Summary
The principal aim was to provide new ethyl formate-based formulations and fumigation methods for:
1) grain growers as alternatives to replace dichlorvos for inloading and outloading treatments and also to replace carbon disulfide and phosphine for in situ fumigation, and
2) bulk handlers as alternative fumigants to replace methyl bromide and phosphine for several reasons; the phasing out of methyl bromide under the Montreal protocol, phosphine is unsuitable for rapid fumigation and increased economically significant resistance to phosphine in several species of stored product pests.

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Ethyl formate## based formulations mixed with methyl isothiocyanate## (MITC) and allyl isothiocyanate## (AITC), as shown in these laboratory studies and trials, provide advantages in terms of worker, consumer and environmental safety. Residues can be reduced to natural levels without aeration. It is highly toxic to insects and has no adverse effect on the quality of the commodity. At the dosage of 40g/t, the formulations give a high level of control of the adult stages of most of the tested insects. At the dosage of 80g/t, all stages of insects including Tribolium variable and Sitophilus oryzae were killed. A disinfectant that kills the adult stages and internal stages will be useful for the grains industry. The new formulation has the potential to replace dichlorvos## for inloading and outloading treatments, as an alternative to phosphine## for resistance management, and in situ quick fumigation in sealed and unsealed farm bins.

Conclusions

Ethyl formate## based formulations provide quick insect control with shorter exposure treatments. Insects should be controlled in on-farm storage, e.g. during the trials, an insect population of more than 20 insect/kg of grain after 6-8 weeks storage of newly harvested grain was found. Therefore, the loss of dry mass and commercial value due to insect damage is quite a common issue for on-farm storage.

Recommendations

1. The registration and commercial availability of ethyl formate## formulations should be strongly supported by the GRDC. There is an urgent need to register new safe fumigants or formulations as alternatives to:
   a) phosphine## so as to avoid over-reliance on phosphine in unsealed bins and sealed bins without gas recirculation systems. The new formulations reduce the occupational health and safety (OH&S) risks and avoid the onset of insect resistance.
   b) dichlorvos## which leaves organic chloride and phosphide residues.

2. Extension officers should be made aware of the advantages of using ethyl formate. Ethyl formate formulations provide quick insect control with shorter exposure treatments. Insects should be controlled in on-farm storage, e.g. during the trials, an insect population of more than 20 insect/kg of grain after 6-8 weeks storage of newly harvested grain was found. Therefore, the loss of dry mass and commercial value due to insect damage is quite a common issue for on-farm storage.

3. Extension of registration of Vapormate®## and other formulations of ethyl formate to a range of commodities should be supported.

Outcomes

The expected outcome is to provide new ethyl formate## based formulations and application methods to be used as an alternative or replacement for dichlorvos## for inloading and outloading treatments, as well as replacing carbon disulfide## and phosphine## for in situ fumigation. These new formulations and application methods will be useful to all grain growers and bulk handlers.
The final outcomes of this project are highly dependent on commercial considerations and overcoming a range of regulatory hurdles. Currently, neither of these appears to create an insurmountable problem, but they may influence progress in an unpredictable manner. During the period 01/07/2002 to 30/6/2005, the outcomes achieved were 1) ethyl formate based formulations were developed for inloading, in situ and outloading treatments; 2) various application methods for the new formulations were developed for use on grain in farm bins; 3) demonstrations of the new formulations and application methods in on-farm storage (50-100t).

An ethyl formate formulation, Vapormate® (cylinderised ethyl formate plus carbon dioxide) is nearing registration for grain, stored seed and structural treatments. Laboratory studies and trials have led to improved efficacy of ethyl formate formulations for on-farm storage (sealed and unsealed bins) inloading, in situ and outloading treatments. All data collected from this project have been submitted for a patent licence and potential registration. Currently, GRDC, CSIRO and BOC are progressing in the registration of the ethyl formate based formulations for grain treatments.

The benefits of this project apply to all overseers of grain and grain products. Since the methyl bromide® phase out in January 2005, phosphine has become the only fumigant available for use by growers and bulk handlers. However, fumigation with phosphine requires a long term (>7 days) exposure in sealed bins at temperatures above 15°C. The majority (e.g. >85% in Queensland), of existing farm bins are unsealed and therefore unsuitable for effective fumigation using phosphine. The over-reliance on phosphine in unsealed bins where it is not possible to maintain concentrations for the length of time required for total control of insects has resulted in 1) frequent resistance at high levels, 2) some dangerous practices, and 3) grain delivered to central storage containing live insects. Dichlorvos is available for disinfection within the bulk handling systems at export terminals in both a complementary and a supplementary role to fumigants, but occasionally problems of dichlorvos residues arise. It will also be phased out soon (dichlorvos has been phased out in the European Union (EU) due to residue issues).

Therefore, development of alternative fumigants, such as carbonyl sulphide (COS) and new formulations (ethyl formate) is necessary as methyl bromide and dichlorvos replacements, and as part of a phosphine resistance management strategy.

Achievements/Benefits

Since January 2005, methyl bromide® has been phased out, and in New South Wales (NSW), since 2002, carbon disulphide® has no longer been registered for use as a fumigant. Phosphine® is the only registered fumigant available for farm and bulk handler use in Australia. However, fumigation with phosphine requires long (>7 days) exposures in sealed bins at temperatures above 15°C to be effective. The majority of existing farm bins are unsealed (e.g. >85% in Queensland) and most manufactured sealed farm bins, unless well maintained, become unsealed after several years of use. The use of less than gas tight enclosures is a widespread issue. A specific problem with poorly sealed bins is that it is not possible to maintain fumigant concentrations for the length of time required for full control of stored product insects. Over-reliance on phosphine in unsealed bins resulted in 1) a higher frequency of resistance, 2) dangerous practices, and 3) grain delivered to grain depots containing live insects and unreacted aluminium phosphide® residues. There is, therefore, an urgent requirement for the development of grain fumigants for on-farm use which should be inexpensive and easy to handle and administer. This project addressed a specific research priority in the GRDC value chain, namely, development of an ethyl formate® formulation and application technology for grain inloading, in situ and outloading treatments. This is part of a general framework for the safe use of fumigants, including their role in resistance management strategies. The planned outcome of the project was access for on-farm use of alternative fumigation methods using ethyl formate based formulations.

The project commenced in July 2002. An extensive literature review covering more than 40 years of published results on the use of ethyl formate and natural products, such as botanical and active constituents, was completed. Fifty one candidate formulations which are mixtures of ethyl formate (60-95%, v/v) with other natural compounds (5-40%, v/v) were designed and tested. The stability, toxicity and phytotoxicity of each formulation were evaluated and completed in January 2004, three months ahead of the milestone. Two potential formulations, which are 95% ethyl formate + 5% MITC® and 95% ethyl formate + 5% AITC® were selected for further systematic laboratory studies. The results showed that 1) both ethyl formate and MITC or AITC are very stable in the formulation for more than two months storage at 25°C, 2) the formulations have no effect on seed germination and colour, and 3) 5% MITC or AITC can doubly increase the toxicity of ethyl formate to insects, particularly the difficult internal stages.

Both ethyl formate and MITC or AITC naturally occur in food, drinks and vegetables. Ethyl formate is currently used in dried fruit for insect control in Australia. There is no Maximum Residue Level (MRL) requirement for ethyl formate on grain and...
previous studies have shown that it has no effect on grain quality. Both MITC and AITC are present in brassica and oilseeds. MITC is used as a biofumigant for soil. AITC is a registered food additive. Current laboratory studies show that MITC and AITC are highly synergistic with ethyl formate with respect to the toxicity of broad insect pests. The new formulations have no effect on grain quality (this includes germination, residues and colour changes). Regarding dosage of ethyl formate (95%) + MITC or AITC (5%), if the formulation is applied at 80g/t of grain, it will contain 4g MITC or AITC per tonne of grain, that is equal to 4mg/kg (ppm). MITC and AITC convert into COS and a primary amine (both are naturally occurring substances) during storage. Two weeks after application, MITC and AITC were not detectable (<0.05mg/kg).

For ethyl formate + MITC or AITC formulations, bioassays, seed quality, formulation stability, phytotoxicity and residue analysis have been completed by 1) laboratory tests, 2) use of a 52kg grain cylinder; this test also included fumigant sorption, desorption, diffusion, penetration and different application methods, 3) one tonne bin trials at the Stored Grain Research Laboratory (SGRL) site, and 4) 40-100 tonne field trials at the SGRL site and Fisherman Island, QLD (Attachment). All results showed the new formulations have potential to replace carbon disulfide#, dichlorvos# and phosphine for on-farm storage inloading, in situ and outloading grain treatments. They also offer quick insect kill, residues which drop down to natural levels without aeration and are environmentally friendly. It is a very exciting result, that has been patented (International Patent Number: PCT/AU2005/000741) by CSIRO.

**Other research**
1. Generation of more data to cover more commodities for registration and extension of the use of the formulations.
2. Development of other formulations for broader fumigation purposes.

**Intellectual property summary**
2. Working with the GRDC to plan for registration and commercialisation of the new formulations.

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