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Fumigation trial on direct application of liquid carbonyl sulphide to wheat in a 2500 t concrete silo

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Abstract

Wheat (Australian Standard White) with a moisture content of 10.2% was fumigated with carbonyl sulphide (COS) at a calculated application rate of 24.14 g m^{-3}, in a sealed concrete vertical silo (3512 m^3, 2500 t wheat) located at Nevertire, NSW, Australia. The COS was applied as a liquid via the top of the silo and released 2 m below the grain surface. The application of 84.5 kg of COS was completed within 30 min. With 2 h of recirculation using a 0.4 kW fan, the in-silo concentrations of COS achieved equilibrium with a concentration variation less than 5% of the mean. After a two-day exposure period, the COS concentration in the silo remained at 29 g m^{-3}. The concentration × time product (*Ct*) was then 1900 g h m^{-3}, and this achieved complete kill of all life stages of mixed-age cultures of *Sitophilus oryzae*, *Rhyzopertha dominica*, *Tribolium castaneum* and *Trogoderma variabile*. After 2-days exposure, the silo was aired overnight with an aeration fan (25 kW) resulting in a COS in-silo concentration of below 4 ppm. This is 2.5 times lower than the Australian Experimental Threshold Limit Value (TLV) of 10 ppm. Residues of COS in the wheat declined to below the Australian Experimental Maximum Residue Limit (MRL) of 0.2 mg kg^{-1} after overnight aeration. The COS was not detected in any outloading samples at concentrations above the detection limit (0.05 mg kg^{-1}). The workspace and environmental levels of COS were monitored during application, fumigation, aeration and outloading. The levels of COS and hydrogen sulphide (H_2S) were less than the detection limit of 0.1 ppm, which was 100 times lower than the TLV of 10 ppm. The treatment with COS had no affect on the wheat germination and seed colour when compared with untreated controls. Oil quality tests showed that COS had no effect on total lipid (made from treated wheat) content or the lipid colour.

Keywords: Fumigant; Fumigation; Carbonyl sulphide; Wheat; Insect; Grain storage; Residue

1. Introduction

Carbonyl sulphide (COS) is a candidate fumigant identified and developed by CSIRO Entomology for stored durable commodities (Desmarchelier, 1994; Plarre and Reichmuth, 1997; Ren, 1997; Zettler et al., 1997; Weller, 1999; Ren et al., 2000, 2003a; Reuss et al., 2003). Its chemistry (Ferm, 1957; Paris and Thomas, 2002), toxicity (Haritos, 2000) and environmental fate (Payton et al., 1978; Mihalopoulos et al., 1989; Ren, 1997) have been reviewed. Many natural sources of COS have been identified, including oceans, soils, volcanoes and marshes (Adams et al., 1981; Khalil and Rasmussen, 1984; Brown et al., 1986; Ren, 1999). The COS is present naturally in plants and thus in a range of raw and processed foodstuffs, including cereals and oilseeds. The natural levels of COS in grains and oilseeds were found to be 0.02–0.07 mg kg^{-1} (Ren, 1997; Desmarchelier et al., 1998b; Ren and Desmarchelier, 2002; Ren et al., 2002).

In previous laboratory studies and commercial-scale (50–500 t) trials on wheat, barley, oats and canola, it has been shown that COS has excellent physical, chemical and biological fumigant functions (Desmarchelier et al., 1998b; Ren et al., 2000, 2003a, b; Reuss et al., 2003) as follows:

- A concentration × time product (*Ct*) of 1650–1950 mg h L^{-1} at grain temperatures of 10–35 °C produced complete mortality of all life stages of *Sitophilus oryzae* (L.), *Rhyzopertha dominica* (F.), *Tribolium*

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castaneum (Herbst), *Trogoderma variabile* Ballion, *Oryzaephilus surinamensis* (L.), *Cryptolestes ferrugineus* (Stephens), *Ephestia cautella* (Walker) and psocids.

- Residues after fumigation and aeration were indistinguishable from levels in unfumigated wheat, barley, oats and canola.
- There was no effect on germination, seed colour, oil colour or the quality of bread, noodles or sponge cakes made from the fumigated wheat.
- In comparison with both gaseous phosphine and methyl bromide, COS gas rapidly penetrated and diffused through the grain bulk.
- During application, fumigation and aeration, the levels of COS in the workspace were <10 ppm (Threshold Limit Value—TLV).

This report describes a commercial-scale silo (2500 t) trial that was needed to satisfy the Australian Pesticides and Veterinary Medicines Authority (APVMA) requirements for registration, as fumigant efficacy and Occupation Health & Safety (OH&S) conditions may vary with application and silo type and size.

2. Materials and methods

2.1. Storage structure and grain source

The silo used was of monolithic concrete construction and was located at GrainCorp Nevertire, NSW, Australia. It was 17.8 m high (wall height), 15 m in diameter with a loading capacity of 2500 t wheat (3512 m^3). It was self-outloading with a conical roof and bottom (Fig. 1). To ensure gas tightness, the top hatch and outloading chute were sealed with rubber gaskets. The silo was fitted with a phosphine recirculation system which was attached to the aeration ducting. Inside the silo, an aeration duct was divided into two arms (0.9 m × 0.9 m × 6.5 m) and was located across the diameters of the cone at the bottom of the silo. This duct served as part of the phosphine recirculation system which included an external metal pipe (100 mm i.d.) running from the top of the silo to the ground where it was connected to a recirculation fan (0.4 kW) with a capacity of 300 $m^3 h^{-1}$. The recirculation fan was flash proofed in accordance with the requirements for fumigation with phosphine. An aeration fan (25 kW) with a capacity of 1500 $m^3 h^{-1}$ was also situated outside the base of the silo and could be connected to force external ambient air upwards into the silo.

The wheat used in this trial was Australian Standard White (ASW) owned by the Australian Wheat Board Limited (AWB).

2.2. Insects and bioassays

Four species of stored product insects were used for bioassays. They were mixed-age cultures of *S. oryzae*, *R. dominica*, *T. castaneum* and *T. variabile* which were established by adding adults (400–500) to media (1 kg) at 25 °C and 55% r.h. The adults were left on the media (sterilised wheat for *S. oryzae* and *R. dominica*, wheat flour + yeast for *T. castaneum* and sterilised crushed canola for *T. variabile*) for 4–5 weeks, by which time there were representative numbers from each stage—egg, larva, pupa, and adult—based on knowledge of development rates (Howe, 1952; Beckett et al., 1994). The insects were sourced from CSIRO susceptible strains (CLS2, CRD2, CTC4 and CTRV3, respectively) held at the CSIRO Entomology Laboratory, Canberra, Australia. Culturing and general handling techniques followed those described in Winks (1982). Data from these strains can be compared with laboratory bioassays and field results on several species of insects. Bioassays were conducted by placing (33) brass cylindrical cages (150 mm × 30 mm inside diameter (i.d.)) at various points within the grain bulk. Each cage contained a mixed-age culture of either *S. oryzae*, *R. dominica*, *T. castaneum* or *T. variabile*, in standard laboratory culture medium, of approximately 80–250 adults, and an unknown quantity of eggs, larvae and pupae. A cage of each of the above species was placed at the various gas sample sites in the grain bulk to be fumigated. A control cage was placed in a bucket of the unfumigated grain to check for residues from any previous treatments. The caged insects were

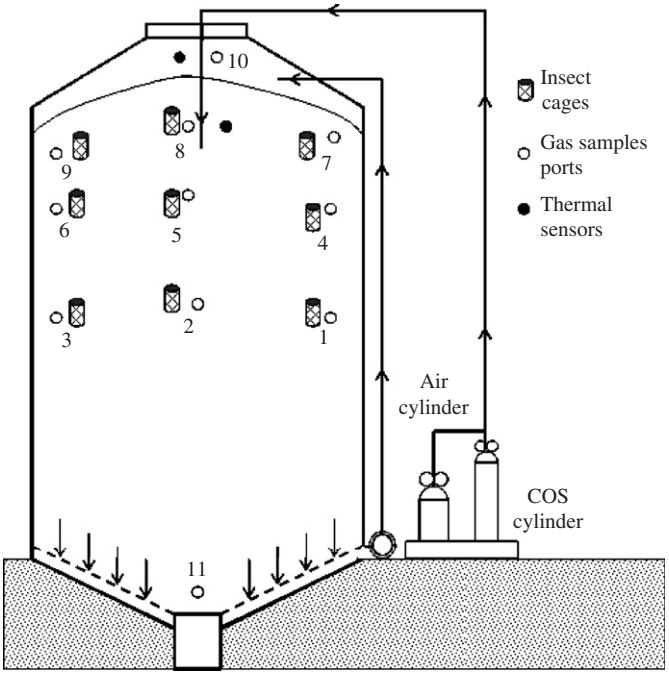

Fig. 1. Schematic representation of a 2500 t concrete silo, gas sampling ports (1–18) and carbonyl sulphide application system at Nevertire, NSW. Gas sample ports 1 and 3 located at 6 m below the grain surface, and 0.5 m from silo wall; gas sample ports 4 and 6 located at 3 m below the grain surface, and 0.5 m from silo wall; gas sample ports 7 and 9 located at 1 m below the grain surface, and 0.5 m from silo wall; gas sample ports 2, 5 and 8 located at 6, 3 and 1 m below the grain surface, and central in the silo; gas sample port 10 located at 0.2 m above the grain surface and central in the headspace; and gas sample port 11 located 20 cm above the bottom of the silo.