RISE AND DEMISE OF CHEMICALS USED FOR AUSTRALIAN GRAIN PROTECTION WITH A FOCUS ON NEW SOUTH WALES

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Summary

Malathion is a key insecticide for the treatment of stored grain pests but its continued use patterns are under review by regulatory authorities. In this literature review, we reflect on grain storage protection issues in Australia but with a focus on New South Wales. Any grain stored for extended times is likely to become infested with storage insect pests. We review storage and export issues in early Australia and observe the challenges and changes created by two world wars, the depression and boom production years. Modern grain protection started with the use of malathion, however the detection of malathion resistance necessitated the introduction of other insecticide options. Fumigants were developed but these also suffered from the onset of resistance. The efficacy of insecticides and fumigants could be improved through combination with other gases or insecticides with different modes of action. Finally, we review the pesticides registered for grain insect pest control and speculate on prospects for grain protection.

Keywords: malathion, phosphine, ethyl formate, insecticides, fumigants, resistance,

INTRODUCTION

Export grain from Australia is a significant contributor to the country's economy; grain production in 2021/22 exceeded 60 million tonnes and AU $14 billion, with ~80% exported (ABS-ACA 2021/22). Currently, Australia enjoys a reputation for exporting "insect-free" grain, but this was not always the case. Waterhouse (1973) reported that insects infested stored grain that arrived with the First Fleet and no doubt that the early settlers tasted the added flavour of insect fragments and pheromone in their daily bread. It was simply accepted that if grain was stored for any length of time, then it became infested. Joseph Banks wrote on the Endeavour in 1769 on his way to Australia: *"Our bread indeed is but indifferent, occasioned by the quantity of vermin that are in it, I have often seen hundreds nay thousands shaken out of a single bisket"* (Waterhouse 1973). Many believed insects germinated spontaneously inside the grain. Winterbottom (1922) noted that "there were numbers of men who have been connected with the wheat trade all their lives who were adamant that every grain of wheat carries a weevil germ". This belief continued into the 1960s (Winterbottom 1922).

In New South Wales (NSW), the main grain pests were *Oryzaephilus surinamensis* (L.) sawtoothed grain beetle, *Tribolium castaneum* (Herbst) rust-red flour beetle, *Rhyzopertha dominica* (F.) lesser grain borer, *T. confusum* (Jacquelin du Val) flour beetle, *Sitophilus oryzae* (L.) rice weevil, and *Cryptolestes ferrugineus* (Stephens) rusty grain beetle (Greening 1969; Herron 1990; Wallbank 1996). Malathion became a cornerstone insecticide to treat these pests. However, currently malathion use patterns are under review by regulatory authorities and some existing use patterns may be withdrawn. Other insecticides such as bioresmethrin have entered the industry but been withdrawn (Daglish and Wallbank 2003). Therefore, it is timely to review stored grain treatments and the place that malathion has in that role. If malathion use patterns are restricted or withdrawn, our review with provide background information to develop a revised stored grain strategy into the future.

The research into the protection of grain has a long history in NSW and Australia. The Journal *General and Applied Entomology* (G&AE), published by The Entomological Society of New South Wales (NSW), has been an important contributor to applied entomology in Australia for 60 years (Volume 1 was published 1 July, 1964) (Greening 1969; Herron 1990; Wallbank 1996). In the intervening decades, GA&E papers covering applied entomology supporting Australian industry (eg Walters and Dominiak 1984; Holtkamp and Horwood 1991; Wallbank and Farrell 2002; Duric et al. 2022). G&AE became centred and managed by entomologists at the *Biological and Chemical Research Institute*, based at Rydalmere in western Sydney. Many of those entomologists, such as Barry Wallbank, Fred Attia, Howard Greening, Grant Herron, and their support staff contributed to grain treatment research. Similarly, many NSW scientists published papers in *The Agricultural Gazette of New South Wales.*

Additionally, during this period, the grain industry benefited from the CSIRO Division of Entomology's Research and Development. The Australian Grain Industry-CSIRO specialist laboratory, Stored Grain Research Laboratory (SGRL) (some 60 scientific and support staff), focussed on protection of grain from stored grain insect infestations (Wright and Morton 1995; Banks and Sharpe 1997; Wright 2003; Waterford et al. 2004). Currently, ongoing support continues with input from Grain Research and Development Corporation (GRDC), Queensland Department of Primary Industries (QDPI), New South Wales Department of Primary industries (NSW DPI), Murdoch University, chemical manufacturers, and grain industry specialists. Research has resulted in the use of many chemicals that played a part in the economic growth in the export and domestic grain markets. Here, we review some of the chemicals used in grain protection technology adopted by the Australia grain industry, with a focus on NSW.

HISTORY

Prior to 1914, most of Australia's two million tonnes of locally produced grain were consumed locally, and any for export was shipped soon after harvest, mostly to Britain. When the First World War broke out, shipping became difficult and Australia was forced to store grain in bags for years (Graver and Winks 1995). Previously, all marketable grain was exported as rapidly as possible and there was no provision for long term storage (Wilson 1953; Graver and Winks 1994). Winterbottom (1922) reported in the Wallaroo, South Australia yard alone, up to 1 tonne of weevils per day were gathered up and destroyed and he estimated a tonne contained over 1 billion insects. The second period of long-term storage of surplus grain was in the 1930's as a result of the depression (Anon 1958). The third period was during World War Two (WW2) when shipping services were diminished (Anon 1958). The peak occurred in 1942 when the carry-over stocks in Canada, USA, Australia and Argentina was equal to several years of export requirements (Druce 1950). The 1949-50 wheat crop was the second largest in NSW history resulting in longer term storage (Graham 1950). Another period occurred in 1957 when the carry-over stocks in USA, Canada and Australia was equivalent to the world export requirements for two years (Anon 1958). In essence, we see patterns where grain needs to be stored for long periods (years), and this raises challenges for protecting grain from storage insects.

As port storage facilities became full, farm storage became increasingly used. However, farm storages were of a lower quality compared to port facilities. Due to poor farm hygiene and poorer storage facilities, grain on-farm became infested and was responsible for subsequent infestations in central and port grain storages (Champ 1962). Regarding farm storage, producers used gravity feed units or spray equipment to apply insecticides to grain on conveyor belts or augers. The gravity feed systems were less costly (Minett *et al*. 1981). In an effort to combat resistant pests in farm storages, azamethiphos and mixtures of fenitrothion and carbaryl were effective treatments of concrete silo walls, and effective for six weeks (Wallbank 1982). Usually, infestations in bagged grain were distributed through most of the mass whereas infestations in bulk grain often was localised in the top layers (Champ 1963).

A wheat committee was established to consider the options which would combat weevils and other insects. These included heat treatment, poison gases, mechanical cleaning, treatment with carbon dioxide in gas-tight containers, lime treatment, sand treatment and underground storage. These are similar to some treatments that are considered today, but the ability to implement them was limited in the past. Nevertheless, in one year alone, approximately 1.7 million tonnes of grain was cleaned and sterilised. It was acknowledged then that the wheat could not be shipped "if infected with weevil" (Winterbottom 1922). Early experiments with poison gases including hydrogen cyanide and carbon disulphide failed, not surprising considering the difficulty of rendering a bag stack gastight. Additionally, the Wheat Committee sponsored experiments with controlled atmospheres. In 1918, the first silo was erected in Australia at Peak Hill, in the central west of NSW (Graver and Winks 1994). Despite grain being traded as bagged wheat into the 1960s (Winks and Ryan 1994), constructions of bulk silos proceeded at a rapid rate from 1918, only disrupted by the onset of the war years (Graver and Winks 1994).

Regarding long term storage of grain, turning of grain could lower the high temperatures caused by insect infestations, but did little to control the insects and, at worse, served to spread insects through a storage facility (Winks and Ryan 1994). Consequently, until the early 1960s, insects were an accepted component of stored grain. The only issue was whether or not their numbers reached levels that were "visible" or at which significant losses or heating/mould development occurred. Chemical treatments used during WW2 were not well documented. DDT and BHC were developed at the time (Champ 1963), and there is some evidence to suggest that after the war these insecticides were added in small quantities to mineral dust for mixing with grain (Winks and Ryan 1994). During WW2, carbon disulphide and hydrogen cyanide were used effectively to disinfect grain (Winks and Ryan 1994). Also, mixtures of ethylene dichloride and carbon tetrachloride were used (Winks and Ryan 1994). There was clearly an improvement in the methods employed to render structures gastight however it is unlikely whether they were of a standard that we now understand as gastight.

The 1949-50 wheat crop was the second largest in NSW history and seaboard storages and terminal elevators in Sydney and Newcastle became full (Graham 1950). Additionally, Britain was slow to import wheat, adding to storage woes and subsequently, the use of farm storage increased. In the 1950s, methyl bromide began to be used to disinfest both in central storage facilities and on-farms storages (Wilson 1953; Winks and Ryan 1994). Considerable and significant research into grain storage problems was undertaken during the war years (Graver and Winks 1994). There was additional funding for 19 new wheat silo storages in NSW to improve longer term storage and grain treatments (Graham 1950b).

In 1948, the Wheat Stabilisation Act created the Australian Wheat Board (AWB) as the only licenced marketer of wheat, leading to a centralisation and coordination of the industry. The AWB provided the vehicle for a centralised decision process to address the choice of pesticides; rate of application; and compliance with health and safety issues. Up until the late 1950s, Australia's principal market was Britain. It was not uncommon to receive reports of infested Australian grain. The importers did not penalise Australia and therefore, there was no specific incentive to improve. In 1958, Australia entered into a contract to sell wheat to mainland China (Graver and Winks 1994). The Chinese Authorities insisted that all shipments be accompanied by certificate stating that the grain should be inspected and that it should be "free on shipment from evidence of injurious diseases and from live insects / pests". In 1963, the federal Department of Primary Industries promulgated the Exports (Grain) Regulations which prohibited the export of grain from Australia unless it was found to be free from insect pests. (Winks and Ryan 1994).

Grain Protectants: and the *"golden age of Malathion"*.

Malathion was an insecticide which was developed after WW2 and was adopted in Australia in 1960/61 to protect wheat for export and domestic use (Watt 1962; Herron 1990; Wallbank 1996). Spraying the grain with liquid insecticides or grain protectant using malathion was trialled during the 1960/61 season (Hodgson 1961). By 1963/64, some 80% of grain shipped from Australia was treated with malathion. Most malathion was applied as grain was received into export terminals, and although the insecticide killed adults, immature stages continued to emerge during the 14-day voyage to China and other long-haul markets. Based on the life cycle of various species, a period of up to six weeks from application to shipment was needed to ensure that all insects present at the time of treatment had emerged and were killed. Clearly, the logical point of the spray application was as the grain was received into country storage. The industry very rapidly relocated their application to country receival points and so commenced the "golden age of malathion". Within the next year, complaints about insect infestations diminished to no more than several per year (Winks and Ryan 1994).

However, malathion resistance was detected in New South Wales (NSW) in 1968 (Greening 1970). The resistance could be managed with addition of the synergist triphenyl phosphate, which achieved complete mortality of malathion-resistant insects (Greening 1970). Resistance to malathion was due to its degradation by carboxyesterase, that can be inhibited by the addition of triphenyl phosphate (Dyte and Rowlands 1968). Dichlorvos was introduced in 1970 as the effectiveness of malathion declined but ultimately dichlorvos was recognised as a short-term solution to resistance (Graver and Winks 1994). Fenitrothion and bioresmethrin mixtures became available in the 1976-77 harvest and served the industry well for about 15 years (Bengston *et al*. 1977; Graver and Winks 1994). Wallbank (1982) found that azamethiphos controlled insects for six weeks and also was effective in completely treated silo cells for over 26 weeks.

Cognisant of the development of insect resistance, the AWB set up a committee to investigate Australia's ongoing technical requirements of the industry. In 1973, the Stored Grain Research Laboratory (SGRL) (located within CSIRO Division of Entomology, Canberra) was established. Using levies, the grain industry funded the SGRL and met annually to consider pest control issues and to plan pest control strategies for the coming season. From the outset of the malathion era, the question of residues was an important consideration and efforts were made to ensure the grain exported from Australia complied with the 8 ppm (malathion; mol. Wt. = 330g/mol) or $0.1g/m^3$ maximum residue-level (MRL). Soon, it was found that it was not always an easy task to meet this MRL or the nil residue standard. To cope with the multiple treatments from the farm onwards, handling authorities needed to supplement their application technology with residue analysis. The ability to control export grain residue levels using analytical laboratories was demonstrated by the WA (Western Australia) Co-operative Bulk Handling Ltd, which led to the National Residue Survey (NRS). NRS operates within the Australian Government Department of Agriculture, Water and the Environment (DAWE), and since 1992 has been funded by industries through levies and direct contracts. NRS residue monitoring programs monitor the levels of, and associated risks from, pesticides and veterinary medicine residues and contaminants in Australian food products.

Malathion protected grain for up to nine months (Anon. 1969) and it was often necessary to disinfect infested grain with other chemicals such as methyl bromide, phosphine, and with hydrogen cyanide in WA (Winks and Bailey 1965). Other chemicals were used to treat surfaces of storage facilities where typically infestations were localised (Champ 1963). Prior to malathion, the most prevalent species in Australian wheat were *T. castaneum* and *S. oryzae*. In 1968, resistance was detected in *T. castaneum* in peanuts, then subsequently in *S. oryzae* from wheat. In 1972, *R. dominica* was by far the most tolerant species to malathion and doses were set to control this species. This *R. dominica* domination was presumeably due to its tolerance to malathion. Grain protectants continue to be needed (exception is WA where a large proportion of grain is delivered directly to port facilities) and are a part of the implementation plan in most states (Winks and Ryan 1994). Protectants are an alternative use especially where gastight storage is not available and where there is an outbreak of insects resistant to alternative chemistry.

WA was able to meet the increasing demand for low or residue-free grain during the late 1980s using fumigants. Up to 1994, no grain protectants were used by WA Cooperative Bulk Handling Ltd (Winks and Ryan 1994). Other states were not so fortunate because few of their storages were sealed and the move to reduce the use of grain protectants during the late 1980s posed significant problems. Progressively over the years, it became necessary to introduce other grain protectants and mixtures of new/existing protectants. For example, a bioresmethrin plus fenitrothion mixture served the industry well over 15 years (Winks and Ryan 1994). Mixtures of fenitrothion and carbaryl controlled *R. dominica* on localised areas for six weeks but provided variable effectiveness against other species (Wallbank 1982). Other chemicals used included malathion, dichlorvos, bioresmethrin, carbaryl, diazinon, pyrethrins (+ piperonyl butoxide – a synergist often used with pyrethroids) (Winks and Ryan 1994). Bioresmethrin was withdrawn from the market in the early 2000's after years of use in Australia (Daglish and Wallbank 2003). Bifenthrin was seen as part of a combined treatment and was effective against a range of grain insects except against pyrethroid-resistant insects (Daglish and Wallbank 2003). Bifenthrin, combined with piperonyl butoxide and chlorpyrifos-methyl, was effective against most grain pests for about seven months. This combination was not effective against species resistant to organophosphates and bioresmethrin (Daglish *et al*. 2003). Magnesite (magnesium carbonate) could protect stockfeed oats for up to two years when applied to oats at >10% moisture (Wallbank *et al.* 2001).

Because of widespread insect resistance, mixtures of current grain protectants were recommended together with rotations over time. The current recommended best practice for protectants is to use mixtures (*below*) and rotate every one or two years, e.g.:

*Spinosad + S-methoprene + **EITHER** chlorpyriphos-methyl **OR** fenitrothion **OR** pirimiphos-methyl*

OR

*Deltamethrin (+Piperonyl Butoxide) + **EITHER** chlorpyriphos-methyl **OR** fenitrothion **OR** pirimiphos-methyl*

OR

*Deltamethrin (+Piperonyl Butoxide.) + S-methoprene + **EITHER** chlorpyriphos-methyl **OR** fenitrothion **OR** pirimiphos-methyl*

Fumigants

Concerns about grain protectant residues and insect resistance issues led to the widespread use of fumigants. Candidate chemicals for fumigant selection need to be either gases or volatile liquids to meet the requirements of uniform distribution in the storage unit to be treated and achieve subsequent effective aeration to ensure efficacy and residue-free status. Effective fumigation depends upon the availability of sealed storage which can reach the required C x t (Concentration x exposure time). In the early 1970's, the SGRL developed the specification for sealing storages to a standard suitable for the effective fumigation (Winks and Ryan 1994); a silo is only deemed truly sealed if it passes a five-minute half-life pressure test according to the Australian Standard: AS 2628 (2010) "Sealed grain storage silos – Sealing requirements for insect control". In the early 1980s, WA commenced sealing their many sheds for effective and cheap fumigation with phosphine gas (Winks and Ryan 1994). WA was able to meet the increasing demand for residue-free grain since the late 1980s because of the decision of WA Cooperative Bulk Handling Ltd to forego grain protectants for fumigants.

Fumigants - Methyl Bromide

Pre-2005, methyl bromide (MBr) (CH_3Br) was the universal fumigant used extensively in agriculture, horticulture, soil, cut timber, logs etc. However, MBr became recognised as an ozone depleting gas and its use should be minimised. The Vienna Convention was adopted in 1985 with the intention to reduce the adverse effects of MBr in the ozone layer. Subsequently, the Montreal Protocol was signed as an international agreement in 1987 (DEP 2023). The Montreal protocol on substances that deplete the ozone layer required a phase out of MBr for applications other than quarantine and pre-shipment purposes (QPS) by January 2005. There were issues with QPS especially the amount used which is a high percentage of the former global methyl bromide consumption. Also, there were WHS concerns for local communities especially with fumigations conducted in urban areas. In keeping with the reduction of MBr use, Williams (1985) found that MBr application could be halved in an atmosphere containing >20% carbon dioxide. MBr toxicity was not reduced in the absence of oxygen although oxygen concentration influenced other fumigants such as hydrogen cyanide and ethylene dibromide (Bond *et al.* 1967). Eventually, the Montreal protocol was successful as it resulted in the replacement of a large number of chemicals that deplete the ozone layer. Specifically for MBr, its large use in soil fumigation was discontinued (DEP 2023).

Fumigants - Phosphine

The fumigants of choice were phosphine (PH_3) and MBr. PH_3 is a naturally occurring gas and is the fumigant of choice for stored products pests. PH_3 is short lived because it reacts with the atmosphere forming phosphoric acid (Fluck 1973) which is an acid used extensively as a food additive. The "solid" metallic phosphide tablets, formulated to release phosphine by reacting with moisture in atmospheric air, was patented in 1935. Phosphine has many of the properties desirable for a fumigant (e.g. high penetrant ability, low sorption on foodstuffs, very low residues, short lived). However, phosphine has a major disadvantage: it is highly flammable and explosive in mixtures with air.

The first gaseous PH_3 formulation in industrial gas cylinders was patented as a non-flammable mixture of 2wt% PH_3 in carbon dioxide (CO_2) which allowed the safe rapid dispensing of the PH_3 into the grain storage being fumigated (Ryan and Latif 1989). Early applications of high-pressure industrial gas cylinders containing a non-flammable gaseous PH_3/CO_2 mixture were successfully completed in gastight horizontal bulk grain storages up to 30,000t in WA using 0.3g PH_3 per tonne (Ryan 1988). Treatments, using gaseous PH_3 with CO_2 plus heat in USA (Mueller 1994), achieved successful fumigations in large silos and flour mills. Noting that effective fumigation depends upon concentration x exposure time (C x t) facilitated by a sealed storage environment, CO_2 aids the movement of PH_3 through commodities and the addition of heat lowers the effective dose of PH_3 required for a lethal C x t product (Zettler 1997). Recirculation of PH_3 improved by Cook (1984) included the closed-loop system (Noyes and Kenkel 1994). These technologies reduced the dosage of PH_3 required to produce a lethal C x t product in grain pests and thus improved the efficiency of conventional types of PH_3 fumigations (Zettler 1997). The CSIRO patented flow-through fumigation (SIROFLO – see below) provided a method for fumigating grain in leaky storage, resulting in many old silos being used for storage without reliance on grain protectants (Winks 1993; Graver and Winks 1994).

An additional patent for on-site mixing of pure phosphine (99% PH_3) with air had advantages of lower costs and reduction in the number of gas cylinders required (Ryan and Shore 2005). Both high pressure gaseous PH_3 cylinder products (2% premix and 99% on-site mixed) compete with the "solid products" because of their shorter exposure time (quick mixing), no spent/unreacted residues requiring disposal and the ability to simply "top-up" PH_3 to maintain the concentration. The concept of on-site mixing of PH_3 with ambient air was adopted by the grain industry

(Ryan and Shore 2005). The mixer is available in a range of sizes covering the treatment of small low flow (SIROFLO®) to large "bunker / pad" bulk storages and currently these units are being globally adopted (Shore, private communication).

Gaseous PH_3 has a long history as a dopant in electronic silicon chip technology manufacture, but initially, it was investigated as a fumigant for the control of fruit fly in mid 1970s (Ryan 1990). The fumigation grade PH_3 (99%) is of lower purity than electronic grade PH_3, however there are critical specifications for impurities such as di-phosphine (P_2H_4) and white phosphorus (P_4) which are pyrophoric (Gallagher *et al.* 1991). On-site mixing of PH_3 (99%) with air to less than 16,000 ppm (2.2g/m^3) (Ryan and Shore 2005) or premix with inert gases overcame flammability issues. Gaseous PH_3 mixtures have benefits over the solid metal phosphide formulations since they eliminate the PH_3 flammability hazard, allow accurate control of PH_3 concentration, deliver PH_3 gas more rapidly, achieve better distribution in the grain mass without disturbing grain, allow controlled flow and dosage maintenance for long periods. Gaseous PH_3 eliminates handling and disposal of the "spent" metallic phosphide tablets but it reacts with oxygen to produce a polymer. This reaction and polymers were issues in dispensing equipment and required pre- & post-purging of gaseous PH_3 dispensing systems with an inert gas. The polymer dust and associated oily phosphoric acid effects gas flow-control equipment (Schonstein *et al.* 1994.).

Flow-Through Fumigation (120 ppm** (0.17g/m^3) **PH_3)

Many grain storages fail to meet the specified standards of gas tightness for PH_3 application (Winks 1987). However, with appropriate modifications to the silo, flow-through technologies such as SIROFLO® (Winks 1993) or other systems using gaseous PH_3 can be used (Bell *et al.* 1993). In flow-through fumigation, a continuous airflow containing a low PH_3 concentration (~120ppm) (0.17g/m^3) is dispensed for an extended time of 3-4 weeks (Ryan 1997). The technique is effective because insect eggs and pupae, which are naturally tolerant to PH_3, continue to develop to larvae and adults while the bulk is still under fumigation (Winks and Ryan 1990). This flow through technique provides a method for fumigating grain in leaky storage and has resulted in many old silos being used for storage again and has enabled grain handlers to decrease their reliance on protectants in eastern Australia (Collins 2010).

Variables (PH_3; O_2; CO_2)

A unique characteristic of PH_3 is that it is not absorbed in the absence of oxygen, and in anaerobic environments is not toxic to insects (Bond *et al.* 1967). Kashi and Bond (1975) found that, in the presence of 4% CO_2, there was a 20% increase in the uptake of oxygen and a 3-fold increase in the toxicity of PH_3 to insects. The action of PH_3 is potentiated by carbon dioxide and the concentration and exposure time can be reduced when both CO_2 and O_2 are present. The optimum CO_2 concentration is in the range of 5-35%. At 5% CO_2, the PH_3 dose for LC_{90} efficacy can be reduced by ~50% (Kashi and Bond 1975).

Insect Resistance (PH_3)

Attia and Greening (1981) found low levels of PH_3 resistance in three grain pests in NSW in 1968-80. By 2003, PH_3 was used to disinfest about 80% of Australian grain compared to grain protectants (about 20%) (Emery et al. 2003). PH_3 was attractive to the Australian grain industry because it was easy to apply, versatile, inexpensive and well accepted internationally (Emery *et al.* 2023). However, fumigation in leaky structures results in a serious reduction in exposure time, with an increased likelihood of the development of resistance (Tyler *et al.* 1983). Since the early 1990's, the major focus in the grains industry was the monitoring of PH_3 resistance development. Research has established three levels of resistance to PH_3 ('weak', 'strong' and 'very strong'). It was suggested that once the frequency of 'weak' resistance reaches about 80% in a population, then there is a strong possibility of developing strong resistance in that species (Collins and Emery 2002). Weak resistance was considered controllable if phosphine was correctly applied (Emery *et al.* 2003). The incidence of weak resistance has grown since 1982 and strong resistance since 1997 (Emery *et al.* 2003). Where insects with strong resistance were detected, they could be eradicated if corrective measures were applied immediately before the infested bulk was moved to further sites or placed onto the market (Emery *et al.* 2003). Newman *et al.* (2004) found that many Australian farm storages did not retain PH_3 levels for the required time to be effective. They highlighted the need to maintain rubber seals in good condition to maintain the gas-tightness of fumigated storage vessels. These measures included moving the infested grain to another silo and treating with an effective grain protectant (Emery *et al.* 2003).

Furthermore, empty bins should be treated with a residual pesticide such as azamethifos (Wallbank and Farrell 2002; Emery *et al.* 2003). Collins (2010) considered that the evolution of strong resistance in *C. ferrugineus* was the greatest challenge facing the Australian grain industry since this resistance is several times greater than in any other species.

Sulfuryl fluoride (SF)

Sulfuryl fluoride (SF) is a broad-spectrum fumigant and has been a fumigant gas for over 60 years. Initially, SF was marketed as Vikane® (Dow Chemical Company) as an effective methyl bromide (MBr) alternative for structural fumigations. It was used to fumigate houses to halt damage to properties by drywood termites, wood-destroying and structure-infesting pests, including bed bugs and rodents. Frequently, MBr was used to control drywood termites but came with the disadvantage that it could react with wool, leather, foam rubber or other sulphur-containing materials to produce lingering malodorous compounds.

In 2004 with additional stored grain product claims, a food-grade SF was registered as a pesticide in the USA and is now marketed globally, including in Australia, as ProFume®. In the interim, there were additional registered SF products available. SF is used in the management of strongly PH_3 resistant *C. ferrugineus* populations in bulk grain. The SF has proven to be successful as a 'resistance breaker' where phosphine resistance is prevalent. Approved label dose for stored product pest fumigations is a maximum of 1500 $g.h/m^3$ CTP – not to exceed a maximum concentration of 128 g/m^3.

Ethyl Formate (EF)

EF is an historical fumigant (Ryan and De Lima 2012) now making a comeback. EF was used as fumigant to disinfest dry fruits and has a history of safe use as a food additive. EF is an effective bulk grain fumigant with sorption issues being accommodated by rapid dispensing. The lower toxicity EF usually requires relatively high dosage ($70g/m^3$) than other fumigants however its predominant attribute, similar to MBr, is short exposure times i.e. hours not days. EF can be used at a much lower temperatures compared to most other fumigants. EF controlled 78 insect species, albeit at different rates or exposure times, or in combination with other gases (Ryan and Dominiak 2021). These insects included five weevils, six aphids, six thrips, seven moths, 18 scale and mealy bugs, and ten beetles. Additionally, the brown marmorated stink bug (*Halyomorpha halys* (Stal)), Khapra beetle *Trogoderma granarium* (Everts), tomato potato psyllid (*Bactericera cockerelli* (Sulc), tramp ants and other biosecurity threats are good candidates for EF fumigation (Ryan and Dominiak 2021).

Therefore, EF application needs to be applied to current fumigation hot spots within grain storages. Currently, there is continuing pressures on fumigants due to registration requirements, atmospheric emissions controls, concerns surrounding operator safety and human health, and the incidence of resistance. These changes are occurring as the world expects increasingly high standards of pest control in international trade (Bell 1993). The in-transit fumigation of shipping containers conducted using a non-flammable mixture of $90g/m^3$ EF in nitrogen, allows travel from Perth to Barrow Island (>2000 km) while fumigating full container loads of food and equipment. The EF in transit fumigation, Fume8 Technology, uses an onsite nitrogen generator or nitrogen bottles with liquid EF to produce a safe, cost effective, fast acting and environmentally friendly gas fumigant (Coetzee 2020).

EF was approved for the quarantine fumigation of containers in New Zealand (NZ) against brown marmorated stink bug *H. halys* (NZ Ministry for Primary Industries, 2023). NZ Biosecurity specify the treatment must achieve the C x t product ($>142g.h/m^3$), minimum concentrations endpoints (EF = $19.5g/m^3$ & CO_2 = 3%), and temperature (>10ºC). Additionally, this approval includes Yellow Spotted Stink Bug (*Erthesina fullo* (Thunberg)), ants and spiders. (Approved Biosecurity Treatments, MPI-ABTRT, 8 June 2023).

We propose that the registrations of EF have not kept pace with recent research due to the existing preference for other fumigants. However, there is an increasing number of plant biosecurity incursions (Anderson *et al.* 2017) and there is a need to ensure registered uses are current to optimise biosecurity needs in Australia.

Resistance continues to develop

Resistance to insecticides and fumigants is a long-standing issue for grain storage. Ideally, grain should be removed from all equipment immediately after harvest has been completed (Greening 1969). For optimal storage, grain should be fully matured and not contain excessive moisture which favours insect infestation (Anon. 1969). Unfortunately, in a survey of 15 farms, Greening (1969) found insect pests in 14 farms reflecting inadequate cleaning and a lack of attention to detail in the clean-down of machinery. Attia (1981) reported insecticide resistance (to malathion, DDT and dieldrin) in moths of grain and stored products. Shortly afterwards, Attia and Frecker (1984) reported low levels of resistance (<10-fold) to DDT, dichlorvos, chlorpyifos-methyl, bioresmethrin and pyrethrins and moderate resistance (<40-fold) to lindane, malathion and pirimiphos methyl. They found synergistic resistance between several insecticides including malathion, fenitrothion and fenitrooxon. There were high levels of resistance (>160-fold) to fenitrothion (Attia and Frecker 1984).

Herron (1990) tested for resistance in bioresmethrin, carbaryl, chlorpyrifos-methyl, fenitrothion, malathion, phosphine and pirimiphos-methyl; resistance levels with as high as 70% to pirimiphos-methyl in one species. Low level phosphine resistance and malathion resistance was detected in all species. Carbaryl and bioresmethrin were used to control multi-organophosphate resistant insects and no resistance was detected. Chlorpyrifos-methyl was used successfully in NSW to control fenitrothion resistant insects despite some levels of resistance to chlorpyrifos methyl (Herron 1990). Resistance to fenitrophion was detected in 50% of tested populations with resistance up to 68-fold. Additionally, Herron (1990) detected resistance to chlorpyrifos-methyl and pirimiphos-methy in 39% and 70% of tested populations with a maximum resistance factor of 8.4 and 44.2 respectively. In subsequent testing, Wallbank (1996) found resistance to fenitrothion was detected in 95% of populations tested with resistance up to 85-fold. Wallbank (1996) detected resistance to pirimiphos-methyl in 95% of tested samples with up to 55-fold resistance. There was resistance to chlorpyrifos-methyl in 67% of tested populations with resistance up to 32-fold (Wallbank 1996). Additionally, 75% of tested populations were resistant to all three insecticides. Combination treatments with different pesticide groups, and different modes of action, was considered to slow the development of resistance to any single insecticide (Daglish *et al.* 2003).

Poor farm practices were a contributor to resistance development (Wallbank 1996). Additionally, the storage of grain beyond the recommended maximum storage period for a given pesticide is conducive to resistance development (Wallbank 1996). Storage units need to be gas tight to minimise the development of resistance to fumigants (Winks and Ryan 1994), and this was not always achieved or possible.

Residues

In the 1980's, pesticide residues gained prominence and became part of quality demands by importers (Graver and Winks 1994). Additionally, Australian flour millers set lower residue limits to ensure compliance with maximum residue limits (MRL) (Graver and Winks 1994). Incorrect use of protectants was one cause of MRL breaches. This was exacerbated in structures that were not gastight (Graver and Winks 1994). The use of SIROFLO® applications enabled industry to meet the increasing demand for low-residue grain (Winks 1993; Graver and Winks 1994). Despite the effectiveness of SIROFLO® technology, grain protectants continue to be used by industry and are expected to be used for some time to come, even with looming insect resistance/tolerance and pesticide residue issues.

Current registrations and pesticide reviews

Currently, amorphous silica, betacyfluthrin, carboxin, chloropicrin, chlorpyrifos-methyl, diatomaceous earth, diazinon, dichlorvos, EF, fenitrothion, malathion, MBr, PH_3 (mostly from aluminium phosphide), pirimiphos-methyl, SF, and methoprene are all registered for stored grain use (APVMA 2023). However, the volumes used vary depending on local preferences.

Most pesticides are reviewed periodically for occupational exposure, efficacy, environmental fate and other reasons. Currently, malathion is under review by the APVMA (Australian Pesticides and Veterinary Medicines Authority), however the review focuses on field crop applications (APVMA 2023). Fenitrothion active constituents, chemical products and labels were nominated for review in response to an invitation to the public made by the APVMA (then the NRA) on 1 November 1994. Eighty of the nominated chemicals, including fenitrothion, were included in the priority candidate review list published in the Gazette on 2 May 1995. In March 2004, the APVMA released the fenitrothion draft review report and publication of the proposed regulatory decision is expected in April 2024 (APVMA 2023).

DISCUSSION

Grain protectants are still used by the industry and will continue to be used for some time to come. To achieve totally pesticide-free storage systems, disinfestation must be conducted by fumigation in certified sealed storages to maintain adequate concentration of fumigant for the desired exposure time prior to ventilation. That is, there should be investment into sealed storages similar to the investment initiated by WA Cooperative Bulk Handling, 40 years ago (Barry 1984).

We speculate that phosphine is likely to continue to dominate grain fumigants over the foreseeable future. However, there are several other alternative fumigants available and utilised by industry. Alternative fumigants include: hydrogen cyanide, EF, cyanogen (EDN) and carbonyl sulphide. However, a great deal of work remains to be done on potential new pesticides before candidate products seek registration for commercial use.

Phosphine satisfies residue considerations and in this regard is not considered a major human health threat when used correctly. However in the context of efficacy, resistance has been recorded since the mid-1960s. Recently, very high levels of resistance were identified and a "resistance break" strategy using a program of alternative fumigants was employed to combat resistant populations.

In addition to alternative fumigants, other options include controlled atmosphere storage using either carbon dioxide or low oxygen atmospheres, currently utilised by niche fumigation of organic grain and food products. The CSIRO division of entomology showed that aeration has a place in the storage of grain in Australia at least in the southern States where suitable ambient conditions were available. Grain aeration can reduce grain temperature to less than 15ºC which ensures that any insects are moribund i.e. no population increase until temperature is elevated which ensures static population growth albeit for the cold months (GRDC 2021).

All levels of the grain storage industry need to be aware of storage pests and to use existing pesticides optimally to minimise and combat the development of resistance. The results of the APVMA review of the malathion use patterns will determine if malathion can continue to be used in much the same way as it currently is. If malathion use patterns are restricted, the grain protection industry will be obligated to re-configure the available pesticides used or develop other management techniques. Any reduction in malathion use patterns is likely to increase the resistance pressure on the remaining pesticides.

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