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Use of fumigation for managing grain quality

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Abstract

Purpose of the review: Fumigation is a vital tool for grain protection against insect and mite pests and quality maintenance. Methyl bromide and phosphine, the principal fumigants, have been facing threats on environmental (ozone depletion) and biological (insect resistance) grounds, respectively. Hence, there have been major developments on the judicious use of phosphine and intensive search on alternative fumigants for grain protection. Recent advances on fumigation for managing grain quality are reviewed in this paper.

Main findings: Due to increased tolerance and development of resistance by stored grain insects, the target concentration of phosphine for effective treatment of grains has been increased (eg, 1,000 ppm for a 7-day treatment). To serve the dual purpose of preventing grain contamination with residual aluminium phosphide and for controlling phosphine-resistant insects, techniques for direct application of gaseous phosphine from cylinder and on-site generator sources have been developed. Rapid penetration into commodities, low to moderate level of sorption by food grains and quick aeration after the treatment have been demonstrated as the favourable properties of sulphuryl fluoride, a new grain fumigant. Reports on the effect of carbonyl sulphide, a promising alternative fumigant, on grain quality (eg, germination and tainting) are conflicting. Improved methods to apply ethyl formate alone and in mixture with CO_2, have been developed. Ethyl formate appears to be a promising fumigant for on-farm storage and space treatments, while ethane dinitrile has shown promise as a devitalising agent for grains.

Directions for future research: Intensive studies are required to exploit natural plant products for grain fumigation. Studies are also necessary to optimise ethyl formate application techniques for on-farm storage. Efficacy of new fumigants against mites in stored grain needs attention. Furthermore, there is a need to ensure quality supply of the fumigants as the impurities present have been noted to be harmful to the produce.

Keywords: fumigation; stored grains; insect control; grain quality

Abbreviations

CT	Concentration Time
HLT	Half-loss Time
QPS	Quarantine and Pre-shipment

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Introduction

Although grain quality has different meanings to different people (producer, trader, store manager and consumer), it generally refers to the physical condition (eg, appearance, kernel size, test weight, presence or absence of insect/ mould/heat damaged grains, immature as well as discoloured grains, dockage, insect pests and pesticide residues) and chemical composition (starch, protein, oil, fibre and mineral contents) of the grain. Quality parameters vary depending on the intended use, ie, food, feed and seed purposes. During storage, grain quality is likely to deteriorate due to environmental (eg, temperature) and biotic factors (pests). Pests include insects and mites among invertebrates, birds and rodents among vertebrates, and microorganisms such as fungi, yeast and bacteria. Among the pests, insects cause depredation of grains to the largest extent. In addition to direct contamination with their fragments, exoskeleton

Table 1. Salient features of present and promising grain fumigants.

Feature	Phosphine	Methyl bromide	Sulphuryl fluoride	Ethyl formate	Carbonyl sulphide	Ozone	Ethane dinitrile
Vapour pressure (mm Hg at 25ºC)	29,260	1,824	13,442	200	9,400	>760 (at 38ºC)	3,600
Flammability (%v/v)	1.8	10–16	Nonflammable	2.8–16.5	11.9–28.5	Nonflammable	6.6–42.6
Water solubility (g/L)	0.35	13.4	0.75	14.5	1.4	1.0	4.5%
TLV-TWA (ppm)*	0.3	5	5	100	10	0.1	10
Tolerant insect stage#	Egg and pupa	Pupa	Egg	Pupa	Egg	All internal stages	Egg
Target concentration time (g h/m^3) or concentration (g/m^3) at 25°C	0.28 g/m^3	3 g/m^3	1,500 g h/m^3	170 g/tonne@	1,950 g h/m^3	No data	13,800 g h/m^3
Minimum temperature for insect toxicity (°C)	15	10	10	15	5	No data	15

*Threshold limit value-Time weighted average concentration. # Excluding diapausing larvae. @Effective dose.

and excreta, insect pests have a role in the dissemination of the pathogenic microbial agents responsible for mycotoxins in grains. They also cause changes in chemical composition, nutritional quality and end use products in food and feed grains [1**]. The presence of live insects and insect damaged grains, therefore, downgrades grain quality resulting in delivery rejections. In industrialised countries like Canada and Australia, there is zero tolerance for detectable insects in stored grain. In view of the advances in detection techniques for pests as well as pest contaminants in food grains and due to international agreements and phytosanitary regulations, in recent times, there has been an increase in quality parameters in the grain market [2].

To maintain grain quality by controlling insect pests, fumigants are applied at various stages, ie, on-farm storage, bulk storage (silos and elevators) and during transport (railcars, shipping containers and ship-holds). At present, phosphine and methyl bromide are the principal fumigants deployed for grain protection. Sulphuryl fluoride, a structural fumigant for dry wood termite and woodborer control, has been recently added to the list [3**]. Methyl bromide has been identified as an ozone depleting substance and as per the Montreal Protocol the fumigant is being phased out globally [4**]. Insect resistance to phosphine is an impediment to its effective use for grain protection [5]. Therefore, new compounds such as carbonyl sulphide, ozone and ethane dinitrile have been investigated as alternatives. Moreover, there has been reappraisal of old fumigants such as ethyl formate and carbon disulphide for grain protection [6**–8]. There have also been several changes in the application of currently used phosphine and extensive studies on alternative fumigants. The objective of the present review is to focus on the recent developments with regard to present and future fumigants for grain protection, their problems and the future directions for their effective use.

Current fumigants

Phosphine

Phosphine is widely used for grain protection because it is cheap, simple to apply and has little effect on grain quality. In view of the phase out of methyl bromide, the role of phosphine in grain protection has increased in recent times. Although its vapour pressure is higher than any other fumigant (Table 1), it is slow acting and requires more than 5 days at temperatures ≥15ºC for effective treatment. Insect eggs are the most tolerant stage to phosphine treatment and in some insects (eg, the psocids, *Liposcelis bostrychophila*) a delay in hatching of eggs for up to 6–9 days in treatments at 30ºC has been noted [9]. Phosphine is effective against mites (*Acorus siro*) in wheat at a dose of 2–3 g/m^3 for 6 days at 10ºC [10]. It also inhibits mould growth and mycotoxin production for a short while only and has no effect on fungal spores [11**]. Although phosphine is considered simple to use, there is ambiguity with regard to its dose, exposure period and target concentration. The recommended dose varies from 0.5 to 5 g/m^3 and the exposure period from 3 to 30 days depending on the temperature, pest type and its resistance status [12, 13].

Food grains, except paddy rice, showed low-level phosphine sorption [14**]. Phosphine caused quality changes in end-use products only when the grain moisture was high (>15%) or in

Table 2. Effects of new fumigants on grain quality.

Parameter	Sulphuryl fluoride	Ethyl formate	Carbonyl sulphide	Ozone	Ethane dinitrile
Sorption	Very low	High	Moderate	No data	No data
Off-odour	No effect	No effect	Taints?	No effect	No data
Chemical composition	No effect	No effect	No effect	No effect	No data
End-use products	No effect	No effect	Affects?	No effect	No data
Germinability	No effect	No effect	Affects?	No effect	Affects
Residue type	Sulphuryl fluoride and fluoride ion	Ethyl formate	Carbonyl sulphide	Not applicable	Hydrogen cyanide

repeated fumigations [15]. When grain stored in silos is treated by admixture with aluminium phosphide tablets, the occurrence of unspent aluminium phosphide residues is a concern [16]. The spent tablet powder could release 0.17 g of phosphine at a slow rate only in 10% acid solution at temperatures >24^{o}C. No phosphine was released from spent tablet residues by wet deactivation using a water-detergent mixture [17]. In addition to chemical cost, unreacted aluminium phosphide residues add to safety hazards to food and feed grains and the environment.

Insect resistance to phosphine is an important issue for effective grain treatment. In view of this, the target concentration of phosphine for effective treatment has increased from 100 ppm to 1,000 ppm in 7-day treatment of food grains [7, 14**]. For quick and even distribution of phosphine throughout the grain mass and to avoid grain contamination with unreacted aluminium phosphide residues, direct application with gaseous phosphine from cylinder sources, ie, VAPOR-PH_3OS® (100% phosphine) and ECO_2FUME® (2% phosphine in CO_2) and on-site generators, have been developed in recent times. Special phosphine generating formulations for application in specific situations (eg, QuickPHlo-R™ and QuickPHlo-C™) have also been developed [18]. Furthermore, specialised phosphine application techniques such as SIROFLO® (continuous low flow of phosphine), SIROCIRC® (controlled low flow recirculation of phosphine) and SIROFUME® (an automated topping up process) in Australia [5] and closed loop fumigation system in the USA [19] have been demonstrated. However, these systems require expertise in application and expensive infrastructure facilities. Alternatively, split application of aluminium phosphide tablets for grain disinfestation resulted in higher concentration-time (CT) products achieving total mortality of insects [20]. The tablets could also be dispensed in such a way (by putting them into perforated polyethylene pouches) that they released phosphine at a slow rate for longer period for effective control of mites in grain [21].

Methyl bromide

Methyl bromide, a broad-spectrum and fast acting fumigant, has been used for grain treatment for more than 50 years. Food grains are effectively disinfested in a short period of 24–48 h at a dose of 24–80 g/m^3. Repetitive treatments and fumigation at higher doses lead to malodour problems and unacceptably high residues in exposed commodities. In view of its phase-out schedule under the Montreal Protocol, the use of methyl bromide for stored grain protection has been reduced substantially. Currently, methyl bromide is applied for quarantine and pre-shipment (QPS) treatments, emergency and certain critical uses [4**]. To avoid environmental contamination during ventilation of methyl bromide-treated commodities, techniques have been developed to recapture released methyl bromide using activated charcoal. These techniques, however, are expensive and have not been adopted much since recapture and emissions reductions have not been made compulsory by regulatory bodies at present [4**].

Sulphuryl fluoride

Sulphuryl fluoride, an inorganic gas, has been recently registered for use on food commodities or in food facilities in Canada, the USA and European countries [3**]. The egg stage of insects is highly tolerant to sulphuryl fluoride [22**]. Recent studies have shown that this problem could be solved by extending the exposure period to 48 h and by increasing the treatment temperature to >20°C [23**]. Sulphuryl fluoride affects the growth of fungi but does not kill the spores [24**]. For efficient use of sulphuryl fluoride (ProFume®), there is software called Fumiguide™ that takes into account the target pests, treatment temperature, half-loss time (HLT) and exposure period [25].

The major advantages of sulphuryl fluoride are high penetrability, low sorption by food commodities and least effect on treated commodities [23**, 26] (Table 2). The United States Environmental Protection Agency has established tolerance limits of sulphuryl fluoride residues in food commodities

[27]. However, there are controversies about the use of sulphuryl fluoride for food commodities and about high maximum residue levels of fluorides [28]. In a 24 h exposure to sulphuryl fluoride at a dose of 50 g/m^3, the fluoride residues in cereal grains ranged from 0.9 to 2.2 ppm and the fumigant did not affect germination of grains [29**]. Reuss *et al.* noted that sulphuryl fluoride has negligible effects on the dormancy breakage capacity of barley [30].

Promising fumigants

Ethyl formate

Ethyl formate, a liquid fumigant with a pleasant aroma, has been extensively studied as a fumigant for food commodities in India [31**]. Subsequently, studies were pursued in Australia particularly for on-farm storage [32]. The compound is naturally present at low levels (0.05–1 ppm) in certain fruits, vegetables, cheese, fish, meat and wine. The fumigant breaks down to naturally occurring formic acid and ethanol. Therefore, ethyl formate is "generally regarded as safe" and the acceptable daily intake is 3 mg/kg body weight/day. Ethyl formate is rapidly toxic to insect pests. However, due to its high water solubility, the fumigant is absorbed heavily by food grains (Table 2). To avoid excessive sorption and for quick and even distribution of the fumigant, a fan or blower has to be used during treatment [33]. Ethyl formate is flammable at levels of 2.8–16.5% (v/v) (Table 1); the flammability risk during fumigation, however, could be overcome by applying the fumigant at split doses (80 + 80 g/tonne) with a 4 h interval. To solve the problems of high sorption and flammability risk, a cylinderised formulation, "VAPORMATE™", containing 16.7% ethyl formate by weight in liquid CO_2 has been registered in Australia [34]. Recently, another formulation containing ethyl formate and allyl isothiocyanate (95:5), which is thought to have synergistic effect on insects as well as microbial organisms, has been developed [35].

Ethyl formate (VAPORMATE™) at a dose of 19–23 g/m^3 for 48 h at 24–28°C does not affect germination of seeds (barley, wheat and sorghum) [36]. It is likely to play a significant role in grain protection at the farm level as a substitute for phosphine, as the latter is difficult to contain in traditional farm storage in developing countries and in unsealed metal silos in developed countries.

Carbonyl sulphide

Carbonyl sulphide, an industrial gas, has been patented as a fumigant for food grains and other commodities and is likely to be registered in Australia soon. It is naturally present in marshes, oceans and volcanoes and is also present in certain foodstuffs at low concentrations (<1 ppm). Carbonyl sulphide is toxic to insect pests at ≥5°C [37**]. Xianchang *et al.* [38**] reported that carbonyl sulphide was effective for wheat and paddy rice at a dose of 50 g/m^3 for 7 days.

There are contradictory views about the effects of carbonyl sulphide on grain quality. In independent studies it has been established that carbonyl sulphide does not affect germinability of cereal grains [37**, 39, 40]. No adverse effect on the quality of bread and noodles prepared from the treated grain and the malting and brewing characteristics of barley has been observed [41]. Ren *et al.* [42**] established that, like phosphine, carbonyl sulphide is less soluble in lipid; fumigation of wheat or wheat oil had no effect on the lipid composition. The fumigant is absorbed moderately by food commodities [39]. Studies in China, however, indicate that carbonyl sulphide imparts off-odour to treated grain, changes the grain colour and affects germination of seed material; the end-use products from treated commodities also get affected [38**]. Desmarchelier, [6**] opined that the off-odour problem in treated commodities, if any, can be attributed to hydrogen sulphide present as an impurity in the supplied product. It has been observed that the fumigant breaks down to produce hydrogen sulphide and CO_2 by its reaction with moisture in grain or by the action of the enzyme carbonic anhydrase; the liberated hydrogen sulphide might affect grain quality [43].

Ozone

Ozone, a known sterilant, that is produced on-site using electricity and air has been investigated for the control of stored grain insects in China, Japan, the UK and the USA. Ozone is environmentally safe as it quickly degrades to molecular oxygen, which is naturally present in air. Ozone treatment controls moulds, bacteria and insects present outside the grain at a dose of 50 ppm for 3 days. Ozone does not penetrate individual grains to affect the mortality of insects developing inside. It needs a longer treatment period, in the first instance to saturate the sorptive sites in the grain and then to act on the pests. In trials on corn (11–13% moisture content), ozone (at a dose of 50 ppm for 3 days) did not affect grain composition (protein, oil and starch contents) and germination [44]. It was shown that treatment of cereal grains (popcorn, wheat, maize and paddy rice) at the same concentration but for a longer period of 30 days did not affect popping volume of popcorn, chemical composition and milling characteristics of wheat and maize, or the texture quality of cooked rice [45**].

Ethane dinitrile

Ethane dinitrile (cyanogen) has been investigated as a fumigant for wood materials and grains in Australia. This fumigant is more toxic to insects in the presence of CO_2 and at higher relative humidity [46]. It has been suggested that the fumigant could be useful as a devitalising agent for grains and for eliminating pathogens at a dose of 115 g/m^3 for 5 days [47]. Current studies indicate that ethane dinitrile has potential as a fumigant for feed grains.

Phytochemicals

There are numerous laboratory studies on the use of plant essential oils and their components as fumigants against stored grain pests. Although plant compounds could show fumigant toxicity in laboratory assays without substrate, their performance in the presence of grain was poor because of very low vapour pressure (<1 mm Hg) and high sorption [48**]. There are only limited studies on the nutritional quality of food commodities exposed to phytochemicals and the persistence of their residues [49]. Till now no plant essential oil or constituent has been exploited commercially for use as a fumigant.

Controlled atmospheres

The application of controlled atmospheres, ie, CO_2-rich and low-O_2 atmospheres, for disinfestation and storage of food grains has been standardised and the sealing levels, dosage and exposure period have also been defined [50]. The quality of grains is not affected by treatment and the application meets the requirements of organic markets. Yet, grain treatment with controlled atmospheres is not widely adopted owing to high cost, longer exposure period and high level sealing requirements.

The future

There has been a drastic change in fumigation technology in recent years. In contrast to the static system as in conventional fumigation, continuous flow and recirculation systems for specific situations employing cylinderised phosphine and ethyl formate formulations have been developed. Hence, a fumigant need not have high vapour pressure to penetrate into commodities and distribute on its own. Fan or blower-aided flow or circulation facilities could supplement the fumigant's ability to achieve rapid and even distribution through bulk grain storages.

To preserve grain at farm level, phosphine is commonly used. However, it is a high vapour pressure (29,260 mm Hg) fumigant and grain treatment under leaky storage conditions at farm level is, therefore, risky and could contribute to resistance development. Hence, there is a need for an alternative fumigant for treating grains at farm level. A liquid fumigant like ethyl formate has the potential for application for on-farm storages. Further studies with ethyl formate in different farm storage structures are necessary.

In stored grains, several species of mites occur as grain feeders, fungus feeders, predators and parasites. Besides causing occupational health problems (eg, asthma and inhalant allergy) to workers, mites impart a musty odour to the grain and disseminate microflora that are responsible for mycotoxins in grains. Mite control in food and feed grains by fumigation has been less focused when compared with that of insect control [51]. The efficacy of alternative fumigants in controlling mites in food grains needs further attention.

It has been noted that in fumigations, the impurities and adjuncts present along with the active ingredient have more harmful effects on the grain than the actual fumigant. Sulphur dioxide, chlorine, hydrogen fluoride and ethylene dichloride, which are likely to be present as impurities along with sulphuryl fluoride, contribute to off-odour problems in treated commodities [24**]. Similarly, hydrogen sulphide present along with carbonyl sulphide causes tainting of grains [43]. Chloropicrin added as a warning agent with methyl bromide is more phytotoxic than methyl bromide itself. Therefore, there is a need to consider the purity of the supply and the adjuncts present when applying a fumigant to food and feed grains.

Fortunately, alternate fumigants such as carbonyl sulphide, ethyl formate and ethane dinitrile have the common feature that they all occur naturally at very low concentrations in foodstuffs or in the environment. Hence, it is advantageous that the food grains treated with these compounds can be aerated until the residues reach the natural levels instead of achieving zero level of residues [52]. There is a general consensus that we may not get a broad-spectrum fumigant like methyl bromide or a cheaper and simpler way to use a fumigant like phosphine in the near future. Alternative compounds could be useful in specific situations, for a particular type of commodity or against particular pests.

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Proceedings of the 9th International Working Conference on Stored Product Protection, Campinas, Brazil, October 2006. Lorini I, Bacaltchunk B, Beckel H, Deckers D, Sundfeld E, dos Santos JP, Biagi JD, Celaro JC, Faroni LRDA, Bortolini L de OF, Sartori MR, Elias MC, Guedes RNC, da Fonseca RG and Scussel VM (eds). Brazilian Post-harvest Association, Campinas, Brazil, 2006; pp. 519–526.

**The author has demonstrated the high penetration and relatively low sorption of sulphuryl fluoride, with no adverse effect on electronic equipments in food facilities; enhanced toxicity of the fumigant against insect eggs at higher temperatures was also proven.

24 Derrick MR, Burgess HD, Baker MT and Binnie NE. Sulfuryl fluoride (Vikane): a review of its use as a fumigant. Journal of the American Institute for Conservation 1990: 29: 77–90.

**In this short review on sulphuryl fluoride, the physico-chemical properties, efficacy against various pests, and toxicity to mammals are described.

25 Schneider BM, Williams RE and Smith MS. Fumigant confinement and half-loss times in food industry structures and shipping containers. In: Proceedings of an International Conference on Controlled Atmosphere and Fumigation in Stored Products, Fresno, CA, 29 Oct-3 Nov 2000. Donahaye EJ, Navarro S and Leesch JG (eds). Executive Printing Services, Clovis, CA, USA; 2001: pp. 471–476.

The concept and importance of half-loss time for prediction of successful fumigation and economical use of fumigants like sulphuryl fluoride are described.

26 Xu GG, Cheng ZM, Seng Z and Qui N. Development of sulfuryl fluoride (SO_2F_2), techniques of vacuum fumigation and circulative fumigation, a comprehensive study. Plant Quarantine 1988: 12: 38–46.

Studies on insect toxicity and sorption by sulphuryl fluoride conducted in China have been reported in this paper.

27 USEPA. 2005. Sulfuryl fluoride; pesticide tolerance. Federal Register, 2005: 70 (135): 40899–40908.

Sulphuryl fluoride residue limits for various food commodities are provided in this document.

28 USEPA. Sulfuryl fluoride; request for study of tolerances. Federal Register 2006: 71(128): 38125–38127.

In this reference, a document requesting the stay of sulphuryl fluoride tolerance limits in food commodities in USA is given.

29 Guogan X, Zhongmei C, Zhao S and Nengzhi Q. The development of sulphuryl fluoride (SO_2F_2), in China- a brief introduction. In: Stored Product Protection; proceedings of the 7th International Working Conference on Stored-product Protection, Beijing, China, October 1998. Zuxun J, Quan L, Yongsheng L, Xianchang T and Lianghua G (eds). Sichuan Publishing House of Science & Technology, 1999: pp. 562–566.

**This article gives a comprehensive report on various studies conducted in China on the use of sulphuryl fluoride as a fumigant for food and non-food commodities. Data on levels of fluoride residues in treated commodities are presented in this paper.

30 Reuss R, Cassells JA and Green JR. Malting barley: storage, dormancy and processing quality. In: Stored Grain in Australia 2003: proceedings of the Australian Postharvest Technical Conference, Canberra, June 2003. Wright EJ, Webb MC and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 44–48.

The authors studied the effect of fumigants on dormancy and viability of barley.

31 Muthu M, Rajendran S, Krishnamurthy TS, Narasimhan KS, Rangaswamy JR, Jayaram M and Majumder SK. Ethyl formate as a safe general fumigant. In: Controlled atmosphere and fumigation in grain storages: Proceedings of an International Symposium on Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages. Ripp, BE. (ed). April 1983, Perth, Australia. Elsevier, Amsterdam, The Netherlands, 1984: pp. 369–393.

**This article presents results of elaborate studies on ethyl formate as a fumigant. Data on field trials with the fumigant on food commodities are also presented.

32 Ren RL and Mahon DA. Fumigation trials on the application of ethyl formate to wheat, split faba beans and sorghum in small metal bins. Journal of Stored Products Research 2006: 42: 277–289.

This paper describes experiments conducted in Australia on ethyl formate for grains in farm storages. The effectiveness of the treatment, and worker and environmental safety of the fumigant are discussed.

33 Damcevski KA, Dojchinov G and Haritos VS. VAPORMATE™, a formulation of ethyl formate with CO_2, for disinfestation of grain. In: Stored Grain in Australia 2003: Proceedings of the Australian Postharvest Technical Conference, Canberra, June 2003. Wright EJ, Webb MC and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 199–204.

In this paper, the authors demonstrated the effectiveness of "VAPORMATE" (ethyl formate and CO_2 mixture formulation) against phosphine-resistant insect pests.

34 Ryan R, Grant N, Nicolson J, Beven D and Harvey A. VAPORMATE (16.7 wt% EtF in CO_2): dispensing techniques. In: Proceedings of the 9th International Working Conference on Stored Product Protection, Campinas, Brazil, October 2006. Lorini I, Bacaltchunk B, Beckel H, Deckers D, Sundfeld E, dos Santos JP, Biagi JD, Celaro JC, Faroni LRDA, Bortolini L de OF, Sartori MR, Elias MC, Guedes RNC, da Fonseca RG and Scussel VM (eds). Brazilian Post-harvest Association, Campinas, Brazil, 2006; pp. 618–623.

The authors report on the effectiveness of a new ethyl formate-CO_2 mixture (VAPORMATE- formulation) for treating grains and grain storage facilities, and its dispensing techniques.

35 Ren YL and Mahon DA. Development of ethyl formate formulation for grain storage. In: proceedings of 2005. Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, San Diego, CA, USA, Oct 31–Nov 3, 2005: pp. 84–1, 84–3.

Results of laboratory and field trials with ethyl formate plus allyl isothiocyanate mixture in treating wheat are presented in this paper.

36 Mahon DA, Ren YL and Burrill PR. Seed store disinfestation trials with VAPORMATE™ (ethyl formate + CO_2). In: Stored Grain in Australia 2003: proceedings of the Australian Postharvest Technical Conference, Canberra, June 2003. Wright EJ, Webb MC and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 205–209.

In this paper, the authors suggest that "VAPORMATE™", a new ethyl formate formulation was safer for treating seed grains.

37 Desmarchelier JM. Carbonyl sulfide as a fumigant for control of insects and mites. In: Proceedings of the 6th International Working Conference on Stored-product Protection, Canberra, April 1994. Highley E, Wright EJ, Banks HJ and Champ BR (eds). CAB, Wallingford, UK. 1994: pp. 78–82.

**In this important paper, data on the chemistry, mammalian toxicity and environmental fate of carbonyl sulphide are presented; the effectiveness of the fumigant against stored grain insects, sorption and effect on germination are also discussed.

38 Xianchang T, Xingwei H, Lizheng C and Jianchun W. Research on carbonyl sulfide as a fumigant for control of stored grain insects. In: Stored Product Protection; proceedings of the 7th International Working Conference on Stored-product Protection, Beijing, China, October 1998. Zuxun J, Quan L, Yongsheng L, Xianchang T and Lianghua G (eds). Sichuan Publishing House of Science & Technology, 1999: pp. 567–571.

**In this article, data on the toxicity of carbonyl sulphide to stored grain insects, sorption and effect on grain quality are reported. The authors demonstrated that the fumigant affected germination and the quality of treated grains.

39 Reuss R and Annis PC. Fumigation of paddy rice and rice products with carbonyl sulfide. In: Stored Grain in Australia: 2000: proceedings of the Australian Postharvest Technical Conference, Adelaide, August 2000. Wright EJ, Banks HJ and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2002: pp. 97–101.

The authors investigated carbonyl sulphide sorption by grain, its residues and effects on grain quality.

40 Ren YL, Mahon DA, van S Graver JE and Head M. Commercial-scale trial fumigation of wheat using carbonyl sulfide (COS). CSIRO Entomology Technical Report No. 99. 2005.

This article describes a large-scale commercial trial of carbonyl sulphide fumigation of wheat. The trials showed that wheat quality was not affected by the treatment.

41 Wright EJ. Carbonyl sulfide (COS) as a fumigant for stored products: progress in research and commercialisation. In: Stored Grain in Australia 2003: proceedings of the Australian Postharvest Technical Conference, Canberra, June 2003. Wright EJ, Webb MC and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 224–229.

The author, in this article, has summarised the results of studies on carbonyl sulphide as a fumigant.

42 Ren YL, Desmarchelier JM and Watson F. Effect of grain fumigants on lipids *in vivo* and *in vitro*. Journal of Agricultural and Food Chemistry 1997: 45: 2626–2629.

**In this paper the authors examined the interaction between fumigants and grain lipids. It was shown that fumigants have the least effect on grain lipids.

43 Weller GL. Sorption of carbonyl sulfide by stored products. In: Advances in Stored Product Protection; proceedings of the 8th International Working Conference on Stored Product Protection, York, July 2002. Credland PF, Armitage DM, Bell CH, Cogan PM and Highley E (eds). CABI, Wallingford, UK. 2003: pp. 493–497.

Levels of carbonyl sulphide sorption in food commodities including grains are reported in this paper; moisture content, age of commodity and previous fumigation history as contributing factors in fumigant sorption were studied.

44 Mason LJ, Strait CA, Woloshuk CP and Maier DE. Controlling stored grain insects with ozone fumigation. In: Stored Product Protection; proceedings of the Seventh International Working Conference on Stored-product Protection, Beijing, China, October 1998. Zuxun J, Quan L, Yongsheng L, Xianchang T and Lianghua G (eds). Sichuan Publishing House of Science & Technology, 1999: pp. 536–547.

The authors studied the toxicity of ozone to stored grain insects, its effect on seed (corn) germination and corrosion property.

45 Mendez F, Maier DE, Mason LJ and Woloshuk. Penetration of ozone into columns of stored grains and effects on chemical composition and processing performance. Journal of Stored Products Research 2003: 39: 33–44.

**The authors demonstrated that treatment of grain with ozone does not affect grain quality (milling property, chemical composition and baking property).

46 Hooper J, Desmarchelier JM, Ren YL and Allen SE. Toxicity of cyanogen to insects of stored grain. Pest Management Science 2003: 59: 353–357.

The toxicity of ethane dinitrile (cyanogen) to stored product insects was investigated; it was shown that the toxicity was comparable to that of methyl bromide.

47 Ryan R, Grant N, Nicolson J, Beven D and Harvey A. Sterigas™ and Cosmic™. Update on proposed new fumigants. In: Proceedings of the 9th International Working Conference on Stored Product Protection, Campinas, Brazil, October 2006. Lorini I, Bacaltchunk B, Beckel H, Deckers D, Sundfeld E, dos Santos JP, Biagi JD, Celaro JC, Faroni LRDA, Bortolini L de OF, Sartori MR, Elias MC, Guedes RNC, da Fonseca RG and Scussel VM (eds). Brazilian Post-harvest Association, Campinas, Brazil, 2006b; pp. 624–629.

The efficacy of ethanedinitrile and carbonyl sulphide during commercial-scale trials conducted in Australia are reported.

48 Rajendran S and Sriranjini V. Plant products as fumigants for stored product insect control. Journal of Stored Products Research 2007. In press.

**In this article, insect toxicity, mode of action, effects on treated commodities, and constraints in application of plant essential oils and their constituents as fumigants are reviewed.

49 Lee BH, Annis PC and Tumaalii F. The potential of 1, 8-cineole as a fumigant for stored wheat. In: Stored Grain in Australia 2003: proceedings of the Australian Postharvest Technical Conference, Canberra, Australia, June 2003, Wright EJ, Webb MC, Highley E. (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 230–234.

The authors studied 1,8-cineole, a natural component of plant essential oils, as a grain fumigant; sorption, effectiveness against insect pests and residues in treated grain were investigated.

50 Annis PC and van S Graver J. Suggested recommendations for the fumigation of grain in the ASEAN Region. Pert 2. Carbon dioxide fumigation of bag-stacks sealed in plastic enclosures: an operations manual. Kuala Lumpur, AFHB/ Canberra, ACIAR; 1991: pp. 58.

Detailed procedures for the application of CO_2 for disinfestation and long time storage of food grains are given in this book.

51 Halliday RB. Health and safety issues related to mites in stored grain. In: Stored Grain in Australia 2003: Proceedings of the Australian Postharvest Technical Conference, Canberra, June 2003. Wright EJ, Webb MC and Highley E (eds). CSIRO Stored Grain Research Laboratory, Canberra, Australia; 2003: pp. 116–118.

In this review paper, the occurrence of mites in stored grain and their health effects to grain industry workers and safety issues are discussed.

52 Ren YL. Philosophy guiding current and future fumigant research. In: Advances in Stored Product Protection: proceedings of the 8th International Working Conference on Stored Product Protection, York, UK, July 2002. Credland PF, Armitage DM, Bell CH, Cogan PM and Highley E (eds). CABI, Wallingford, UK, 2003: pp. 553–555.

The author discusses future directions of fumigation research with particular reference to alternative fumigants such as carbonyl sulphide, ethane dinitrile and ethyl formate.