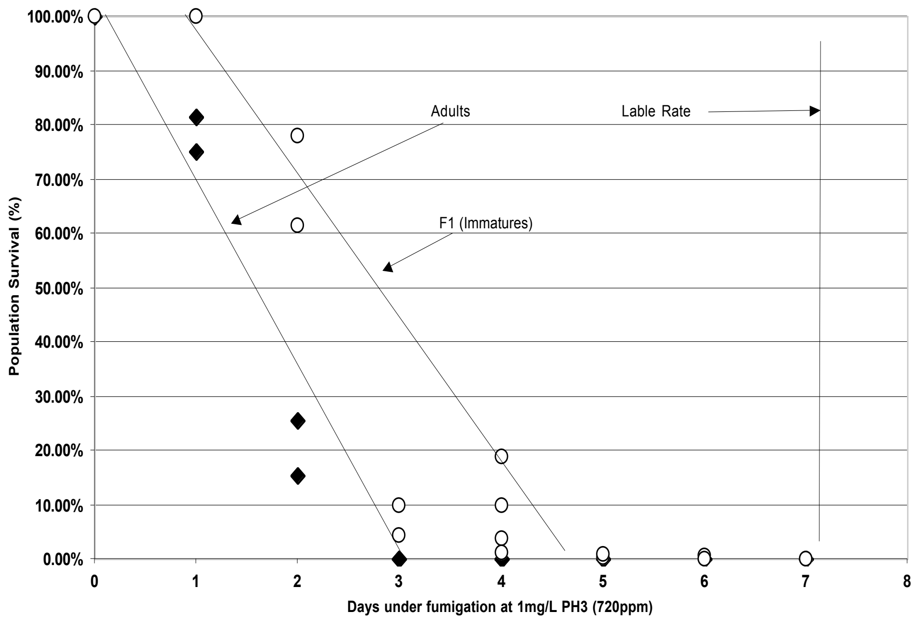

Fig. 1. Survival against time curves of the resistant strain QRD569 of *Rhyzopertha dominica* when exposed to phosphine at 720 ppm .

Comparison to the data matrix

The data extracted from the field tests was then retrofitted to the data matrix along the accumulated Ct product for the duration, to confirm when population extinction occurred.

The data displayed indicates the accumulated Ct product achieved over time. The fumigation rates, when plotted over the laboratory data matrix indicate the point at which significant efficacy occurs. This is represented graphically for each of the concentrations used in the trial. The field data concurred with the data matrix constructed from the laboratory trials.

Cost Comparison

A cost comparison between the various methods was carried out. The costs compared in Fig. 4 represent the cost of fumigant only. The cost of application was taken as being constant, despite observations of significant differences during the trials.

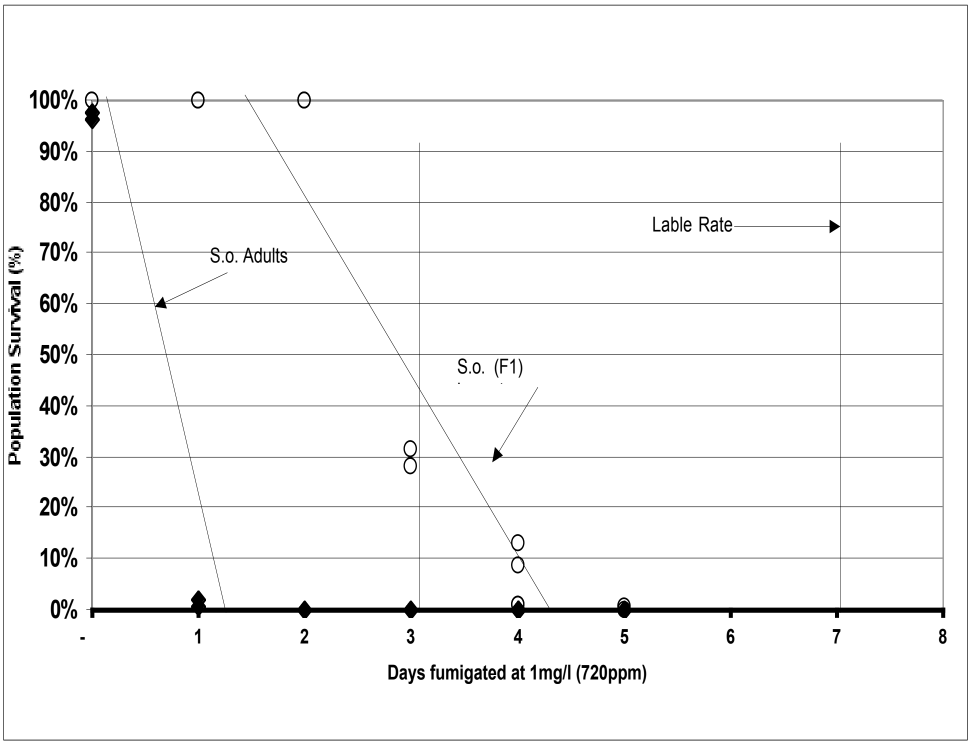

Fig. 2. Survival against time curves of the strain QSO335 of *Sitophilus oryzae* when exposed to phosphine at 720 ppm .

The comparison of costs between the fumigations using liquid formulation techniques varied directly with the dosage employed. Comparison with fumigations involving solid formulations of aluminium phosphide revealed that these were the most cost effective, while Siroflo was the most expensive. MB fumigation compared well cost-wise and was far more time efficient than any of the other methods.

Comparison of effective fumigation duration

The fumigation duration (required exposure time) of each of the methods was compared with data collected from other methods in common use. Both of the methods used in the above trials achieved the desired 60-80 min initial purge and distribution time as well as the 4-6 h target time for fumigant clearance from the grain bulk.

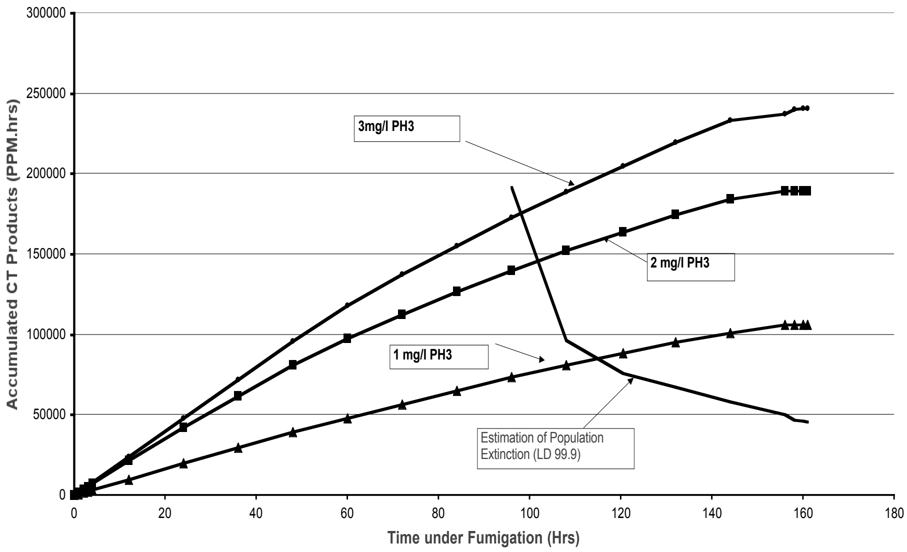

Fig. 3. Ct products for high dose phosphine fumigations at the Globex Gladstone port facilities of Grainco Australia, 2000.

The duration of a typical MB fumigation is about 12 h including sealing and clearance times. The use of the large doses of liquid PH_3 fumigant was successful in reducing purging and clearance times. This allowed some scope for a reduction in the total fumigation time required for PH_3. The bioassay indicated that a reduction in exposure time from the 7 days label rate, to 5 days was justifiable under these conditions.

DISCUSSION

The results indicate that at 25ºC, it will take a minimum of 5 days to achieve 99.9% control of the strains of typical grain-storage pests tested in these trials. The bioassays were conducted using resistant strains from the field (Collins *et al*. 2000). Fumigations of this duration would not be suitable for most of the current fumigations carried out at Grainco Australia Ports. However it does mark a significant improvement on the 7–10 days required as a label stipulation. A reduction of PH_3 duration to 5 days would allow direct substitution of MB with PH_3 in a significant proportion of port fumigations. This potential substitution could result in an approximate 60-80% reduction in pre-shipment MB fumigation at

Globex ports. The remainder of the shipped commodities arrives at port less than 5 days before loading, and some even arrives as the ship is being loaded. However, less than 60% of exported commodities are fumigated at port, even though all (100%) ships are loaded with some MB treated commodity in the cargo. These statistics indicate that it is theoretically possible to fumigate ~ 60% of grain cargoes with PH_3 while the remaining 40% would linger as a pre-shipment use of MB. This scenario is based on the prerequisite that the logistics of grain movements and the scheduling of shipping must be accurately coordinated. This task appears to pose a considerable challenge, though, if achieved, further reductions in MB dependence could be realised.

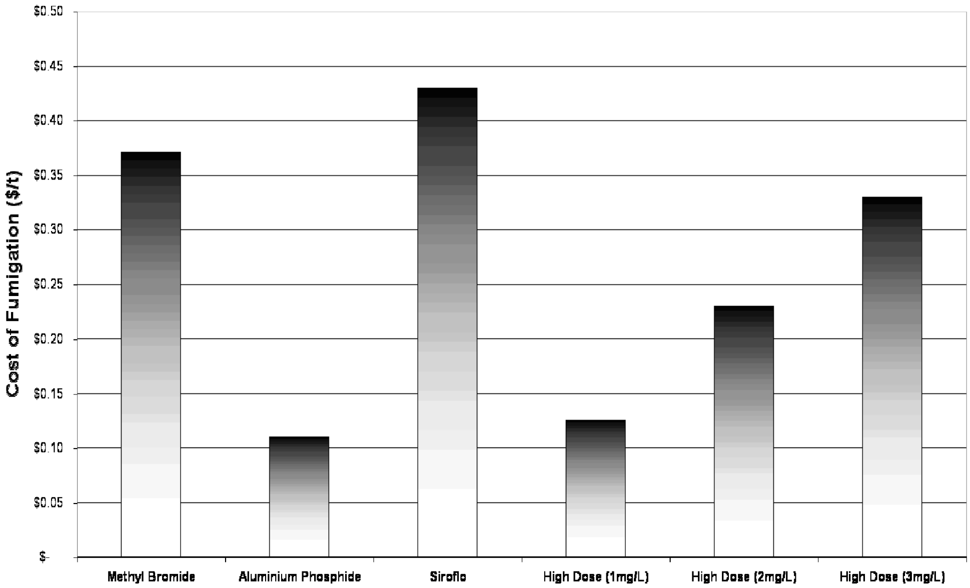

Fig. 4. Comparative costs of different fumigation procedures and formulations at an 8,000 tonne storage silo at the Globex, Grainco port facility.

A major concern not often highlighted in the imminent demise of MB is the consideration of its role as a resistance management strategy (Collins and Bridgeman 1991; Bridgeman 1999). At present, the use of MB at port ensures that populations exhibiting PH_3 resistance that are surviving in the commodity (which may have been previously fumigated with PH_3 several times), are extinguished prior to export. The introduction of another PH_3 fumigation at this critical point merely adds another selection for resistance in the surviving population. It has been very clearly demonstrated recently that the tolerance of target insects to PH_3 is increasing significantly and rapidly. A grain protection strategy based on a total dependence on a single chemical fumigant for an indefinite period is fundamentally flawed

(Bridgeman 1999, Collins and Bridgeman 1991). While research into alternatives to MB is progressing, it is the search for a substitute to PH_3 that really needs to be at the focus of our attention.

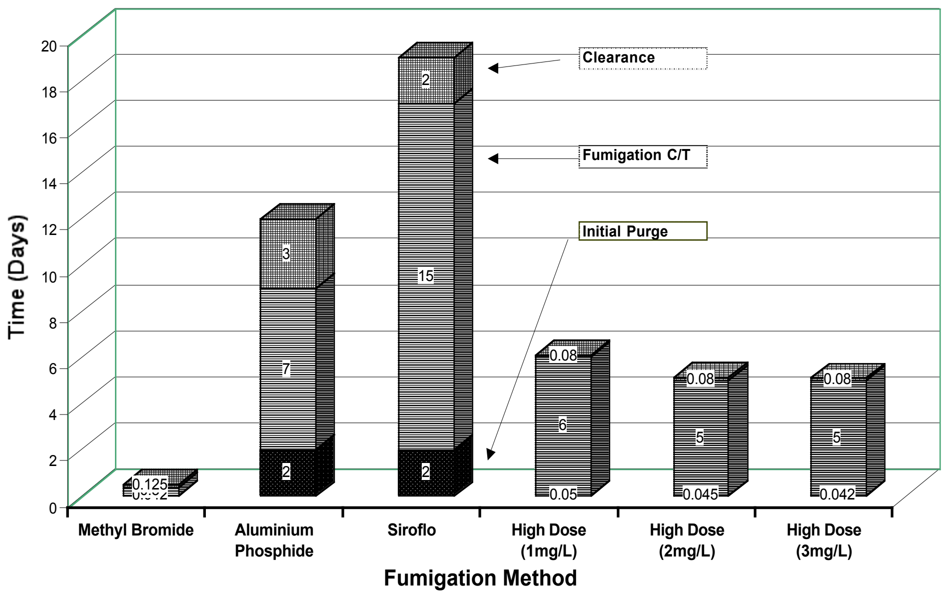

Fig. 5. comparison of exposure duration of different fumigation procedures and formulations at an 8,000 tonne storage silo at the Globex, Grainco port facility.

CONCLUSION

The data collected in this series of trials clearly indicates that there is scope to reduce the duration of high dose liquid PH_3 fumigation from 7 days to 5 days when the grain temperature is above 25ºC. Fumigation using liquid formulations of PH_3 was shown to be a very effective pest management technique. It is also concluded that high dose PH_3 fumigation can play a significant role in replacing MB applications. Once development is fully complete the process will find application in many other aspects of commodity disinfestation.

Further research is required into the technical aspects of mixing PH_3 with air to ensure that all safety aspects of this technique are considered.

ACKNOWLEDGEMENTS

The entire project outlined in this paper has been the work of a focused team. Without their combined efforts the considerable work required to do this study could never have been accomplished. We recognise the considerable efforts of the staff of the Farming Services Institute, QDPI, Indooroopilly; the Grain Quality Staff of Globex Gladstone Port; the Grainco Australia Fumigation Staff; BOC Gases and Cytec Australia and thank them all.

REFERENCES

Bridgeman B.W. (1999) Grainco Australia, Integrated Pest Management Plan. Internal Publication, Grainco Australia Limited, Australia.

Bridgeman B.W., and Collins P.J. (1994) IPM in the Grainco, Australia, storage system. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.) Canberra, Australia, 17-23 April 1994, CAB International, Wallingford, Oxon, UK, **2,** 910-914.

Bridgeman B.W., Collins P.J. and Davis D. (2001) Assessment of the effectiveness of fumigation protocols in the field. In: *Proc. Australian Postharvest Technical Conference,* Adelaide, 1-4 Aug. 2000, (in print).

Collins P.J. and Bridgeman B.W. (1991) Bulk Grains Queensland Integrated Pest Management Plan Strategies for the Nineties. Internal Publication Grainco Australia Limited, Australia.

Collins P.J., Daglish G.J., Nayak, M.K., Ebert, P.R., Schlipalius, D., Chen, W., Pavic, H., Lambkin, T.M., Kopittke, R. and Bridgeman, B.W. (2001) Combating the evolution of strong resistance to phosphine in Australia. In *Int. Conf. on Controlled Atmosphere and Fumigation in Stored Products*, Fresno, California. 2000, (this publication).

Desmarchelier, J.M. (1998) Potential new fumigants. In: *Stored grain in Australia. Proc. Australian Post-harvest Technical Conference.* (Edited by Banks, H.J., Wright, E.J., Damcevski, K.A.), 1998. Canberra, Australia, 133-137.

Winks R.G. and Hyne E.A. (1994) The use of mixed-age cultures in the measurement of response to phosphine. In: *Proc. Int. Conf. on Controlled Atmosphere and Fumigation in Stored Products*, (Edited by Donahaye, E.J., Navarro, S. and Varnava, A.), 21-26 April 1996, Printco Ltd., Nicosia, Cyprus, 3-15.