A reappraisal of an old fumigant, carbon disulphide, under modern farm storage conditions

YongLin Ren and Sylvia E Allen[1]

Abstract

Carbon disulphide, an old fumigant fallen into disuse, is re-examined and trialed under modern sealed farm storage Results for carbon disulphide are compared with methyl bromide, a fumigant in the process of being withdrawn, and also with phosphine, where insect resistance may limit its use The possibility of reintroducing carbon disulphide as an alternative fumigant is supported by new data from Australia, and by published Egyptian and Chinese data which is not widely known The data covers grain quality, natural emissions and residues of carbon disulphide in processed food Using sealed storage lower doses of carbon disulphide ($27g/m^3$) were found to be efficaceous The sorption of carbon disulphide on grain is lower than that for methyl bromide, and is mainly physical in origin yet it leaves residues on grain These residues are extensively degraded during storage and processing Residues in processed products were indistinguishable by current methods of analysis (limits of quantification were <0 005 mg/kg, 5ppb w/w) and the same as levels present in products made from unfumigated wheat from the same source Unlike methyl bromide, carbon disulphide had no effect on germination and plumule length even at high doses (150 mg/L) Results reported in this paper indicate that carbon disulphide can be used in sealed storage to replace many of the uses of methyl bromide and in particular where the maintenance of seed viability is desirable

Introduction

New fumigants are required as replacements for fumigants in the process, or under the threat of being withdrawn from use In response to this need an old fumigant, carbon disulphide was re-examined and trialed in sealed storage Comparisons are made with methyl bromide, which is in the process of being phased out and also with phosphine Carbon disulphide (CS_2) is the oldest fumigant used for commercial large scale insect control in grain storage It was the first patented fumigant (U S Patent No 64667), patented in 1867 and used as a fumigant for grain in the US in 1896 It was used in France, in 1869, against the grape vine pathogen phylloxera and for many years CS_2 was widely used as a grain, soil and space fumigant Being the first fumigant used for commercial bulk grain, the use of CS_2 as a fumigant to control insects in grain and soil is a landmark in the history of applied entomology (Bond 1984) Carbon disulphide has now largely fallen into disuse because of its high flammability, relatively higher and longer term residues than phosphine (PH_3) which along with methyl bromide (MeBr) replaced CS_2 as a grain fumigant However, it is the only fumigant used in certain parts of the world (Bond 1984) As carbon disulphide penetrates a grain mass well and compares favourably with phosphine, CS_2 mixed with nonflammable components such as carbon dioxide (CO_2) are still used in vertical silos without recirculation in China (Ni 1983, Tan 1994 and Yang et al 1998) Carbon disulphide is also used currently by Australian growers in NSW (Hilton et al 1998)

Extensive work in China on more than 20 seed species showed that unlike methyl bromide, CS_2 does not affect seed viability even at a concentration of 200 mg/L (Xiu et al 1987) Ghaly (1960) showed that CS_2 had no effect on the germination and plumule length of Nahda variety rice even at high doses (400 − 800 mg/L) The physical characteristics of rice (e g hardness, broken ratio and milling output) and qualities (such as cooking test, iodine value, starch and alkali test) were not affected by CS_2 fumigation at a concentration of 400 mg/L and moisture content of 13 − 19% (Ghaly 1960) Sorption of CS_2 on grains, wheat flour, polished rice and legumes is lower than that for methyl bromide, and seems to be mainly physical sorption as most of this is recoverable (Rafie 1954 and Tan 1994) Mapes and Shrader (1957a) reported that CS_2 residues found in commercially fumigated wheat treated with 120 and 40 ppm of CS_2 had declined 3 months after fumigation, and before any turning, to < 2 5 ppm and <0 25 ppm respectively Munsey et al (1957) added 10ppm CS_2 to commercial baker's flour, and then carried out commercial baking studies They found no extra CS_2 in the bread compared with bread from untreated flour For example, Mapes and Shrader (1957) found by reducing CS_2 rates of application by one third (from 120 ppm to 38 ppm),

[1] Stored Grain Research Laboratory, CSIRO Division of Entomology, Canberra GPO Box 1700 ACT 2601, Australia

residues of CS_2 can be reduced 40 times (from 6 0 ppm to 0 14 ppm) in flour New evidence has shown that CS_2 rates of application can be reduced by applying it in a sealed storage, and CS_2 residues can be further reduced by forced airing (Hilton et al 1998)

The object of this paper is to re-examine CS_2 as a fumigant under today's storage conditions and quality management Also to bring CS_2 use up to modern standards of safety and efficacy, through being able to reduce the dose of CS_2, and further reduce residues and the risk of explosion This re-examination of CS_2 in response to the phasing out of methyl bromide is part of a general philosophy of having alternatives, both new fumigants and old where applicable, so that there is not reliance on any one chemical

Materials and Methods

Laboratory procedures

Samples and Chemicals

Wheat samples used in laboratory tests were Australian Standard White (ASW, 10 6% moisture content, w/w wet basis) Australian barley (var Schooner, 10 3% moisture content, w/w), chick peas (Desi-type var Amethyst, 11 5% moisture content, w/w), peas (10 5% moisture content, w/w), paddy (10 5% moisture content, w/w) and sorghum (11 5% moisture content, w/w) were used for germination and sorption tests All of the above samples were free of insecticide

Carbon disulphide as a liquid (99 9% purity and 1250 g/L density) was purchased from Ajax Australia Methyl bromide (99 8% purity) was purchased from Matheson Gas Products (Cucamonga, CA) Phosphine was prepared by the FAO method (Anon 1975)

Germination Tests

Wheat, barley and chickpeas samples (10 g) were exposed at 25(±2)℃ to CS_2(150 mg/L) in 250 ml bottles capped with a Mininert injection system The concentration of CS_2 in the headspace was measured at timed intervals, and the samples were used for germination tests after 7 – 14 days exposure

Germination tests were carried out according to the principles stated in International Seed Testing Association Methods (1976), adapted by Ghaly and Van Der Touw (1982) Fifty seeds were saturated with approximately 40 mL of distilled water and wrapped in 2 rolled crepe filter papers (500 mm × 330 mm each) The seeds were arranged 30 mm apart on the top half of the sheet (i e 250 mm × 330 mm), using a seed counting board, and the lot covered by folding the lower half over them Each doubled sheet was saturated with water and loosely rolled from one side to the other, perpendicular to the base It was then held together with a rubber band and put in an upright position in the germination cabinet, at 25℃ The number of germinated seeds was counted after 8 days (total germination test) and the plumule length was measured at 8 days Each experiment was also replicated four times The data were analysed statistically for standard error and variance

Determination of Sorption of CS_2 on Grain and Pulses

Grain and pulse samples (wheat, barley, paddy, sorghum, peas and chick peas) of 180 g were placed in bottles (250 ml) which were equipped with a screw on mininert valve (Alltech 24 mm Mininert Valves, Code 95326) Fumigant to achieve 25 mg/L was injected into the bottles, and also into bottles without sample This empty flask was used as a control to calculate the concentration applied Fumigant in the headspace was injected into a gas chromatograph at timed intervals, and the concentration (C) in the headspace determined The ratio (C/Co) of the headspace concentration (C) and initial concentration (Co) is expressed as sorption It represents the proportion of original dose remaining and it is plotted against time after dosing Samples were tested at 25(±2)℃ and 90 – 95% filling ratio and all samples were made in triplicate

Determination of CS_2 Movement Through Wheat

The procedure used was as described in Desmerchelier (1994) Fumigants were blown through a 1 1 m column of wheat, of total volume 7 9 L, at an airflow rate of 200 ml/min Fumigants (10 ml of PH_3 and MeBr gas and 20 μl of CS_2 liquid) were applied simultaneously to the column via a 500 ml flask at the bottom of the column and their concentrations were measured at the top of column

Analysis of Carbon Disulphide Residues

Two methods were used for determining CS_2 residues in wheat, wheat fractions (such as flour, germ, pollard and bran) and wheat products (such as sponge cake, bread, uncooked pasta and uncooked noodles)

(a) Method A This method was developed by Ren (1997) and Ren and Desmarchelier (1998) In this procedure, a Panasonic model microwave oven equipped with time and power programming was used The microwave power emission ranged from 270 to 900 W The sample (15 g) was placed in a compressed bottle of 250 ml, which was equipped with a screw on mininert valve (Alltech 24 mm Mininert Valves, Code 95326) A cycle of microwave irradiation and headspace analysis followed by 50 sec standing was repeated until the amount of fumigant in the headspace either remained constant or started to decline

(b) Method B This method was based on an AOAC procedure modified by Daft (1987) and further modified (Desmarchelier et al 1998a) by using gas-tight systems and headspace chromatography The wheat sample (50g) and 50 ml 'Daft solution' (acetone (80%) in 25% phosphoric acid solution) (Daft 1988) was placed in a 270 ml Erlenmeyer flask, fitted with a septum Concentrations in the headspace were determined after steeping for 31 ± 3 hours, at room

temperature (25 ± 3℃)

Diluted CS_2 standards were prepared by addition of a known volume of liquid CS_2 into a 500 ml Erlenmeyer flask containing 5 glass beads (e g 2 μL in 500 ml gives 6 25 mg/L of CS_2) After mixing by shaking, the diluted gas standard was used to prepare both fortified samples and standards The fortified samples were prepared by injecting a known volume of the diluted gas standard into 'Daft solution' (50 ml) in a 270 ml Erlenmeyer flask containing 50 g of untreated wheat

Determination of CS_2 Concentrations

Carbon disulphide levels were determined using a Shimadzu GC6AM gas chromatograph equipped with a flame photometric detector (FPD), sulphur filter and a 1 m × 3 mm glass column packed with HayeSep Q (Alltech 2801) Operation conditions were an oven temperature of 140℃ and an injection temperature of 200℃

Analysis of CS_2 in the headspace over solvents or in the liquid phase required complete elution of the solvent or solvent vapour from GC column before further injections, so a minimum interval of 15 min was kept between injections

Commercial scale studies

Field Trails

Field trials were conducted on wheat in a silo at the SGRL (Stored Grain Research Laboratory) site in Canberra, ACT in May, 1997 The silo used was a welded steel, self outloading silo of 55 m^3 capacity Before loading, the bin was sealed by coating rivets bolts and holes with a silicone putty, Silastic™ from inside the bin The bin was filled with approximately 40t wheat and pressure tested, as described in Banks and Annis (1980) A half-life of greater than 4 minutes was achieved The wheat was treated with 1500 g (1200 ml) CS_2 38 ppm, w/w or 27 g m^{-3} by pouring CS_2 through a plastic funnel and pipe onto hessian placed on the surface of the wheat Safety considerations of time taken to dose and any spills were the major concerns To minimise risk, gloves were worn and a dry run without CS_2 was carried out prior to dosing The bin remained sealed for 6 days, outloading after airing for 1 day Gas samples were taken with a DYNAVC pump (Model OD1) through Nylon lines (3 mm internal diameter), and collected in Tedlar bags Gas sampling positions were in the centre of the bin, at distances of 1, 2, 3 and 4 m below the grain surface, at the bottom and the top of the bin (inside) in 4 equidistant directions and in the central headspace Concentrations of CS_2 were measured by GC On outloading, wheat (3 t) was transferred into three Bulka bags, each of 1 – 1 5 t capacity Ten to fifteen samples of 0 5 kg were taken from the wheat streams, with a glass jar as it entered each Bulka bag

Insect tested were stored product insects *Tribolium castaneum* strain CTC4 (50 adult and 50 larvae), *Rhzopertha dominica* strain CRD2 (50 adult) and *Sitophilus oryzae* strain CLS2 (50 adult) The media within the test insect containers was 95% wheat and 5% wheat flour The containers were placed 1 5 m below the surface of the grain, at different distances from the center of the bin prior to fumigation They were constructed of a perforated stainless steel cylinder, diameter 22 mm, height 100 mm, with a cone at each end, to enable them to be inserted into the grain The containers were removed during outloading of the grain Insects were counted when removed from the bin, and again after holding periods of 4 and 8 weeks at 30℃

Wheat samples used in field trails were Australian Standard White (ASW, 10 6% moisture content, w/w wet basis) and insecticide free Carbon disulphide as a liquid (99 9% purity and 1250 g/L density) was purchased from Ajax Australia

Milling and Baking Trails

The outloading wheat (3 t) was transferred to the BRI (Bread Research Institute) site within 5 hours of outloading to carry out wheat cleaning and milling studies, which represent usual commercial practice The usual BRI commercial formula and procedure were used in the baking, noodle and pasta processing studies Levels of CS_2 were measured by GC

Results and Discussion

Laboratory studies

The Effect of CS_2 on Germination and Plumule Length

The germination rate of wheat, barley and chick peas was unaffected by exposure to 150 mg/L of CS_2 as shown in Figure 1 The standard error from 4 replicates of 50 seeds was less than 2 5% in all cases The time of exposure ranging from 7 – 14 days at a dose of 150 mg/L, did not diminish the germination potential for all three type of seeds. That is, CS_2 had no deleterious effect on the germination of wheat, barley and chick peas at either higher levels (150 mg/L) of CS_2 or longer periods (14 days) of exposure. This result is consistent with that found on 20 fumigated seed and grain species which included grains, legumes, oil containing seeds and vegetable seeds, where the CS_2 concentration reached 200 mg/L for exposure periods of 48 hours (Xiu et al 1987) Xiu also indicated that the order of effect of fumigants on germination of 20 seed species was ethylene oxide > methyl bromide > sulphuryl fluoride > carbon disulphide Here CS_2 had the lowest phytotoxicity Ghaly (1960) reported that CS_2 has no effect on the germination and plumule length of Nahda variety rice even at high doses (400 – 800 mg/L), 48 hours exposure and 16% moisture content Verma (1988) had examined the effect of CS_2 on seed germination, where the germination rate of drier wheat is unaffected at high

concentrations for long periods, but the germination rate decreases with increasing moisture content.

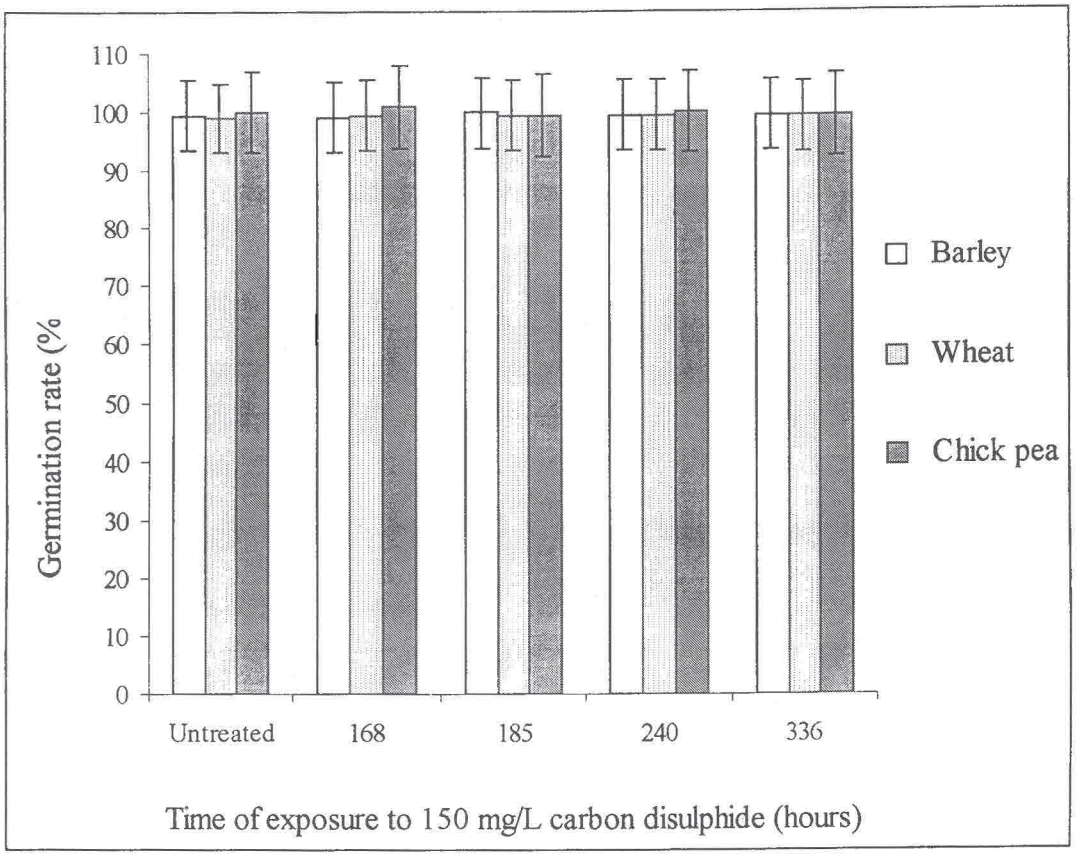

Fig. 1. Percentage germinability of wheat, barley and chick pea at initial dose 150 mg/L of CS_2 and different lengths of exposure compared with untreated grains.

Carbon disulphide had no affect on the plumule length of germinated wheat, barley and chick pea (Figure 2). The standard error in plumule length was less than 8% of the mean value in all cases. Unlike hydrogen cyanide (HCN), CS_2 can be used at higher levels without decreasing plumule length. This result is similar to the effect of carbonyl sulphide on plumule length of germinated wheat at a dose of 100 mg/L (Ren et al. 1997).

Sorption of Fumigants on Grains

Results for sorption show that CS_2 is much less strongly sorbed than MeBr. The decay of the fumigants in the headspace is shown in Figure 3, which plots the ratio of concentration to applied concentration (C/Co) against time (the standard error in sorption of fumigants was < 4 % of the mean value in all cases). They are typical sorption curves, that is, the loss of fumigants from the gas phase followed the expected pattern, with an initial rapid sorption giving way to a long term trend after about 10 hours from dosing. Sorption of CS_2 on tested grains and pulses was less than for MeBr.

The decay of CS_2 is relatively slow and concentrations that are effective against insects are still present over the exposure period in all commodities tested. Even after 160 hours fumigation, loss was less than 50% and 30% for wheat, barley respectively. For sorghum, paddy, peas and chick peas $> 30\%$ of the dose remained after 6 days. Conversely there was a remarkably rapid sorption rate for MeBr found for all tested grains and pulses in this study. Methyl bromide will disappear by reaction in few days when applied to peas and chick peas or paddy and sorghum.

Movement of Fumigants Through Wheat

Fumigant concentrations in the effluent gas are shown in Figure 4, for all concentrations greater than 1 ppm, v/v. Carbon disulphide moved through wheat in a similar manner to the two most widely used fumigants, PH_3 and MeBr. The chromatography of PH_3 and CS_2 was essentially identical with respect to retention time, peak width and degree of tailing. However, methyl bromide has a broader peak and greater tailing, consistent with stronger sorption. Differences in sorption are less obvious in this system of blowing fumigants in an airstream than in a static test. Carbon disulphide moved rapidly through or was blown out of a wheat column, to levels below 1 ppm in the intergranular air.

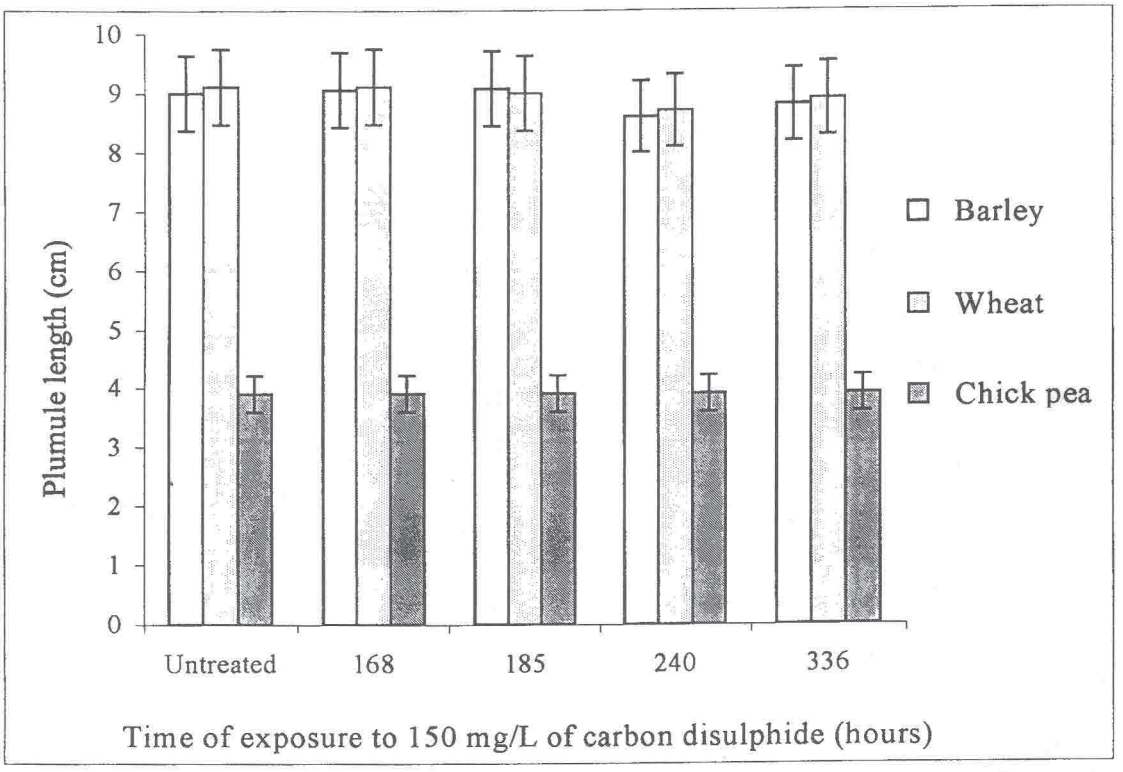

Fig.2. Plumule length of wheat, barley and chick pea at initial dose 150 mg/L of CS_2 and different lengths of exposure compared with untreated grains.

The ability of a fumigant to move through a column of grain shows an integrative effect of factors such as sorption, desorption, penetration and diffusion of the fumigant (Muthu 1973). Because CS_2 can more easily and quickly move through wheat in an air stream, it can be blown away from fumigated grain by ventilation in a short period of time. These advantages are essential requirements for an ideal fumigant, which should be able to be easily passed through bulk grain, and thus improve worker safety during unloading and transportation of grain after fumigation.

Commercial scale fumigation and wheat processing trials

The Effect of CS_2 on Control of Insects in Sealed Storage

Results for insect mortality are shown in Table 1. Mortality at the end of exposure was complete for the tested insects, and no progeny had developed after a holding period of 4 weeks and 8 weeks at 30℃. In this trial, concentration of CS_2 averaged 10.5 mg/L at day 4, and this concentration fell to 7.7 mg/L at day 6. That is, the ($C \times T$) values of CS_2 against all tested insects of species were in the range of 1000 – 1500 mg h L^{-1}. This result showed that CS_2 was highly toxic to all tested insects, and killed them quickly.

The Effect of Cleaning and Conditioning on CS_2 Residues in Wheat

Residues of CS_2 were determined at various stages of the standard cleaning and conditioning of wheat from the field treatment with CS_2. Residues of CS_2 are progressively reduced during cleaning and conditioning of wheat before milling (Figure 5). Levels of CS_2 in wheat on outloading from the silo at the SGRL site were approximately 7 mg/kg (ppm, w/w), which is below the Australian MRL of 10 mg/kg. There was a small amount of CS_2 (0.03 – 0.08 mg/kg) in unfumigated wheat, which we believe to be natural levels. Under natural conditions, CS_2 can be produced from carbonyl sulphide (COS) and conversion and decomposition of thiocyanate (Ren 1999).

Table 1. Insect mortality and progeny in field trials.

Species	Mortality(%) at end of fumigation	Progeny after 4 weeks	Progeny after 8 weeks
T. castaneum (adult)	100	0	0
T. castaneum (larvae)	100	0	0
R. dominica (adult)	100	0	0
S. oryzae (adult)	100	0	0

Cleaning of wheat reduced residues of CS_2 from 6.7 mg/kg to 4.5 mg/kg. That is, approximately 30% of the CS_2

residues were removed during wheat cleaning (Figure 5) Conditioning of wheat further reduced residues of CS_2 from 4 5 mg/kg to 2 2 mg/kg, approximately another 30% of the CS_2 residues were removed during this stage (Figure 5) Of the total residues 67% of the CS_2 was removed from outloading, during cleaning and conditioning In all cases, concentrations of CS_2 in the work space were below the TLV of 10 ppm (v/v)

The Effect of Processing on CS_2 Residues in Wheat milled Products

Residues of CS_2 were determined at various stages of the milling and baking of wheat from the field treatment with CS_2 Residues of CS_2 in milled products are shown in Figure 6 Of the milled fractions, flour or pollard final flour had the lowest residue and germ had the highest, where residues were 5 45 mg/kg This level of residue was below the MRL, but higher than those in conditioned wheat, that is the residues are to an extent concentrated in the germ Residues of CS_2 (2 62 mg/kg) in bran were slightly above the levels in conditioned wheat Residues of CS_2 in flour and pollard final flour were 3 and 10 times the natural level of CS_2 respectively

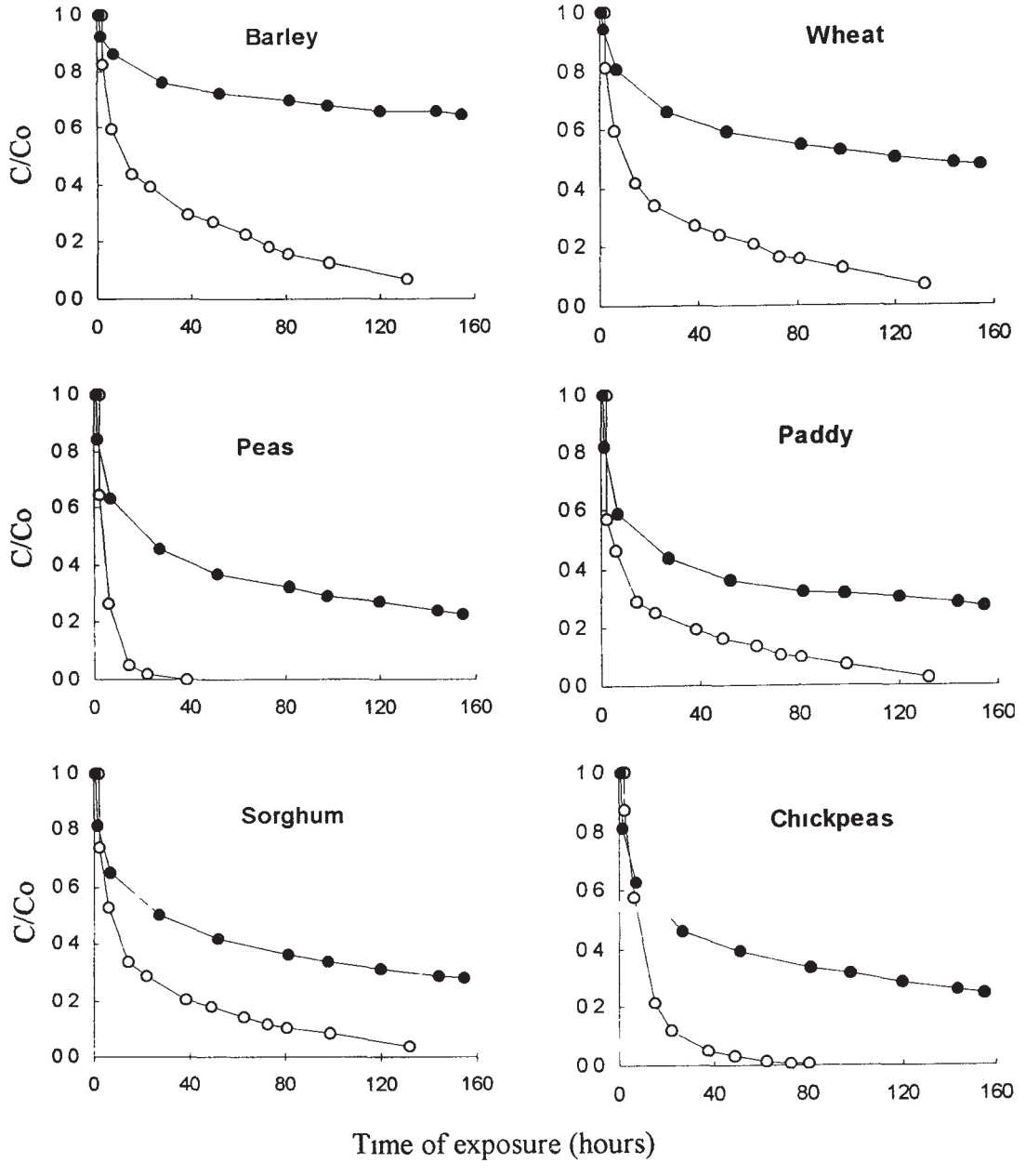

Fig. 3. Comparative sorption data for CS_2 and MeBr, taken from measurement of loss of fumigant concentration in the headspace (—o— MeBr and —●— CS_2)

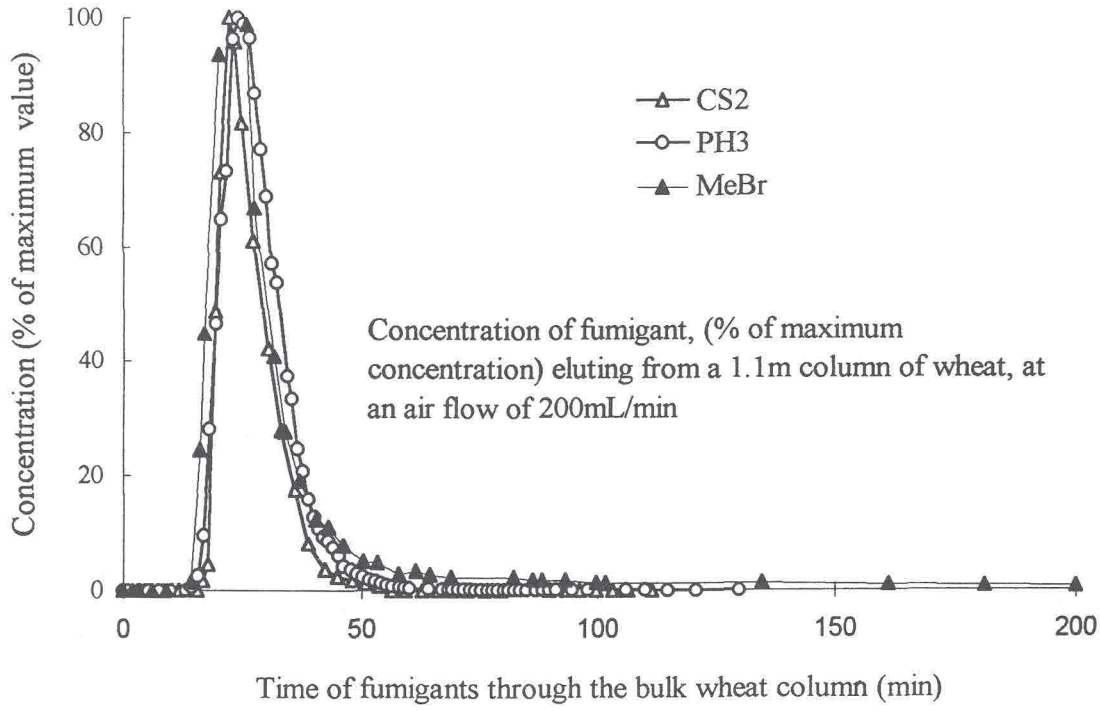

Fig. 4. Concentration of fumigant, (% of maximum GC area) eluting from a 1.1 m column of wheat, at an air flow of 200 ml min^{-1}, plotted against time (—o— CS_2, —●— PH_3 and —▲— MeBr).

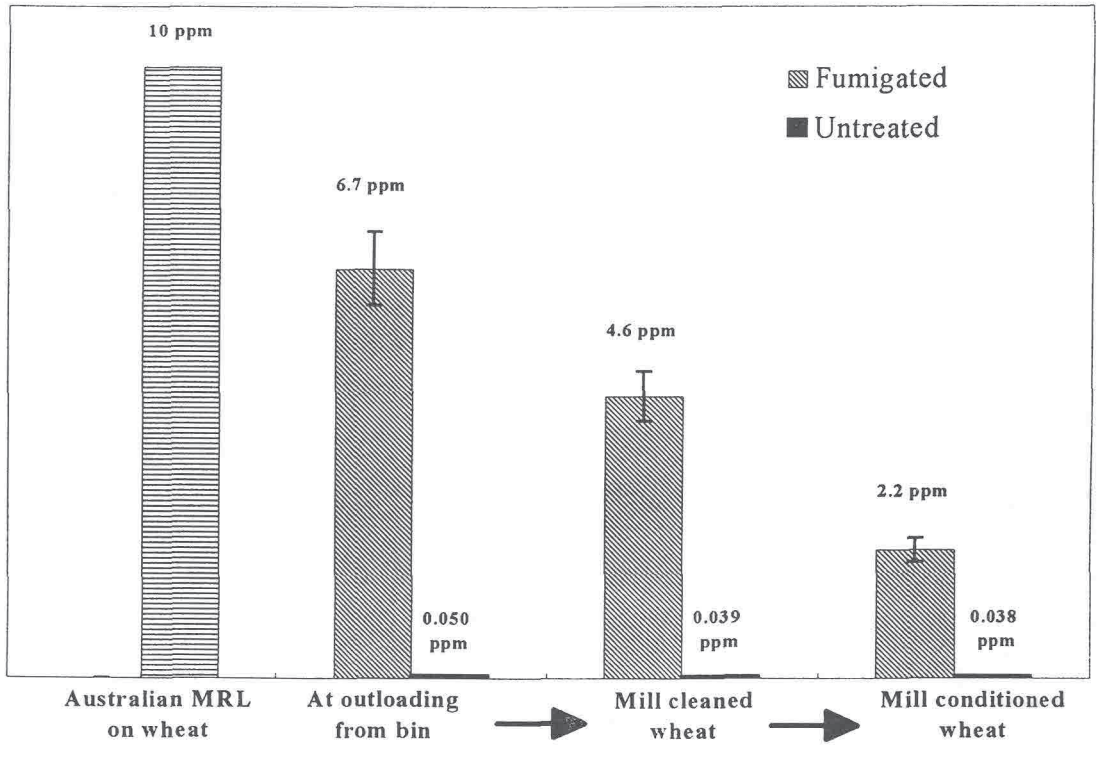

Fig. 5. Carbon disulphide residues in CS_2 fumigated and untreated wheat during processing of wheat.

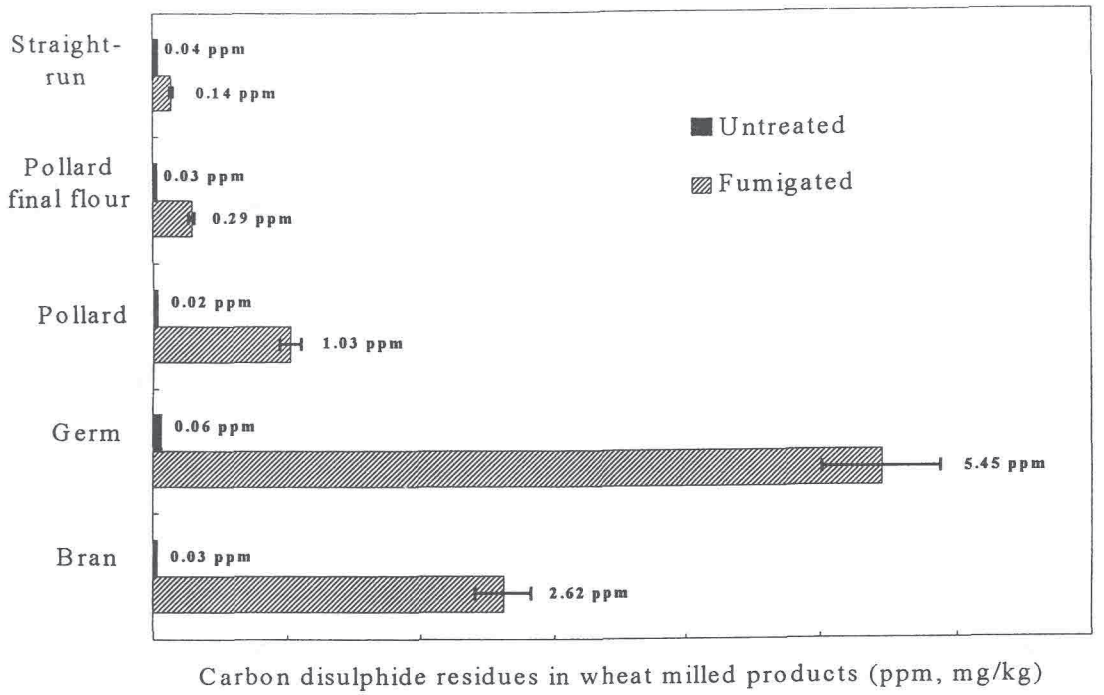

Fig.6. Carbon disulphide residues in milled wheat products of on CS_2 fumigated and untreated conducted commercial scale milling trials at the BRI site.

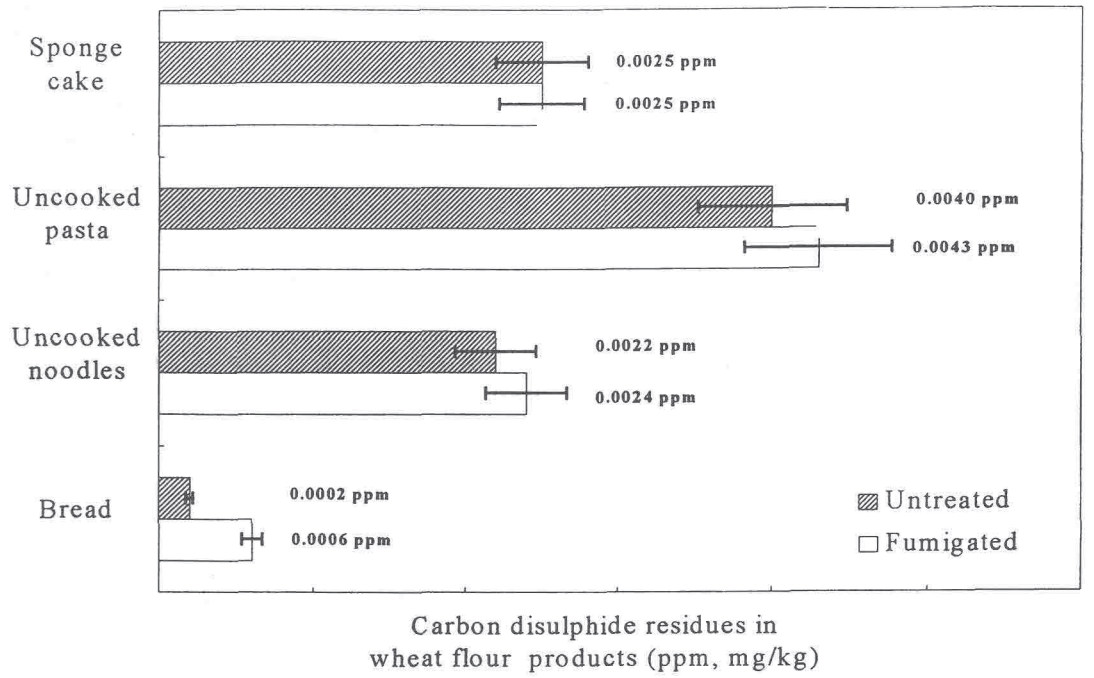

Fig.7. Carbon disulphide residues on processed CS_2 fumigated and untreated wheat products conducted on a commercial scale milling trial at the BRI site.

The Effect of Baking and Processing on CS_2 Residues in Wheat Flour Products

The flour milled from fumigated wheat and unfumigated wheat was used in baking studies Residues of CS_2 in baked and processed products are shown in Figure 7 Small amount of CS_2 residues, in the range 0 0002 – 0 0025 mg/kg was found in bread and sponge cake In uncooked pasta and uncooked noodles, only small residues of CS_2 were found (0 0022 – 0 004 mg/kg) In most cases, these values were not significantly different from those in the controls These results are consist with Munsey et al (1957) who found no additional CS_2 in the bread, which was made from CS_2 treated wheat flour, compared with bread from untreated flour

Conclusion

In this study, the results indicate that CS_2 is highly toxic to insects ($C \times T$ value of 1000 – 1500 mg h L^{-1}) and kills insects quickly Unlike methyl bromide, it is low in phytotoxicity and has no effect on germination and plumule length even at very high concentrations (>150 mg L^{-1}) on a diverse variety of seed types The sorption of carbon disulphide on grain is lower than that for MeBr, and is mainly physical in origin It leaves residues on grain, but these are extensively degraded during storage and processing There were no residues above that found as natural levels in untreated samples of wheat end products So carbon disulphide applied in sealed storage can be used as a fumigant to replace many of the uses of MeBr particularly where high rates of seed germination must be preserved

Acknowledgements

The authors thank J M Desmarchelier, E J Wright, P C Annis and V Haritos for helpful advice and to the Grain Research Development Corporation (GRDC) and the participants in the Stored Grain Research Laboratory Agreement for financial assistance The authors wish to thank Le Trang Vu for technical assistance

References

Anon 1975 Recommended methods for the detection and measurement of resistance of agricultural pests to pesticides 16 FAO Plant Protection Bulletin, 23 12 – 25

Banks, H J and Annis, P C 1980 Conversion of existing grain storage structures for modified atmosphere use Shejbal, J , ed , *Controlled atmosphere storage of grains* Amsterdam, Elsevier, Developments in agricultural engineering 1, 461 – 473

Bond, E J 1984 Manual of fumigation for insect control FAO plant production and protection paper 54 Room, FAO

Datt, J 1987 Determining multifumigant in whole grains and legumes, milled and low-fat grain products, spices, citrus fruits and beverages *J Assoc off Anal* Chem 70 734 – 739

Desmarchelier, J M 1994 Carbonyl sulphide as a fumigant for control of insects and mites In Proc 6th *Internat Working Conf Stored prod* , Edited by E Highley, E J Wright, H J Banks and B R Champ, Canberra, Australia, 17 – 23 April 1994 CAB International Wallingford, UK, Vol 1 78 – 82

Desmarchelier, J M , Allen, S E and Ren, Y L 1998a Modifications of a method for determining multifumigants residues J AOAC Int 81(3) 638 – 644

Desmarchelier, J M , Allen, S E , Ren, Y L and Le Trang Vu 1998b Commercial-scale trials on the application of ethyl formate, carbonyl sulphide and carbon disulphide to wheat (CSIRO Entomology Technical Report No 75)

Ghaly, T H 1960 Fumigation of rice against insect pests and its effects on the quality of the grain Master, Thesis, Cairo University, Egypt

Ghaly, T H and Van Der Touw, J W 1982 Heat damage studies in relation to high temperature disinfestation of wheat *J Agric Eng Res* 27 329 – 336

Greening, H G 1984 Fumigation trials with farm-stored grain Proceedings of an international symposium 'Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storage' held from 11 to 22 April 1983 in Perth, Western Australia [Edited by Ripp, B E] 673 – 682

Hilton, S J , Cassells, J A and Banks, H J 1997 Fumigation of unsealed farm bins with carbon disulphide CSIRO Division of Entomology, Stored Grain Research Laboratory (Research report)

International Seed Testing Association 1976 International Rules for Seed Testing *Seed Sci Technol* 4 3 – 177

Mapes, D A and Shrader, S A 1957a A Residues in laboratory fumigated wheat and its Buhler mill fractions *J Assoc off Agric Chem* 40(1), 191 – 192

Mapes, D A and Shrader, S A 1957b C Residues in commercially fumigated grains *J Assoc off Agric Chem* 40(1) 196 – 198

Munsey, V E , Mills, P A and Klein, A K 1957 2 Effect of cooking on fumigant residues *J Assoc off Agric Chem* 40(1) 201 – 202

Muthu, M 1973 Some aspects of phosphine as a fumigant Fumigation and gaseous pasteurisation Edited, by Majumder, S K and Venugopal, J S, Mysor, India , Academy of pest control sciences pp 28 – 29

Ni, Z Z 1989 Fumigation trials with carbon disulphide

carbon tetrachloride (20 80) in silo bins Proceedings of an international symposium 'Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storage' held from 11 to 22 April 1983 in Perth, Western Australia [Edited by Ripp, B E] 657 – 662

Raie, M S 1954 Fumigation of agricultural products X – Sorption of carbon sulphide by wheat and flour *J Sci Food Agric* 5 536 – 541

Ren, Y L 1997 Carbonyl sulphide as a fumigant for grain timber – efficacy towards organisms and formation of residues Ph D thesis, University of Canberra, Australia

Ren, Y L and Desmarchelier, J M 1998 Release of fumigant residue from grain by microwave irradiation *J AOAC Int* 81(3) 673 – 678

Ren, Y L , O'Brien, I G and Desmarchelier, J M 1996 Effect of hydrogen cyanide and carbonyl sulphide on the germination and plumule vigour of wheat *Pestic Sci* 47 1 – 5

Ren, Y L 1999 Is carbonyl sulfide a precursor for carbon disulfide in vegetation and soil? – inter-conversion of carbonyl sulfide and carbon disulfide in fresh grain tissues in Vitro (in press)

Tan, X C 1994 Residue of common chemicals in stored grain and hygiene evaluation *Grain Storage* 23(2) 43 – 55

Verma, B R 1988 Effect of multiple fumigants on seed germination *Seed Research*, 16(2) 241 – 244

Xiu, G G , Zhang, Y H , He, G C , Tang, Z , Wang, Y J , Jia, K S and Li, X Y 1987 The safety of cropseeds fumigated with four fumigants and the effects of the vacuum and carbon dioxide to control the stored product insects *Grain Storage* 16(2) 8 – 20

Yang, S H , Wang, Y N and Xu, X Z 1998 Experimental report of control *Rhyzopertha dominica* with mixture of CS_2 and CCl_4 Paper present in *7th Internat Working Conf Stored prod* , Beijing , China, 14 – 19 October 1998