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Australian research into methyl bromide alternatives: Possible applications for Rice

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Introduction

The Stored Grain Research Laboratory (SGRL) is part of CSIRO Entomology, a Division of the Australian Government's national research body CSIRO. The SGRL was set up in 1973 to research storage issues for the Australian grain industry with the main focus on insect control. This was aimed at improving the standard of grain exports and reducing the reliance on contact pesticides, particularly on bulk wheat. Over thirty years of research the SGRL has also done research on rice on a contract basis. In recent years the SGRL has focused on its alternatives to methyl bromide as a result of phase-out under the Montreal Protocol. The results of much of this research has application in rice storage, and this paper presents an overview of the main results of this research, including assessment of fumigants, controlled atmospheres and aeration strategies. References to some other supporting documentation are included.

The rice industry in Australia began in the 1920's in the newly established Murrumbidgee Irrigation Area (MIA) of New South Wales (NSW). The industry started with a bag storage system where rice was stripped at low moistures (16.5%) prior to further drying, storage and milling. Today, the industry is characterised by large scale machinery, advanced aerated storage facilities, automatic control, and purpose built in-situ moisture sensing systems in a highly capital intensive industry. The 1.6 million tonne rice crop is aeration dried in 6 to 7.5 metre deep bins using ambient and burner supplemented inlet air. The Australian industry trades rice to a variety of international and domestic markets, and therefore caters to a range of quality requirements. These include minimised kernel breakage, a range of polished rice appearance and presentation characteristics, cooking texture and performance, eating qualities, and a range of downstream processing functionalities. Methyl bromide is an important part of the treatment of milled products before shipment.

Alternative insect control approaches for disinfesting bulk paddy through to finished product, and for structural treatments, are also being pursued by the Australian rice industry. This is in response to increased infestation occurrences caused by larger crop sizes with more storage over summer months. The rice industry is investigating the use of alternative fumigants such as carbonyl sulphide, phosphine and ethyl formate.

Fumigant and controlled atmosphere strategies developed within the SGRL for pest control include:

- fumigation of rice with ethyl formate, a fumigant used in Australia on dried fruit, that acts quickly but is strongly absorbed and rapidly broken down,

- fumigation of rice with carbonyl sulfide, a new fumigant that has been patented by the SGRL and which is being developed in Australia for cereal grains,
- ethanedinitrile (C_2N_2), a new fumigant that acts quickly and may have applications in rice mills, particularly for structural treatment,
- controlled atmospheres as a means of disinfesting stored products such as rice, and
- treatment of paddy rice with phosphine.

Developments in aeration control are also being pursued to improve performance in several areas. A new control method, Adaptive Discounting (ADC), is being trialled on natural air and burner assisted aeration drying facilities within the Australian rice industry. The aims are to improve the milling quality of the dried rice, increase aeration efficiency, enable chemical free insect control, and provide a user friendly operating interface.

Fumigation of Paddy Rice and Rice Products with Carbonyl Sulfide

With the phase-out of methyl bromide in 2005 under the Montreal Protocol the Australian rice industry is looking for alternatives for this function. One such alternative is carbonyl sulfide (COS). While the interaction of COS with commodities such as barley, wheat and canola has been investigated previously, more data on the fate of COS during fumigation of rice commodities, and its effect on their quality was needed. Reuss et al (2000a) investigated the effects of fumigating paddy rice, brown rice, white rice and rice flour for 5 d with COS (20 g m^{-3}) at two temperatures (10 and 25℃). They found that sorption of COS in rice commodities was higher than in wheat and was especially high in paddy rice and rice flour. The removal of fumigant by airing after fumigation was found to be rapid for all of the commodities. Residue levels after airing were found to be below the proposed MRL of 0.2 mg kg^{-1} and indistinguishable from natural background levels in rice. There were no phytotoxic effects of COS on paddy rice and the viability of paddy rice was unaffected after fumigation at 20 g m^{-3}.

High loss rates of COS from rice commodities during fumigation mean that higher doses of fumigant to achieve efficacious insect control in these commodities than are required for wheat. However, Ruess et al (2000a) show that fumigation of milled rice products at 25℃ is a possible replacement for methyl bromide fumigations. At lower temperatures, longer exposure periods than those commonly used for methyl bromide fumigations would be necessary. Paddy rice and rice flour will need to be treated at higher doses to achieve the same insecticidal concentrations of COS.

Fumigation of Paddy Rice and Rice Products with Ethyl Formate

Ethyl formate is registered and used in Australia for dried fruit under the trade name Erinol™ and distributed by Orica. The SGRL has re-evaluated this very old and almost forgotten fumigant and found that it has a remarkably fast action.

Ethyl formate is naturally present in high concentrations in many fresh fruits and vegetables and as a result may not be as phytotoxic as other compounds. It is strongly absorbed into commodities and it breaks down very quickly into two other components that occur naturally in food. The problem is that it breaks down so rapidly that it is difficult to hold concentrations long enough to be effective against the target pests. Therefore there is a technical uncertainty about what may be possible on cereals.

While the interaction of ethyl formate with commodities such as barley, wheat and canola has been investigated previously, specific data on the fate of ethyl formate during fumigation of rice commodities or its effect on their quality was needed. Reuss et al (2000b) investigated the effects of fumigating paddy rice, brown rice, white rice and rice flour for 2 d with ethyl formate (60 g m^{-3}) at two temperatures (10 and 25℃). They found that ethyl formate loss in rice commodities was especially high in paddy rice and rice flour. Removal of ethyl formate from all commodities by airing was found to be rapid at 25℃. At 25℃ ethyl formate residues after treatment were indistinguishable from background levels. However, at 10C substantial residues were detected immediately after airing off. Phytotoxic effects of ethyl formate on paddy rice were negligible and the viability of paddy rice after fumigation at 60 g m^{-3} was unaffected.

The high loss rates of ethyl formate from paddy rice and rice flour requires the application of higher doses of fumigant to achieve efficacious insect control in these commodities. Fumigation of milled rice products with ethyl formate at 25℃ promises to be an effective pest control measure. This is likely to also apply at lower temperatures, although more research into ethyl formate toxicity to insects at low temperatures is required. At the applied dose at 25℃, ethyl formate residues in fumigated commodities were indistinguishable from background levels. At lower temperatures residues might be a problem immediately after treatment, especially in paddy rice and rice flour.

Phosphine Sorption by Paddy Rice

Sorption behaviour of fumigants by a commodity under fumigation can significantly affect the concentration of active material in the gas phase and has a major influence on the outcome, success or failure, of fumigation. Even if the correct amount of fumigant is applied and leaks to atmosphere minimised, the concentration of fumigant gas can drop to non-lethal concentrations due to the action of the commodity prior to the completion of fumigation period.

As some materials sorb and retain more fumigant than others it is necessary to consider the sorption profile of a commodity when planning fumigations. To compensate for low to moderate levels of sorption, it is usually sufficient to increase the initial applied concentration, thereby ensuring that the concentration of fumigant in the headspace remains appropriate throughout the exposure. However, when a commodity is highly sorptive it is often preferable, safer, and legally necessary to 'top up' the concentration of fumigant in the fumigation enclosure during the fumigation.

Paddy rice is typically a highly sorptive commodity with respect to phosphine. Annis (1990) and Rajendran and Muralidharan (2001) both observed very high loss rates from sealed stacks fumigated with phosphine.

The amount and rate of sorption of fumigant on a commodity is influenced by temperature, moisture content and the history of the commodity (Banks 1990). Increased moisture content and lower temperatures are usually associated with higher levels of sorption. The conditions under which a grain has been grown and stored may also influence sorption; perhaps the most significant influence of storage is previous treatments. Re-treatment of a commodity generally results in a reduced loss of fumigant due to sorption, however it is difficult to distinguish whether ageing or repeated treatments is the main component of reduced levels of sorption.

Experiments were undertaken to determine the feasibility of fumigating current varieties of paddy rice with phosphine. Paddy rice is highly sorptive of phosphine and the current label rate of 1.5 gm^{-3} applied as aluminium phosphide resulted in an inadequate concentration x time profile. The concentration of phosphine fell too quickly to kill all life stages of pest species likely to be present in the paddy rice. A single top-up with gaseous phosphine after 1 week of fumigation, was found to be sufficient for an adequate fumigation concentration to be maintained to the end of the fumigation period.

The results from this study (Weller 2001) agree with previous findings that paddy rice is highly sorptive of phosphine gas and that the rate at which it is sorbed is dependent on temperature, fill rate and whether the paddy has been fumigated with phosphine previously. The sorptive properties of the paddy rice observed in this study should be seen as indicative, as the sorptive properties of grains are known to change depending on growing conditions, variety and moisture content. The two samples tested in this instance were similar and resulted in comparable rates of sorption. However, significantly different levels of sorption have been noted in apparently standard samples of wheat (Banks 1990).

Under the current label rates for aluminium phosphide preparations in Australia, the maximum application rate is 1.5 gm^{-3} for grain in a well-sealed structure, based on the empty silo/shed to be fumigated independent of the fill rate. This study suggests that such an application will maintain the concentration of phosphine above 100 ppm for 8 days, after which a top up with gaseous phosphine will be required to maintain the concentration above 100 ppm for the required 14-day exposure period. If the label rate is increased to 3.0 gm^{-3}, an initial application of aluminium phosphide preparation would probably ensure that the 14 days above 100 ppm was achieved.

These predictions have been made from experiments undertaken on a very small scale compared with actual field application. Several issues need to be addressed in scaling up from these laboratory scenarios to a field situation:

1. The concentration of phosphine in the headspace may approach the lower flammability limit of 1.8% (18000 ppm) during the initial release of phosphine from the formulations.
2. The gas may need to be actively distributed by forced recirculation through the grain bulk to ensure that it reaches all parts of the bulk at effective fumigation concentrations.
3. The vacuum/vortex created by the use of a fan during forced distribution when high concentrations of phosphine exist may result in phosphine concentrations exceeding the flammability limit as the gas passes across the fan (Green et al, 1984).
4. The health and safety issues of applying blankets to the top of the grain mass also need to be addressed. Fumigators' applying the blankets should use appropriate personal protection equipment. As

the blankets begin to produce phosphine on contact with the moisture in air, the level of phosphine in the vicinity of the fumigator could very quickly exceed safe levels.

If the label rate is increased to 3.0 gm^{-3}, the decision to increase the application rate, should readdress issues 1, 3 and 4 raised above. These will be critical to the safety of the fumigation. Furthermore, the spatial distribution of the number of blankets required could be an issue in the restricted headspace of the pyramidal shed design being constructed for the Australian rice industry.

Controlled atmospheres using CO_2 in Containers

The aim of the work reported here (Annis and Reuss 2001) was to investigate the use of shipping containers as fumigation enclosures for alternatives for methyl bromide. Carbon dioxide (CO_2) has been examined in this study, but phosphine is also a currently available alternative to methyl bromide. However, phosphine requires a substantial increase in time to be efficacious and would not be logistically feasible without a huge increase in available containers and fumigation space for the current shipping program. In addition in-transit fumigation using toxic substances is not allowed in Australia.

Rice products are shipped from Australia in containers. Methyl bromide is used before shipment to control any residual infestation. With the phase-out of methyl bromide an alternative treatment that is capable of fitting into the current shipping pattern is required. For this reason trials to assess controlled atmospheres using CO_2 which can be used in suitable containers with a sufficient level of gas tightness to provide an opportunity for in-transit treatment, have been conducted with the Australian rice industry.

Four standard shipping containers were used, as is the routine for containers delivered to Ricegrower's. It was not possible to select them for gas-tightness as those that come by rail empty are the ones that leave the site full, i.e. there is no opportunity for selection. These containers were far too leaky for the simplest form of CO_2 addition, and showed no overall improvement on sealing compared to studies of 20 years ago.

The following recommendations on this technique from the results of this trial were:

- Containers used for CO_2 treatments should have pressure decays from 200 to 100 Pa of longer than 10 seconds.
- 30kg of loose dry ice, pellets or snow, should be added as an initial charge
- 30kg of dry-ice in an insulated box made of 75mm polystyrene foam should be added for sustained gas release to maintain an effective concentration during the in-transit period.
- Protection from excessive solar heating and cooling and wind during the exposure period improves the efficacy of the treatment.

Containers not meeting the pressure standard could be individually sheeted and treated statically on a fumigation pad (gas proof slab). These recommendations apply directly to CO_2 treatments but also have implications for phosphine and methyl bromide fumigations. It is more than likely that current methyl bromide or phosphine treatment in any of the four containers would be of marginal efficacy.

Based on the observed trial data, in-transit fumigation with CO_2 may have been possible with 3 of 4 containers tested especially if > 30 kg of dry ice had been used both in the initial charge and the make up gas. Protocols for clearing gas from containers after an in-transit disinfestation need to be in place to ensure the safety of workers.

Aeration control-Adaptive Discounting control (ADC)

A new grain aeration control method has been developed within the SGRL (Darby 2002). This method has application in:

- All aeration modes: Dry, Cool and Maintain
- All grains and locations in Australia
- All aeration systems and stores

ADC meets contemporary trends in harvest flexibility, maintenance of grain quality during storage, is a non-chemical method of insect control and can provide a safe long-term storage option.

The main advantage of ADC is that it removes the need for a high level of understanding of the aeration processes. Users are not required to monitor the drying process or adjust set points. They input specific information at filling the store including average grain moisture content, average grain temperature, target grain moisture content, e.g. 14.0%, target grain temperature, e.g. 10℃, store filling extent as %. [or Tonnes], whether burners are to be used or not (Yes or No), the overdrying limit or minimum moisture content, e.g. 12.0%. These user inputs are dynamic and can be updated at any time.

Results of a comparative trial with the Australian rice industry showed the ADC method dried rice from an average moisture content of 20% to a target of 14% where the final average moisture of the ADC bin was 13.4 to 14.1%, with a moisture profile across the bin depth of approximately 0.5% and a drying rate of 5 to 6 weeks. This compared with an "expertly supervised" bin which dried rice from an average moisture content of 20% to a target of 14% where the final average moisture of the supervised bin was 13.4 to 14.5%, with a moisture profile across the bin depth of approximately 1.0% and a drying rate of 6 to 7 weeks. The breakage results showed negligible losses from either control method.

ADC matched the drying performance of the "expertly supervised" control method for the final moisture level and profile.

ACIAR Projects Fumigation Manuals

The SGRL has participated in a range of research projects that have led to important documents on fumigation practice. These are included as references against which the results of the rice work can be assessed along with some other web based references on related issues.

References

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Some useful web based information sources

Note: All web sites listed below were accessed and opened successfully on 17 October 2003.

AGIRD - Australian Grain Insect Resistance Database. A National database of pesticide resistance in grain insects. http://www.agric.wa.gov.au/ento/agird1.htm

Annual International Research Conferences on Methyl Bromide Alternatives and Emissions Reductions. The proceedings of the past nine conferences (1994-2002) can be accessed on the web at: http://www.mbao.org/

APTC98. Stored Grain Australia. Proceedings of the 1998 Australian Postharvest Technology Conference (APTC98): http://www.sgrl.csiro.au/aptc1998/default.html

APTC2000. Stored Grain Australia 2002. Proceedings of the 2000 Australian Postharvest Technology Conference (APTC2000): http://www.sgrl.csiro.au/aptc2000/default.html

APTC2003. Stored Grain Australia 2003. Proceedings of the 2003 Australian Postharvest Technology Conference (APTC2003). Due early in 2004: http://www.sgrl.csiro.au/aptcabstracts2003/default.html

Australian Centre for International Agricultural Research (ACIAR): http://www.aciar.gov.au/

AQIS. Methyl Bromide Fumigation Standard (accessed 30 September 2003). http://www.affa.gov.au/content/output.cfm?ObjectID=D2C48F86-BA1A-11A1-A2200060A1B01797#subb414

CSIRO Stored Grain Research Laboratory: http://sgrl.csiro.au/

MBTOC 2002. 2002 Assessment Report of the Methyl Bromide Technical Options Committee http://www.teap.org/REPORTS/downloads/MTOC2002.pdf

MBTOC 1998. 1998 Assessment Report of the Methyl Bromide Technical Options Committee. http://www.teap.org/REPORTS/downloads/MBTOC98.pdf

MBTOC 1995. 1994 Assessment Report of the Methyl Bromide Technical Options Committee. http://www.teap.org/REPORTS/downloads/MBTOC94.pdf

Phosphine. National awareness campaign: http://www.agric.wa.gov.au/ento/publications/national_phosphine_awareness_campaign.htm

Phosphine. Use it responsibly: http://www.agric.wa.gov.au/ento/publications/Phosphine_Use_it_responsibly_or_lose_it.htm