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二硫化碳作为谷物熏蒸剂的新观点（中英文）

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摘　要：虽然二硫化碳（CS_2）是一种古老的熏蒸剂，但澳大利亚新数据以及中国和埃及已发表的研究数据使它可被人们重新关注。这些数据包括谷物质量、自然释放和加工食品中的残留，但目前并不广为人知。埃及研究数据显示，即使在 400 mg/m^3 高剂量下，二硫化碳对水稻的发芽率和幼芽长度都没有影响。中国研究数据显示，200 mg/m^3 高剂量对大麦、小麦、玉米、高粱、棉花、胡萝卜等大多数种子发芽率没有影响。本研究中 150 mg/L 剂量对澳大利亚小麦、大麦以及鹰嘴豆发芽率和幼芽长度的影响数据也证明了这一点。澳大利亚储藏谷物研究实验室（SGRL）的商业规模实验数据表明，二硫化碳在 1 000~1 500 mg·h·L^{-1} 的 CT 值（浓度×时间）范围内可杀死所有受试昆虫，并且对小麦最终产品质量没有影响。二硫化碳在谷物上的吸附力低于甲基溴，且主要是物理吸附。它会在谷物上有残留物，但这些残留物在储存和加工的过程中会被大量降解，而剩余的二硫化二苯醚残留物会在小麦制粉前的清理和润麦过程中减少。在制粉和烘烤的过程中，二硫化碳的残留量会逐渐减少。例如，将含有 27 g/m^3 二硫化碳的小麦在仓内密封放置 6 d，然后通风 24 h，清理会使制粉前的残留量从 6.7 mg/kg 降至 4.6 mg/kg，润麦会使残留量从 4.6 mg/kg 降至 2.2 mg/kg。在制粉的过程中，残留量会进一步减少，而在面条（甚至在烹饪前）、意大利面以及面包的制作过程中，残留量还会进一步减少。当前检测分析方法无法检测加工产品中的残留量（定量限值<0.005 mg/kg），且其残留水平与同一来源未经二硫化碳熏蒸的小麦制品相同。

关键词：熏蒸剂；二硫化碳；吸附性；发芽率；残留

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A New Look at Carbon Disulphide as a Grain Fumigant (Chinese and English versions)

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Abstract: Although carbon disulphide (CS_2) is an old fumigant, the possibility of reintroducing it 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 in processed food. Egyptian data shown that CS_2 has no effect on the germination and plumule length of rice even at high doses (400 mg/m^3). Chinese data has shown that CS_2, at high doses (200 mg/m^3), has no effect on the germination of a large number of seeds, including malting barley, wheat and maize, sorghum, cotton, carrot etc. This is supported by current Australian data (150 mg/m^3) on germination and plumule length of wheat, barley and chickpeas. Australian data from the Stored Grain Research Laboratory (SGRL) commercial scale trial showed that all tested insects are killed by CS_2 at a range of C×T (concentration×time) values of 1 000~1 500 mg·h·L^{-1} and has no effect on the quality of end products of wheat. The sorption of carbon disulphide on grain is lower than that for methyl bromide, and is mainly physical in origin. It leaves residues on grain, but these are extensively degraded during storage and processing. Remaining residues of CS_2 are reduced during cleaning and conditioning of wheat before milling. Residues of CS_2 are progressively reduced during the milling and baking processes. For example, wheat was treated at 27 g/m^3 of CS_2 for 6 days in sealed farm bin and then aired for 24 hours. Cleaning reduced residues from 6.7 to 4.6 mg/kg, and conditioning reduced residues from 4.6 to 2.2 mg/kg before milling. They are further reduced during milling, and further still during formation of noodles (even before cooking), pasta and bread. Residues in processed products were indistinguishable by current methods of analysis (limits of quantification were <0.005 mg/kg) and the same as levels present in products made from unfumigated wheat from the same source.

Key words: fumigant; carbon disulphide; sorption; germination; residues

二硫化碳（CS_2）是一种古老的熏蒸剂，用于谷物大规模商业储藏的虫害防治，是美国第一种获得专利的熏蒸剂（1867 年，第 64667 号），1896 年在美国登记注册为谷物熏蒸剂。1869 年，法国曾用它来防治葡萄根瘤蚜。将二硫化碳用作谷物和土壤的熏蒸剂来控制害虫是应用昆虫学史上的一个里程碑[1]。此后多年，二硫化碳广泛用作谷物、土壤和空间熏蒸剂。但当时由于二硫化碳易燃且残留时间较磷化氢长，二硫化碳已被弃用，磷化氢和甲基溴取代其成为谷物熏蒸剂。

二硫化碳制剂，如与二氧化碳（CO_2）等不可燃气体的混合，仍在世界上某些地区使用，如中国[2-4]。澳大利亚新南威尔士州的种植者也在使用这种熏蒸剂[5]。中国对 20 多个种子品种进行大量研究后表明，即使二硫化碳的浓度为 200 mg/m^3 也不会影响种子的活力[6]。Ghaly[7]研究表明，即使在 400~800 mg/m^3 高剂量下，对 Nahda 水稻品种的发芽率和幼芽长度也没有影响。在 400 mg/m^3 浓度和 13%~19%含水量情况下，二硫化碳熏蒸对稻米的物理特性（如硬度、破碎率和出米率）和品质（如蒸煮实验、过氧化值、淀粉和酸价）均无影响[7]。

二硫化碳穿透性很好，不逊色于磷化氢。在中国，二硫化碳用于无环流系统的立筒仓中[1-2]。谷物、小麦粉、精米和豆类对二硫化碳的吸附量比甲基溴低，主要是物理吸附，大部分气体可回收[3,8]。Mapes 和 Shrader[9]在使用 120 mg/m^3 和 40 mg/m^3 二硫化碳进行商业化熏蒸处理小麦时发现，二硫化碳残留在熏蒸 3 个月后和之前相比分别降至<2.5 mg/m^3 和<0.25 mg/m^3。Munsey[10]等在商业烘焙面粉中添加了 10 mg/m^3 的二硫化碳，然后进行了烘焙研究，与未经处理的面粉制成的面包相比，处理组面包未检出额外二硫化碳。Mapes

和 Shrader[11]通过降低二硫化碳的浓度，可以减少制粉馏分中的残留，即将二硫化碳的剂量降低 3 倍（从 120 mg/m^3 降至 38 mg/m^3）时，面粉中的残留量可降低 40 倍（从 6.00 mg/m^3 降至 0.14 mg/m^3）。新研究表明，在密闭环境下应用二硫化碳可以降低应用剂量，通过强制通风可以进一步降低残留量[5]。

本文旨在重新评估二硫化碳在当今储存条件和质量管理下作为熏蒸剂的可能性。特别由于磷化氢是一种登记注册的谷物熏蒸剂，易于获得且成本低，因此全世界过度依赖磷化氢（PH_3），导致昆虫对其抗药性越来越强[12]。另外，硫酰氟（SF）需要高浓度或长时间暴露才能完全控制卵态，且它是一种氟化气体，寿命为 36 年，20 年的全球变暖潜能值（GWP）为 7510（GWP 是衡量温室效应的指标），使用硫酰氟作为熏蒸剂存在潜在的环境安全挑战[13-14]。因此，迫切需要开发快速杀死全虫态的经济熏蒸剂，我们从降低应用剂量、减少残留和燃爆风险、安全和防效标准等方面重新对二硫化碳进行了评估。

1 材料与方法

1.1 实验室小试研究

1.1.1 样品与化学试剂

实验室测试中使用含水量 10.6%澳大利亚白麦（ASW）、含水量 10.3%（w/w 湿基）澳大利亚大麦：var.Schooner；含水量 11.5%（w/w 湿基）鹰嘴豆：Desi-typevar.Amethyst；含水量 10.5%豌豆(w/w 湿基)、含水量 10.5%水稻和含水量 11.5%高粱测试发芽率和吸附性，含水量均为 w/w 湿基法，所用样品均不含杀虫剂。

99.9%纯度液体二硫化碳，密度为 1 250 g/L：澳大利亚 Ajax 公司；纯度 99.8%甲基溴：Matheson Gas Products（加利福尼亚州，库卡蒙加）购买；磷化氢采用 FAO 方法制备[15]。

1.1.2 仪器与设备

螺旋式微量钝化阀：Alltech 24 mm 螺口瓶盖阀，代号 95326；螺旋式微压阀：Alltech 24 mm 螺口瓶盖阀，代号 95326；微波炉：配备有时间和功率编程功能，松下；气相色谱仪：GC6AM，岛津。

1.1.3 发芽实验

分别取 10 g 小麦、大麦和鹰嘴豆样品装入带有 Mininert 注射塞的 250 mL 瓶中，注入 150 mg/m^3 浓度的二硫化碳，温度设定为（25±2）℃，每隔一段时间测定瓶内空间的二硫化碳浓度，熏蒸暴露 7~14 天后测定发芽率。

发芽实验参照国际种子检验协会方法[16]，该方法由 Ghaly 和 VanDerTouw[17]进行了改编。用 40 mL 蒸馏水将 50 粒种子浸泡，并用 500 mm×330 mm 滤纸包好、喷湿并平铺于实验台上，一半滤纸压上 250 mm×330 mm 的种子计数板，计数板上铸有 30 mm 间距排列的圆孔，在圆孔里放入浸泡样品籽粒，然后将空白的另一半滤纸折叠，从 250 mm 端卷曲成卷，用橡皮筋将其固定，装入自封袋中，悬挂在 25 ℃培养箱中。第 8 天记录发芽种子率和测量幼芽长度。每个实验重复 4 次，数据进行了标准误差和方差统计分析。

1.1.4 测定谷物和豆类对二硫化碳吸附性

将 180 g 的谷物和豆类样品（小麦、大麦、稻谷、高粱、豌豆和鹰嘴豆）装入带有螺旋式微量钝化阀的 250 mL 瓶子中，注入 25 mg/m^3 熏蒸剂。空瓶也注入 25 mg/m^3 熏蒸剂，作为对照计算所用浓度。从注入熏蒸剂开始按时间间隔抽取瓶顶空的熏蒸剂，注入气相色谱仪进行分析，制作浓度和时间曲线，按照顶空浓度（C）与初始浓度（Co）的比值（C/Co）计算（25±2）℃和 90%~95%填充率条件下的吸附量，所有样品均一式三份。

1.1.5 测定二硫化碳在小麦粮堆的扩散情况

按照 Desmerchelier[18]方法，采用长 1.1 m、容积为 7.9 L 的小麦柱，将 10 mL PH_3 和 MeBr 气体以及 20 μL CS_2 液体分别注入柱底部的 500 mL 烧瓶中，通过 200 mL/min 的气流速度将熏蒸剂带入柱中，并在柱顶部测量通过的熏蒸剂浓度。

1.1.6 二硫化碳残留分析

采用两种方法测定小麦、小麦各部分（如表皮、糊粉层、胚乳和胚）和小麦粉制品（如海绵蛋糕、面包、未煮熟的意大利面和未煮熟的面条）中的二硫化碳残留量：

（1）方法 A：该方法由 Ren[19]和 Ren 与 Desmerchelier[20]开发。将 15 g 样品放入 250 mL

带有螺旋式微压阀的压缩瓶中，利用微波炉进行微波辐照，然后抽取顶空气体进行气相色谱分析，静置50 s，重复操作，直到顶空气体浓度保持不变或开始下降。

（2）方法B：该方法基于Daft[21]修订的AOAC标准方法，通过结合气密系统和顶空色谱法作进一步修改[22]。将50 g小麦样品和50 mL“Daft溶液”（80%纯度丙酮溶于25%磷酸溶液）[21]混合物放入270 mL装有隔膜的锥形瓶中，在（25±3）℃下浸泡（31±3）h后，测定顶空气体浓度。

将已知体积的二硫化碳液体加入装有5粒玻璃珠的500 mL锥形瓶中制备稀释的二硫化碳标准物质，如在500 mL中加入2 mL得到6.25 mg/m^3。经振荡混合后，稀释的气体用于制备加标样品和标准品。将已知体积的稀释气体标准品注入装有50 g未处理小麦和50 mL“Daft溶液”混合物的270 mL锥形瓶中，制备加标样品。

1.1.7 测定二硫化碳浓度

气相色谱参数：进样口温度，200 ℃；柱温，140 ℃；检测器，FPD；硫过滤器；玻璃填充柱，HayeSep Q（1 m × 3 mm）（Alltech2801）。

分析溶剂或液相顶空的二硫化碳，每次气相色谱进样前需要对色谱柱中的溶剂或溶剂蒸汽完全洗脱，因此进样间隔时间最少为15 min。

1.2 商业规模研究

1.2.1 实仓实验

实仓实验在SGRL的一个小麦筒仓进行，筒仓结构为焊接钢制自卸式，仓容为55 m^3。入粮前，用Silastic^{TM}对仓内铆钉和螺栓孔进行密封。装入约40 t小麦，按照Banks和Annis[23]的方法进行气密压力测试，半衰期大于4 min。将1 500 g（1 200 mL）二硫化碳（38 mg/m^3，w/w或27 g/m^3），密闭6天，出仓后继续通风散气1天。气体采样点包括粮仓中心、粮堆表层下1、2、3和4 m处、以及粮仓底部和顶部空间的4个等距方向和中心。通过DYNAVC泵（ODI型）从引出的尼龙管（内径3 mm）采集气体样本，装入Tedlar气体采样袋中，利用气相色谱法测量。出仓时，取3 t小麦接入三个Bulka袋中，每袋装1~1.5 t，装袋过程中用玻璃瓶从小麦流中抽取10~15个0.5 kg的样本。

试虫为赤拟谷盗（50只成虫和50只幼虫）、谷蠹（50只成虫）和米象（50只成虫）。所用虫笼为直径22 mm、高100 mm的不锈钢带孔圆筒，两端制成锥状体，以便插入粮堆中。虫笼内装有由95%小麦和5%小麦粉组成的试虫饲料。将虫笼埋入粮堆表层1.5 m深处，以中心位点和四周布置五个不同检测点。熏蒸散气后取出虫笼，检查记录即时害虫死亡率，并将这些试虫样品在30 ℃下继续培养4周和8周，统计死亡率。

实仓实验中使用含水量10.6%的澳大利亚白麦（ASW），不含杀虫剂。

1.2.2 制粉和烘焙实验

出仓后5 h内将3 t小麦送至面包研究所（BRI），进行小麦清理和制粉实验。烘焙、面条和意大利面加工方法参照面包研究所的常规商业配方和步骤。采用气相色谱法测量二硫化碳的含量。

2 结果与讨论

2.1 实验室研究

2.1.1 CS$_2$对发芽和芽长的影响

150 mg/m^{3}二硫化碳熏蒸后小麦、大麦和鹰嘴豆的发芽率如图1所示。所有实验重复4次，50粒种子的标准误差均小于2.5%，3种种子的萌发潜力均没有降低，即无论是150 mg/m^{3}高浓度还是14 d的长时间暴露，二硫化碳都不会对小麦、大麦和鹰嘴豆的萌发产生有害影响。这一结果与前期对用200 mg/m^{3}二硫化碳熏蒸20种种子和谷

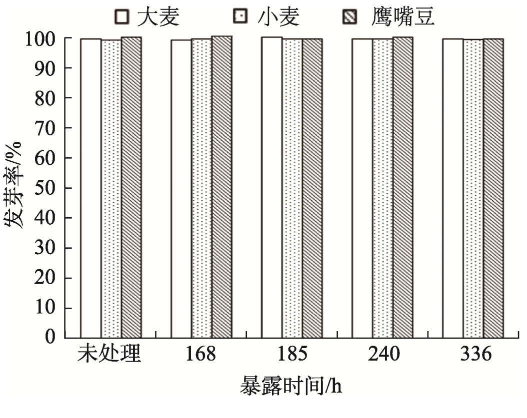


图1 暴露于150 mg/m^{3}浓度二硫化碳不同时间的样品发芽率

Fig.1 Percentage germinability of samples at dose 150 mg/m^3 of CS$_2$ and for different time of exposure

物（包括禾谷、豆类、含油种子和蔬菜种子）48 h 后结果一致[6]。Xiu 还指出，熏蒸剂对 20 种种子发芽的影响顺序为环氧乙烷 > 甲基溴 > 硫酰氟 > 二硫化碳，其中二硫化碳的植物毒性较低。Ghaly[7] 研究表明，即使 400~800 mg/m^3 高剂量和 48 h 长时间暴露，二硫化碳对 16%含水量的 Nahda 品种水稻的发芽率和幼芽长度也没有影响。Verma[24] 也研究了高剂量二硫化碳长时间熏蒸对种子发芽率的影响，发现低含水量小麦的发芽率不受影响，但随着含水量的增加，发芽率会降低。

所有处理组幼芽长度的标准误差都小于平均值的 8%。二硫化碳对小麦、大麦和鹰嘴豆的发芽幼芽长度没有影响（图 2）。与氰化氢（HCN）不同，较高浓度的二硫化碳也不会使幼芽长度降低，与用 100 mg/m^3 硫化二羰基对小麦幼芽长度的影响相似[19]。

2.1.2 熏蒸剂在谷物上的吸附作用

吸附结果表明，二硫化碳在所测谷物和豆类上的吸附量比甲基溴弱。图 3 表示测定浓度与施用浓度比值（C/Co）与时间的关系曲线（所有处理组熏蒸剂吸附的标准误差都小于平均值的 4%），均为经典吸附曲线，熏蒸剂衰减模式符合预期，即最初快速吸附到 10 h 后趋于平缓。

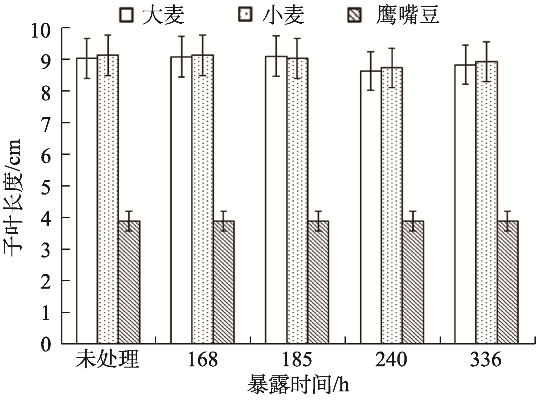


图 2 暴露于 150 mg/m^3 浓度二硫化碳不同时间的样品幼芽长度

Fig.2 Plumule length of samples at dose 150 mg/m^3 of CS_2 and for different time of exposure

熏蒸 10 h 后，二硫化碳浓度下降平缓。熏蒸 160 h，小麦、大麦和豌豆中的损失率分别在 50%、30%和 75%以下，而高粱、水稻和鹰嘴豆在 70%以下。二硫化碳衰减速度相对较慢，整个暴露时间仍然存在有效防治剂量。本研究中，所测禾谷和豆类对甲基溴吸附速度非常快，如在豌豆和鹰嘴豆或稻谷和高粱几天后就会发生反应而消失。

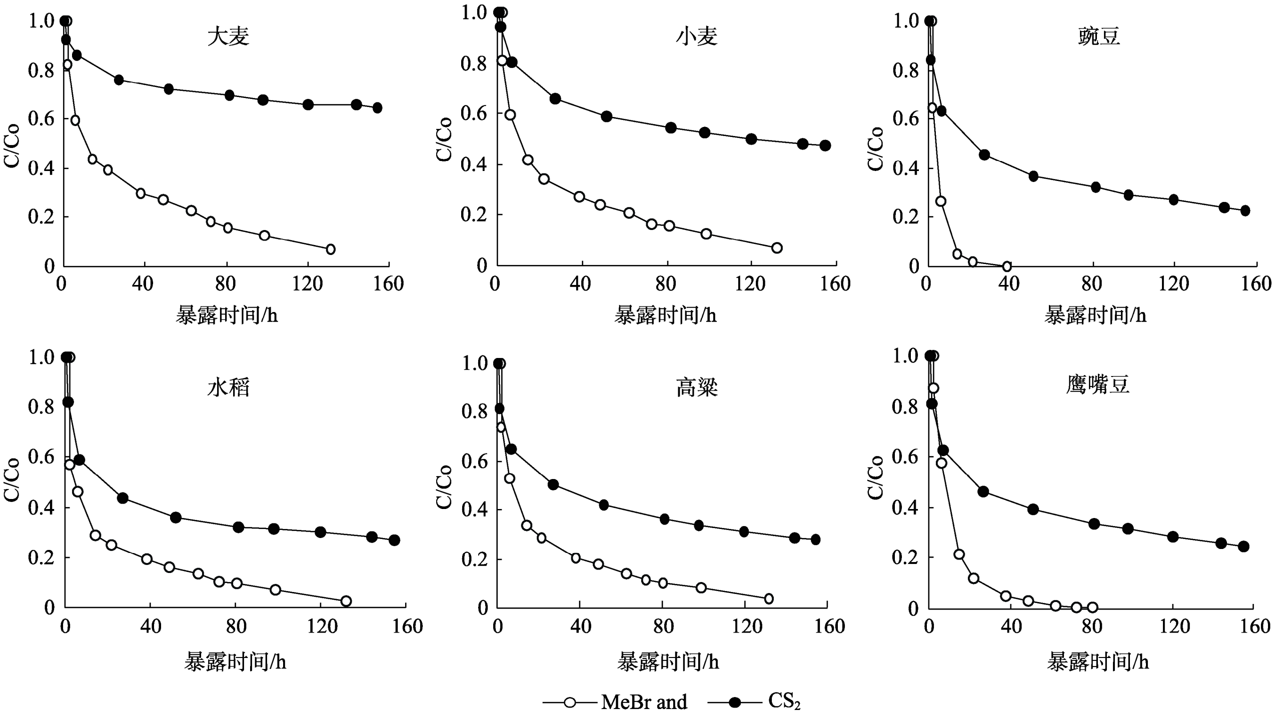
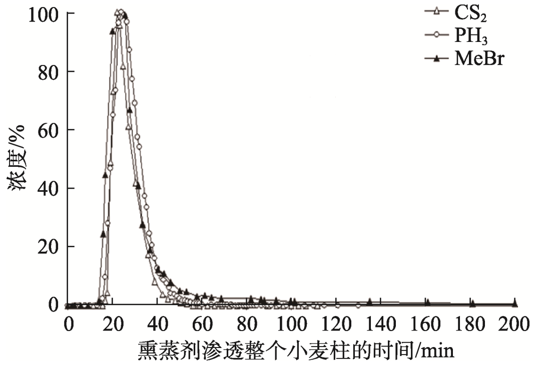


图 3 二硫化碳和甲基溴在谷物豆类上的吸附曲线

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

2.1.3 熏蒸剂在小麦中的扩散

图 4 显示三种熏蒸剂在小麦柱中的扩散性，从小麦柱远端排出气体浓度均大于 1 mg/m^3（v/v）。二硫化碳在小麦中的扩散特性与磷化氢和溴甲烷两种最广泛使用的熏蒸剂相似。磷化氢和二硫化碳的色谱分析图在保留时间、峰宽和拖尾程度方面基本相同，甲基溴峰宽更宽，拖尾明显，吸附性更强。二硫化碳能快速穿透麦柱，麦粒间空气中的含量低于 1 mg/m^3。



注：熏蒸剂浓度（%，为最大浓度的占比），从 1.1 m 的小麦柱中洗脱，风速为 200 mL/min。

Note: Concentration of fumigant, (% of maximum concentration) eluting from a 1.1 m column of wheat, at an air flow of 200 mL/min.

图 4 在 200 mL/min 的气流流速下，1.1 m 麦柱远端熏蒸剂浓度与时间的关系图

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, plotted against time

熏蒸剂在麦柱中穿透性是熏蒸剂吸附、解吸、渗透和扩散等因素的综合效应[25]。由于二硫化碳能快速且容易穿透小麦粮堆，所以它也可以通过通风方式快速从熏蒸谷物中解吸。这些优点是作为理想熏蒸剂的基本要求，由于能快速扩散解吸，从而保障谷物出仓和运输环节操作工人的健康安全。

2.2 商业规模熏蒸和小麦加工实验

2.2.1 密闭仓中二硫化碳的防虫效果

防虫效果如表 1 所示，熏蒸结束后，受试昆虫死亡率为 100%，并在 30 ℃条件下培养 4 周和 8 周后，没有后代出现。实验发现，二硫化碳平均浓度在第 4 天时降至 10.5 mg/m^3，第 6 天 7.7 mg/m^3。二硫化碳对所有受试昆虫的 CT 值（浓度×时间）在 1 000~1 500 (mg/h)/L，说明其对受试昆虫都有剧毒，起到快速防治作用。

表 1 实仓实验中害虫死亡率和子代数量

Table 1 Insect mortality and progeny in field trials

种类	熏蒸死亡率/%	4 周后子代数	8 周后子代数
T. castaneum（成虫）	100	0	0
T. castaneum（幼虫）	100	0	0
R. dominica（成虫）	100	0	0
S. oryzae（成虫）	100	0	0

2.2.2 清洗和润麦对小麦中二硫化碳残留的影响

本研究测定了熏蒸后的小麦经过清洗和润麦不同工序后二硫化碳的残留量，如图 5 所示，残留量逐渐减少。从 SGRL 工厂的筒仓出仓时，小麦中的二硫化碳含量约为 7 mg/kg（ppm，w/w），低于澳大利亚规定的最高残留限量 10 mg/kg。未经熏蒸的小麦中天然含有少量二硫化碳（0.03~0.08 mg/kg），这是因为在自然条件下，硫化羰基（COS）和硫氰酸盐的转化和分解可产生二硫化碳。本实验残留水平比 Hilton[5]使用 80 mg/m^3 二硫化碳处理气密性差且无通风散气农场仓中的燕麦时低 4~6 倍。

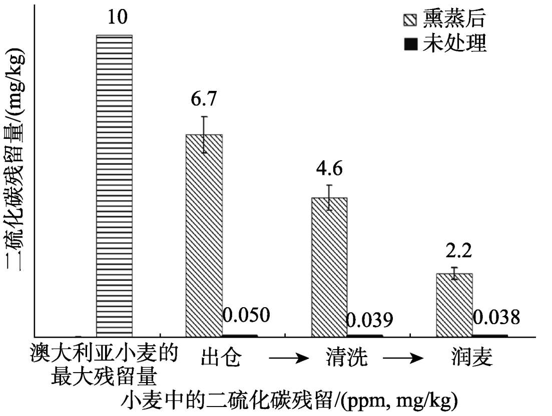


图 5 在小麦加工过程中二硫化碳残留量逐渐减少

Fig.5 Carbon disulphide residues in wheat are progressively reduced during processing of wheat

小麦清洗后，二硫化碳残留量从 6.7 mg/kg 降至 4.5 mg/kg。也就是说，清洗过程可清除大约 30%的二硫化碳残留物（图 5）。小麦的润麦可进一步将残留量从 4.5 mg/kg 降低到 2.2 mg/kg，约 30%残留量（图 5）。67%的二硫化碳残留物可在出仓、清洗和润麦过程中去除。在所有情况中，工作环境中的二硫化碳浓度都低于 10 mg/kg （v/v）的有害物最高允许浓度（TLV）。

2.2.3 加工对小麦粉制品中二硫化碳残留的影响

测定了制粉和烘烤不同工序对二硫化碳熏蒸后的小麦粉制品中残留量的影响，结果如图 6 所示。碾磨产品中，面粉或后路粉中的残留量最低，胚中的残留量最高，为 5.45 mg/kg，但这一水平也低于最高残留限量，高于润麦小麦的平均残留水平。也就是说，残留集中在胚中。麸皮中的残留量(2.62 mg/kg)略高于润麦后的平均残留水平。面粉或后路粉中的二硫化碳残留量分别为未处理小麦中含量的 3 倍和 10 倍。

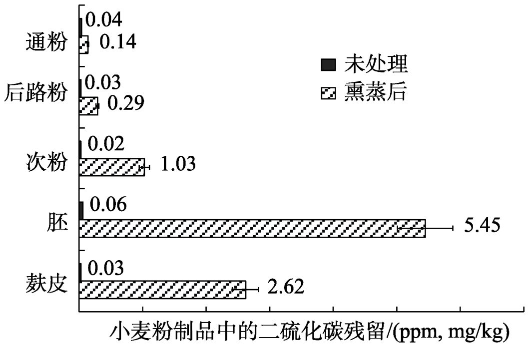


图 6 BRI 商业规模制粉实验小麦粉制品中的二硫化碳残留量

Fig.6 Carbon disulphide residues in wheat milled products on a commercial scale milling trials at the BRI site

2.2.4 烘焙和加工对小麦粉制品中二硫化碳残留的影响

采用熏蒸和未熏蒸的小麦磨出的面粉进行烘焙研究，烘焙和加工产品中的二硫化碳的残留量如图 7 所示。在面包和海绵蛋糕中含有少量二硫化碳残留物，含量为 0.2~2.5 ng/kg。即使在生的通心粉和生的面条中也仅发现少量二硫化碳残留物含量，为 2.2~4.0 ng/kg。在大多数情况下，处理组与对照组的数值差异不显著，与 Munsey[10]的研究结果一致，在用二硫化碳处理过的小麦粉制成的面包中检测出二硫化碳，与对照组不存在显著差异。

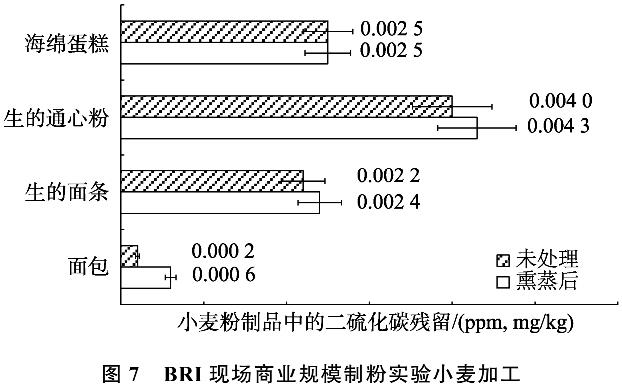


图 7 BRI 现场商业规模制粉实验小麦加工最终产品中的二硫化碳残留量

Fig.7 Carbon disulphide residues on processed wheat end products on a commercial scale milling trials at the BRI site

3 结论

本研究结果表明，二硫化碳对昆虫活性高，CT 值为 1 000~1 500 mg/m^3/h，杀虫速度快。与甲基溴不同，它的植物毒性低，即使在>150 mg/m^{3}高浓度下，对各种测试种子的发芽率和幼芽长度无影响。二硫化碳在谷物上的吸附性低于甲基溴，主要是物理吸附。二硫化碳会在谷物上残留，但在储藏和加工过程中能得到很大程度地降解。小麦最终产品中的二硫化碳残留量没有超过天然含量。因此，二硫化碳可取代甲基溴，用于密封农仓中种子熏蒸处理。

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A New Look at Carbon Disulphide as a Grain Fumigant (英文原文)

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Abstract: Although carbon disulphide (CS_2) is an old fumigant, the possibility of reintroducing it 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 in processed food. Egyptian data shown that CS_2 has no effect on the germination and plumule length of rice even at high doses (400 mg/m^3). Chinese data has shown that CS_2, at high doses (200 mg/m^3), has no effect on the germination of a large number of seeds, including malting barley, wheat and maize, sorghum, cotton, carrot etc. This is supported by current Australian data (150 mg/m^3) on germination and plumule length of wheat, barley and chickpeas. Australian data from the Stored Grain Research Laboratory (SGRL) commercial scale trial showed that all tested insects are killed by CS_2 at a range of C×T (concentration×time) values of 1 000~1 500 $mg \cdot h \cdot L^{-1}$ and has no effect on the quality of end products of wheat. The sorption of carbon disulphide on grain is lower than that for methyl bromide, and is mainly physical in origin. It leaves residues on grain, but these are extensively degraded during storage and processing. Remaining residues of CS_2 are reduced during cleaning and conditioning of wheat before milling. Residues of CS_2 are progressively reduced during the milling and baking processes. For example, wheat was treated at 27 g/m^3 of CS_2 for 6 days in sealed farm bin and then aired for 24 hours. Cleaning reduced residues from 6.7 to 4.6 mg/kg, and conditioning reduced residues from 4.6 to 2.2 mg/kg before milling. They are further reduced during milling, and further still during formation of noodles (even before cooking), pasta and bread. Residues in processed products were indistinguishable by current methods of analysis (limits of quantification were <0.005 mg/kg) and the same as levels present in products made from unfumigated wheat from the same source.

Key words: fumigant; carbon disulphide; sorption; germination; residues

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1 INTRODUCTION

Carbon disulphide (CS_2) is the oldest fumigant used for large commercial scale insect control in grain storage. It was the first US patented fumigant (1867, No. 64667), and used as a fumigant for grain in the US in 1896. It was used in France, in 1869, against the grape pathogen phylloxera. The use of CS_2 as a fumigant to control insects in grain and soil is a landmark in the history of applied entomology[1]. For many years afterwards, CS_2 was widely used as a grain, soil and space fumigant. Carbon disulphide has 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) have replaced CS_2 as a grain fumigant.

Carbon disulphide formulations, such as mixtures with nonflammable components such as carbon dioxide (CO_2) are still the only fumigant used in certain parts of the world, such as China[2-4]. It is also currently used by Australia growers in NSW[5]. The extensive work in China on more than 20 seed species showed that CS_2 does not affect seed viability even at a concentration of 200 mg/m^3[6]. Ghaly[7] showed that CS_2 had no effect on the germination and plumule length of Nahda variety rice even at high doses (400~800 mg/m^3). 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/m^3 and moisture content of 13%~19%[7].

Carbon disulphide penetrates well and compares favourably with phosphine, it is used in vertical silos without recirculation in China[1-2]. Sorption of CS_2 on grains, wheat flour, polished rice and legumes is as lower than that of methyl bromide, and seems to be mainly physical sorption, most of this is recoverable[3,8] Mapes and Shrader[9] 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.[10] 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 comparied with bread from untreated flour. The data of Mapes and Shrader[11] suggested that residues of CS_2 in milled fractions can be reduced by reducing CS_2 application rates. For example, Mapes and Shrader[11] found by reducing CS_2 rates of application 3 times (from 120 ppm to 38 ppm), 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[5]. The object of this paper is to re-examine CS_2 as a fumigant under today's storage conditions and quality management. Particularly, overreliance on phosphine (PH_3) which is used worldwide, as it is a registered grain fumigant, readily available and cost effective has resulted in increasing levels of insect resistance to PH_3[12]. Consequently, sulfuryl fluoride (SF) requires high concentrations or extended exposures to ensure complete control of egg stages. Moreover, SF is a fluorinated gas with a lifetime of 36 years and a 20-year Global Warming Potential (GWP) of 7510 (GWP is a measure of how a greenhouse gas's warming effect over a period compares to the warming effect of carbon dioxide over the same period)[13, 14]. Therefore, it is potential environmental safety challenge to use SF as fumigant. There is now an urgent requirement for the development of a fumigant that can kill all stages of insects quickly, and that is economic in comparison with other existing methods. Here, we re-evaluate 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.

2 MATERIALS AND METHODS

2.1 Laboratory trials

2.1.1 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), chickpeas (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 insecticide free.

Carbon disulphide as a liquid (99.9% purity and 1 250 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[15].

2.1.2 Germination Tests

Wheat, barley and chickpeas samples (10 g) were exposed at (25±2) ℃ to CS_2 (150 mg/m^3) 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[16], adapted by Ghaly and Van Der Touw[17]. 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 (e.g., 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.

2.1.3 Determination of Sorption of CS_2 on Grain and Pulse

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 (25 mg/m^3) was injected into the bottles, and also to 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 was plotted against time from addition of fumigant. A ratio (C/Co) of the headspace concentration (C) and initial concentration (Co) expressed as sorption at (25±2) ℃ and 90%~95% filling ratio. All samples were made in triplicate.

2.1.4 Determination of CS_2 Movement Through Wheat

The procedure used was as described in Desmerchelier[18]. 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.

2.1.5 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[19] and Ren and Desmarchelier[20]. 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[21] and further modified[22] by using gas-tight systems and headspace chromatography. The wheat sample (50 g) and 50 mL "Daft solution" (acetone (80%) in 25% phosphoric acid solution)[21] 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/m^3 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.

2.1.6 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.

2.2 Commercial Scale Studies

2.2.1 Field Trails

Field trials were conducted on wheat in a silo at the SGRL (Stored Grain Research Laboratory) site. The silo used was a welded steel, self outloading silo of 55 m^3 capacity. Before loading, the bin was sealed by coating rivets and bolt holes with Silastic^{TM} from inside the bin. The bin was filled with approximately 40 t wheat and pressure tested, as described in Banks and Annis[23]. A half-life of greater than 4 minutes was achieved. The wheat was treated with 1 500 g (1 200 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. The bin remain 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* (50 adult and 50 larvae), *Rhzopertha dominica* (50 adult) and *Sitophilus oryzae* (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 1 250 g/L density) was purchased from Ajax Australia.

2.2.2 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. 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.

3 RESULTS AND DISCUSSION

3.1 Laboratory Studies

3.1.1 The Effect of CS_2 on Germination and Plumule Length

The germination rate of wheat, barley and chickpeas after exposure to 150 mg/m^3 of CS_2 is 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/m^3, did not diminish the germination potential for all three types of seeds. That is, CS_2 had no deleterious effect on the germination of wheat, barley and chickpeas at either higher levels (150 mg/m^3) 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/m^3 for exposure periods of 48 hours[6]. 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 lower phytotoxicity. Ghaly[7] reported that CS_2 has no effect on the germination and plumule length of Nahda variety rice even at high doses (400~800 mg/m^3), 48 hours exposure and 16% moisture content. Verma[24] 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.

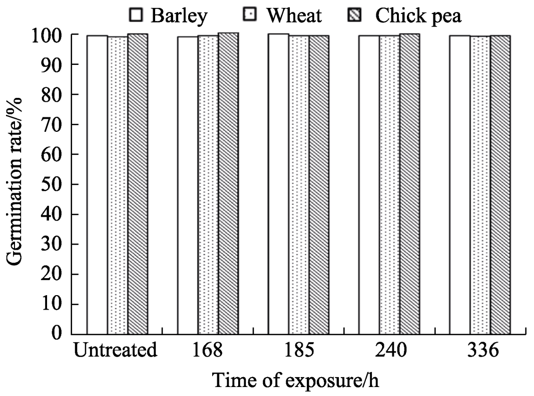

Fig.1 Percentage germinability of wheat at dose 150 mg/m^3 of CS$_2$ and for different time of exposure

The standard error in plumule length was less than 8% of the mean value in all cases. Carbon disulphide had no affect on the plumule length of germinated wheat, barley and chickpea (Figure 2).

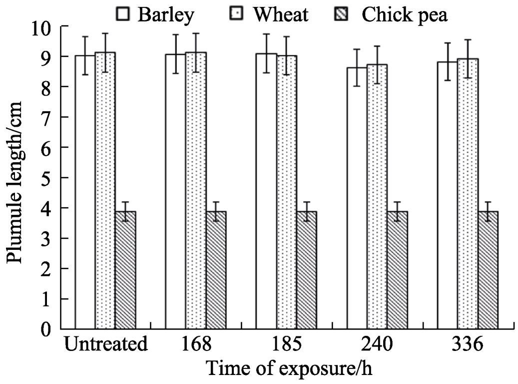

Fig.2 Plumule length of wheat at dose 150 mg/m^3 of CS$_2$ and for different time of exposure

Unlike hydrogen cyanide (HCN), it 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/m^3[19].

3.1.2 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 more less than MeBr.

The apparent loss of CS$_2$ after 10 hours from dosing was small. Even after 160 hours fumigation, loss was less than 50%, 30% and 75% for wheat, barley and peas respectively, and in the case of sorghum, paddy and chickpeas where less than 70% of CS$_2$ was lost. The decay of CS$_2$ is relatively slow and concentrations that are effective against insects are still present over the exposure period. 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 chickpeas or paddy and sorghum.

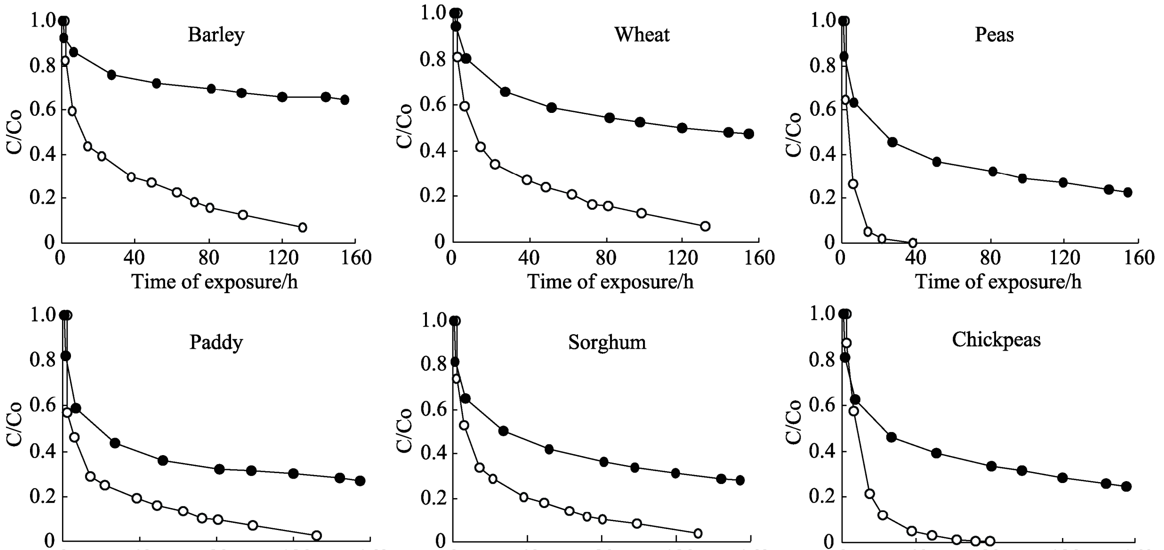

Fig.3 Comparative sorption data for CS$_2$ and MeBr, taken from measurement of loss of fumigant concentration in the headspace (—O—MeBr and —|—CS$_2$)

3.1.3 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. Carbon disulphide moved rapidly through or was blown out of a wheat column, to levels below 1 ppm in the intergranular air.

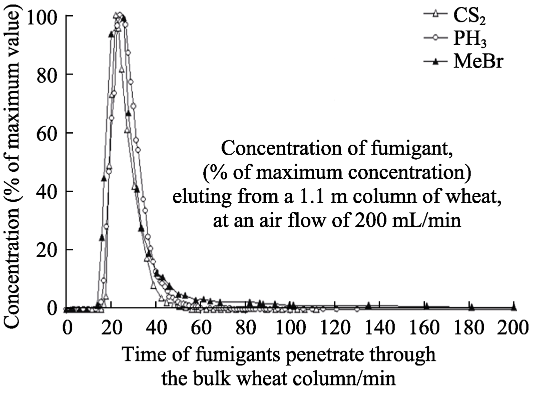

Fig.4 Concentration of fumigant, (% of maximum GC area) eluting from a 1.1 m column of wheat, at an air flow of 200 mL/min, plotted against time (—O—CS_2, —l—PH_3 and —s—MeBr)

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[25]. 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.

3.2 Commercial scale Fumigation and Wheat Processing Trials

3.2.1 The Effect of CS_2 on Control of Insect 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/m^3 at day 4, and this concentration fell to 7.7 mg/m^3 at day 6. That is, the (C×T) values of CS_2 against all tested insects of species were in the range of 1 000~1 500 mg h/L. This result showed that CS_2 was highly toxic to all tested insects, and killed them quickly.

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

3.2.2 The Effect of Cleaning and Conditioning on CS_2 Residues in Wheat

Residues of CS_2 were determined at various stages of the 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. The residue levels of CS_2 from this trial are 4~6 times lower than the data from Hilton et al.[5] using CS_2 to treat oats at 80 mg/m^3 in an unsealed farm bin without aeration.

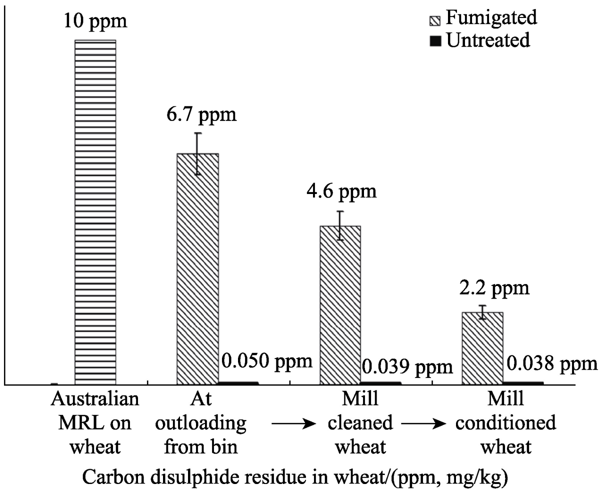

Fig.5 Carbon disulphide residues in wheat are progressively reduced during processing of wheat

Cleaning of wheat reduced residues of CS_2 from 6.7 to 4.5 mg/kg. That is, approximately 30% of the CS_2 residues were removed during wheat cleaning (Figure 3). Conditioning of wheat further reduced residues of CS_2 from 4.5 to 2.2 mg/kg, approximately another 30% of the CS_2 residues were removed during this stage (Figure 3). 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 workspace were below the TLV of 10 ppm (v/v).

3.2.3 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.

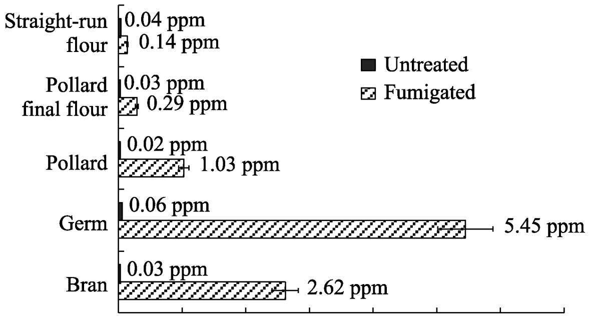

Fig.6 Carbon disulphide residues in wheat milled products on a commercial scale milling trials at the BRI site

3.2.4 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 0.2~2.5 ng/kg was found in bread and sponge cake. Even in uncooked pasta and uncooked noodles, only small residues of CS_2 were found (2.2~4.0 ng/kg). In most cases, these values were not significantly different from those in the controls. These results are consistent with Munsey et al.[10] who found no additional CS_2 in the bread, which was made from CS_2 treated wheat flour, compared with bread from untreated flour.

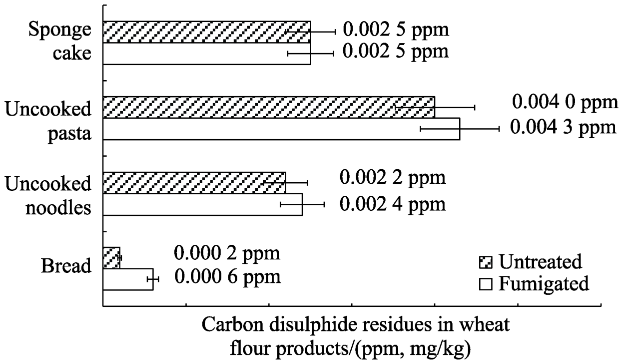

Fig.7 Carbon disulphide residues on processed wheat end products on a commercial scale milling trials at the BRI site

4 CONCLUSION

In this study, the results indicate that CS_2 is highly toxic to insects (C×t value of 1 000~1 500 mg h/L) and kills insects quickly. Unlike methyl bromide, it is low in phytotoxicity and has not effect on germination and plumule length even at very high concentrations (>150 mg/m^3) on the diverse variety of seed types tested. 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. Therefore, carbon disulphide can be used as a fumigant to replace MeBr in sealed farm bins, particularly for seed treatments.

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