Practical synergism of fumigant action: ethyl formate and carbon dioxide

Summary
The increasing incidence in the detection of phosphine® resistance in stored grain insects and the phase out of other fumigant options have left grain storers with few alternatives to phosphine for low residue insect control. This project aimed to develop a fumigant product using ethyl formate® and carbon dioxide through research into insect mortality, residue breakdown, safe application technology to grain silos and the potential development of resistance. The data generated in this project will be used by BOC Ltd to update its new Australian Pesticides and Veterinary Medicines Authority (APVMA) registration for Vapormate™® within the next six months for its use as a rapid-acting fumigant for farm grain storages.

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Conclusions

The Australian grains industry is heavily dependent on phosphine®️ for the effective insecticidal and low residue treatment of stored grain. Phosphine is the main fumigant used throughout the grain industry and has come under pressure due to the development of resistance in insects. Although very useful and cheap, phosphine is slow acting and should not be used for rapid disinfestation of grain as it is ineffective and the practice can lead to development of phosphine resistance.

CSIRO Entomology, with the support of GRDC in project CSE009, researched an ethyl formate®️ and carbon dioxide mixture as a fast insecticide fumigant for small grain storages (50-200 tonnes). It was registered as Vapormate™️ by BOC Ltd and is faster and more effective than dichlorvos®, which is becoming less useful through insect resistance. The new fumigant will support phosphine in resistance management.

Project CSE0009 aimed to develop a data package to support the agricultural chemical registration of ethyl formate and CO₂. This aim has been achieved.

The major outcome of project CSE0009 has been the successful delivery of a new grain fumigant for the Australian grain industry and in particular, farm-scale storers of grain. The new label for Vapormate™️ will be updated based on the outputs of the project.

Fast treatment: The new treatment is fast. Application takes less than 15 minutes and fumigation from as little as three hours to as much as 72 hours. The grain can be immediately outloaded for sale and use for human and animal purposes after venting of excess fumigant. Silo requirements include an aeration fan and some level of sealing.

Vapormate™️ can be used as a phosphine resistance management tool and as a fast disinfestant.

Vapormate™️ is the only registered grain fumigant, apart from methyl bromide®, that can legally be applied to a farm silo and outloaded within 24 hours. However, methyl bromide’s use is restricted to bulk grain handlers.

Recommendations

Vapormate™️ is the first new fumigant registered in Australia in more than 40 years for the treatment of stored grains. Applications for two other grain fumigants -sulfuryl fluoride®️ (Profume®️) and carbonyl sulfide®️ have also been recently submitted to the APVMA.

There are several reasons why there are very few new fumigants registered for grain. Grain is a staple food, therefore a fumigant used on grain needs to demonstrate a high level of safety in terms of residues and alteration products in the commodity and to fumigant applicators, as well as to the environment. Discovering a fumigant that is also relatively safe to humans can be difficult to achieve. Moreover, grain fumigation is a marginal business in which all major fumigants,
disinfestants and protectants are currently available at a very cheap rate. This results in low costs per tonne for treatment and is a significant disincentive for new products coming on the market because of the high cost of registration.

A recommendation is that the GRDC and the wider grains industry strive to protect and develop available effective treatments (and perhaps those coming on line) as there may be limited options in the future. Currently there are no financial incentives for new products to be developed. This may mean investment in extension to increase Vapormate's uptake by growers and other storers as a phosphine resistance management measure and as a superior alternative to dichlorvos.

Outcomes

Economic benefits

The major economic benefit stemming from this project is the provision of a rapid, low residue treatment for controlling stored product pests that is an alternative to phosphine. Most Australian grain is fumigated with phosphine. The effectiveness and low residues resulting from phosphine fumigation have allowed Australian grain to obtain a premium in clean and green markets. The loss of or restrictions into these markets has been estimated at potentially hundreds of millions of dollars by the Australian Wheat Board (AWB) Ltd. However, as phosphine is almost the only fumigant used throughout the grain industry, resistance development has become a great threat to the industry. The availability of effective alternative treatments is one method of supporting phosphine's use in the industry. Ethyl formate is completely effective against phosphine-resistant insects.

Vapormate is also an alternative to methyl bromide which is being phased out of use worldwide as its release into the atmosphere eventually depletes the ozone layer. Methyl bromide's use in the grain industry is virtually restricted to bulk grain handlers seeking alternatives for the fast treatment of grain.

Project research has developed an application technology for Vapormate that is specifically designed for small scale silos (50-200 tonnes) thereby directly benefiting growers who choose to store on-farm.

Vapormate acts rapidly to kill insects. It is applied in less than 15 minutes, the fumigation period can be as short as three hours and venting of the gas at the end of fumigation takes less than two hours. Grain can then be safely outloaded without a withholding period. This means growers who want to sell grain quickly but find it is infested can treat and outload in less than a day. This is currently not possible with any treatments routinely available to growers. The economic benefit of this is difficult to estimate but could be very valuable in situations where there are no alternatives.

Environmental and health benefits

Ethyl formate + carbon dioxide (Vapormate) has low toxicity toward humans and when used for fumigation of grain, results in very little environmental release and therefore low impact on the environment. In the case of an accidental release, there would be minimal impact on the environment. Ethyl formate occurs naturally in a wide range of foods. The residues of ethyl formate remaining in grain after fumigation were not considered of any health consequence by the APVMA and as a result, Vapormate does not attract a withholding period for residues. Ethyl formate and CO₂ have large margins of safety in relation to potential occupational health and safety for applicators. The occupational exposure limit for ethyl formate is 300 times higher than phosphine. Phosphine and methyl bromide are highly toxic to humans and the venting of these gases post-fumigation has come under greater regulation from various State Environmental Protection Agencies (EPAs).

Achievements/Benefits

Background to CSE0009

The Australian grains industry is heavily dependent on phosphine for the effective insecticidal and low residue treatment of stored grain. Phosphine has helped our grain obtain a premium in international markets and supports Australia's clean and green reputation. As phosphine is about the only fumigant regularly used throughout the grain industry it has come under pressure due to the development of resistance in insects. CSIRO Entomology with the support of the GRDC developed an ethyl formate and carbon dioxide mixture as a fast insecticide fumigant for small grain storages (50-200 tonnes). A
formulation of 166.7 g/kg ethyl formate in liquid carbon dioxide as the solvent and propellant was registered by BOC Ltd for use on stored grain. Vapormate™ can replace dichlorvos™, which is becoming less useful through insect resistance, and support phosphine resistance management.

Major achievements of CSE0009

Project CSE0009 aimed to develop a data package to support the agricultural chemical registration of ethyl formate and CO₂. The project team identified and worked with the registrant resulting in a registered product (Vapormate) with a label for stored grain use. This label will be updated based on the outputs of the project.

Project achievements include:

1. Collaboration with the product registrant.
2. Efficacy data for Vapormate against stored grain insects.
3. No regulatory requirement for residue analysis or withholding period.
5. Field trialing of Vapormate.
6. Current and proposed new label rates for stored grain applications.

1. Collaboration with product registrant

The project team worked closely with BOC Ltd to provide data for the initial registration application and had an on-going contribution to this event. Discussion topics with BOC Ltd included registration, presentation material for conferences; progress on cheap and efficient vaporisers to aid fumigant application; sensors for measurement of occupational health and safety (OH&S) and fumigant concentrations; residue measurement methods; other grain-related uses; work with potential end-users of the fumigant; formulation delays; field trial outcomes; publicity for Vapormate and issues such as cylinder design. This collaboration has been key to the success of the project.

2. Efficacy of Vapormate against stored grain insects

Insect selection

Three stored grain insects were chosen for the major efficacy studies based on the frequency these insects are found in storages, the economic damage they cause to stored grains and their known tolerance of insecticidal treatments. These included a highly phosphine-resistant field strain of the lesser grain borer, and laboratory strains of the flour beetle and the rice weevil. Mixed age cultures which contained representative numbers from each stage i.e. egg, larval, pupal and adult were used in the efficacy studies. It is well known that the immature stages of insects can be much more difficult to control with fumigant insecticides.

Application of Vapormate

Exposures were carried out at 25 or 15°C in a sealed model silo for 3, 24 or 72 hours and a range of Vapormate concentrations were bioassayed. The formulation was applied to the model silo at a flow rate that achieves an even distribution of ethyl formate in the quickest time possible and within the capacity of aeration fans available for grain silos. One gas exchange of ethyl formate formulation was pumped into the model silo, taking approximately 12 minutes.

Optimal concentrations and times for more than 99% mortality for each species were obtained. Rice weevils, in particular the juveniles, were the most difficult to control.

Conclusions from the insect efficacy studies

- Vapormate can achieve very high levels of control (>99%) of all stages of stored grain insects at exposure times of three hours except the rice weevil which achieves only a moderate level of control (82-91%).
- A single application of 450 g/cu.m of formulation is sufficient to obtain high level control (>99%) of all stages of flour beetle and lesser grain borer when grain is held for 24 hours. Rice weevil is moderately controlled (86%) at this combination of concentration and exposure time.
- Very high levels of control of rice weevil can be achieved with a single treatment at 940 g/cu.m formulation held for 72 hours.
Contrary to expectations, lowering the grain temperature to 15°C did not affect efficacy of Vapormate as an application of 380 g/cu.m formulation at 15°C achieved very similar mortality to an application at 25°C.

In the presence of a light infestation of rice weevil, the lower rate of application (450 g/cu.m Vapormate formulation) held for 24 hours would be sufficient to greatly reduce the insect load in the grain. Heavy infestations of rice weevil would require the higher rate of 940 g/cu.m formulation for high level control.

3. No regulatory requirement for residue analysis or withholding period

A review of human toxicology conducted under project CSE159 was made available to BOC Ltd to submit with its initial registration application for Vapormate. This review demonstrated the safety and natural occurrence of ethyl formate in the diet. The APVMA deemed that ethyl formate residues resulting from fumigation were safe for humans and animals to consume and therefore ruled out the need for a withholding period for the grain. Residue analysis was no longer a requirement as all residues resulting from fumigation are considered safe to consume.

4. Application technology for Vapormate

Vapormate cannot simply be added to the headspace of a silo and left to diffuse through the grain like other fumigants. Ethyl formate is a liquid at room temperature and is highly sorbed to grain when compared to phosphine. Therefore, the ethyl formate and CO₂ mixture needs to be applied with force through the grain to achieve penetration. The most effective method to achieve this is to use an aeration fan. Firstly, the optimal flow rate for the fan was determined to ensure an even distribution of fumigant through the grain bulk. Once the flow of fumigant had penetrated the bulk, the fan was switched off and the lid of the silo closed for the fumigation period. The fan was turned on again after the fumigation period to assist in expelling the remaining fumigant. This application technology has never previously been used for a fumigant and required field trialling to ensure that it worked effectively.

5. Field trialling Vapormate

Six field trials were conducted under experimental use permit no. 7555 (plus amendments) from the APVMA. Each trial was conducted in the presence of a licensed fumigator. The trialling was a valuable experience to help in understanding where problems can occur in application of the fumigant.

In bin fumigant monitoring: In each trial, ethyl formate and CO₂ levels were measured in five critical places in the silos except Trial 6 in which measurements were taken from one position only. A Draeger X-AM 7000 multi gas detector was used to measure ethyl formate and CO₂. The highest achieved concentration of fumigant was always at the bottom of the silo close to a fan inlet and the lowest concentration was always at the centre top surface.

Insect bioassay: Large numbers of lesser grain borer, flour beetle and rice weevil mixed age cultures were placed in cages and co-located with the gas sampling lines in the silo. Flour beetle and lesser grain borer were completely controlled and more than 98.2% rice weevils were controlled in all trials except Trial No. 6.

The first three trials were conducted at Walla Walla, New South Wales, in a purpose-built new silo as a result of collaboration between Modern Engineering & Construction Co. Pty. Ltd (Kotzur silos) and CSIRO Entomology. Vapormate was introduced into the intake of the fan at a rate that applied fumigant in 12 minutes. The aeration fan had a relatively small capacity of two litres of air per second per tonne of grain. This flow rate is easy to achieve with existing commercial aeration fans.

CSIRO Black Mountain was the site of the fifth trial and Warwick, Queensland, of the fourth and sixth trials. In Trial No.6, a silo of sorghum was available for fumigation whereas wheat was fumigated in all other trials. In this trial, either the high moisture content of the sorghum (13.4%) or the nature of the grain itself resulted in most of the fumigant rapidly sorbed to grain and not reaching the upper parts of the silo. This resulted in a substandard fumigation and less than 50% of the insects were controlled. However, these had been placed in the position of lowest gas concentration in the bin i.e. the upper surface of the grain.

Occupational and environmental exposure monitoring

Air sampling and monitoring were conducted during all field trials for compliance with the occupational exposure limit for ethyl formate (100 ppm) and carbon dioxide (5000 ppm) in the workspace surrounding farm bins during set-up, fumigation, venting and before outloading.
Monitoring systems: The Miran® SapphIRe (Thermo Environmental Instruments) programmable infra-red gas analyser was used to measure ethyl formate without interference by CO₂ at occupational exposure levels (100 ppm) and below. Draeger detector tubes for carbon dioxide and formic acid within occupational exposure ranges were also used. Discussions have been held with Draeger which has shown interest in developing an ethyl formate tube for occupational exposure level detection.

In all six field trials, the occupational exposure level, for ethyl formate (100 ppm) and formic acid (5 ppm), was not exceeded within the five metre fumigation barrier in the fumigator’s workspace during application, venting or outloading. If the occupational level was not exceeded within the barrier, the air concentration was probably even lower outside the barrier. Carbon dioxide concentrations were not routinely monitored.

6. Current and proposed new label rates for stored grain applications

The team worked with BOC Ltd to submit data generated in this project to the APVMA to support registration and label requirements of Vapormate.

7. Outcome of resistance testing

While there appears to be natural variation in the tolerance of some insect species to Vapormate, studies that included mutagenesis and inbreeding have as yet found no evidence of resistance. 800 individual mutagenised insect lines have been challenged with the discriminating dose of ethyl formate. This is consistent with the lack of resistance detected in insects collected from a dried fruit processing plant where ethyl formate had been used for many years. If commodities are treated only once with Vapormate prior to sale or processing, it is unlikely that resistance to the treatment will develop, however if multiple treatments are undertaken on the same commodity, there will always be the prospect of resistance occurring, being selected for and becoming an issue for this treatment.

Phosphine resistant insects were found to be completely susceptible to Vapormate i.e. there is no cross resistance between the two fumigants.

How achievements will benefit the grain industry

The major outcome of project CSE0009 has been the successful delivery of a new grain fumigant for the Australian grains industry and in particular, farm-scale storers of grain.

Fast treatment: The new treatment is fast. Application takes less than 15 minutes, fumigation as little as three hours to as much as 72 hours and the grain can be immediately outloaded for sale and use for human and animal purposes after venting of excess fumigant. Silo requirements include an aeration fan and some level of sealing.

Phosphine resistance management: Vapormate can be used as a phosphine resistance management tool and as a fast disinfectant.

Methyl bromide alternative: Vapormate is the only registered grain fumigant, other than methyl bromide, that can legally be applied to a farm silo and outloaded within 24 hours. However, methyl bromide is restricted to bulk grain handlers.

Other research

Commodities other than wheat

The project was designed to achieve its goals by focussing on the fumigation of wheat, by far Australia’s most important crop. However, during the course of the project, representatives of other commodities (e.g. Pulse Australia and the Malting and Brewing Industry Barley Technical Committee (MBIBTC)) showed interest in Vapormate™ and its potential for grains such as pulses and barley. It is important for the GRDC to consider research proposals that will extend the use of Vapormate. This will help phosphine’s effectiveness as a fumigant for grain. Experience in the field trial with sorghum has shown that simply extending the fumigation conditions developed for wheat to other commodities is not possible without extra research and development.

Although wheat is Australia’s biggest crop, it is not the only crop that requires a rapid fumigant. Smaller production commodities such as pulses could greatly benefit from a rapid, residue free treatment.
Collaboration with Modern Engineering & Construction (MEC) Pty Ltd

CSIRO entered a non-commercial agreement with MEC regarding the construction of a purpose built ‘Vapormate’ silo. The first three field trials were conducted at Walla Walla in the purpose-built new silo as a result of that collaboration. This silo was a modified Kotzur drying silo to accommodate requirements for forced flow fumigation on the basis of CSIRO input. The silo was fully sealed and equipped with an adjustable flow aeration fan that allowed Vapormate to be introduced into the silo within 12 minutes.

Collaboration with Draeger

Draeger Safety Pacific has been very supportive of the CSE0009 project. Draeger made available a highly versatile fumigant monitor (X-AM 7000) for use in field trials free of obligation for nearly 12 months. In addition, the Draeger Head Office in Germany has been developing an ethyl formate# detector tube for use in handheld gas monitoring meters. Occupational health and safety is increasingly becoming a more important issue for regulatory bodies such as APVMA and among farming groups. Having the ability to quickly (and cheaply) monitor the environment or workspace for presence of the fumigant is now considered obligatory for the safe use of fumigants.

International linkage of research groups on Vapormate

Researchers at Crop & Food Sciences in New Zealand and at the University of California Davis are evaluating Vapormate for use with horticultural commodities. The project team has liaised with these groups and exchanged ideas and approaches to determine insect efficacy and data requirements for registration.

Intellectual property summary

The model of delivery for this project was one of collaboration between CSIRO, GRDC and a potential registrant of the ethyl formate# and CO₂ mixture to make the data available to the registrant in return for a label covering stored grain uses. The efficacy data obtained in the laboratory and the field trial data remain the property of CSIRO and GRDC and are recognised as such under the data protection procedures introduced recently by the APVMA.

Additional information


Further publications:


