



Sorption and desorption of sulfuryl fluoride by wheat, flour and semolina



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ABSTRACT

Sulfuryl fluoride (SF) has been developed as a fumigant for control of insect pests in stored grain. However, there is very limited information on the sorption behaviour of this fumigant, which can be critical to its bioactivity, application and potential for residues. We undertook a comprehensive laboratory study of the sorption and desorption of SF by wheat (bread and durum), flour and semolina at 15, 25 and 35 °C, moisture contents 12% and 15%, and concentration × time combinations at CT = 1500 mg/h/L (4.167 mg/L × 360 h, 8.928 mg/L × 168 h and 31.25 mg/L × 48 h).

At each dosage, sorption rate increased as commodity temperature and moisture content increased. The highest rates of sorption occurred at 35 °C and 15% m.c., and lowest rates at 15 °C and 12% m.c., and the rate was independent of initial concentration. Sorption followed first order reaction kinetics described by the exponential decay equation, $C_t = C_0 \cdot e^{-k \cdot t}$, where k is the sorption rate constant. The most important factors determining the rate of sorption were commodity particle size (exposed surfaces) and temperature. Little sorption of fumigant occurred within the first 24 h whereas longer fumigation times resulted in significant sorption. Unbound SF was rapidly lost from the commodity upon aeration with no further desorption detected under any of the test conditions.

SF possesses a number of characteristics that recommend it as a commodity fumigant. It is sorbed slowly by commodities relative to methyl bromide and carbonyl sulphide although it is sorbed about 4–5 times faster than phosphine. It desorbs rapidly upon aeration, and the lack of continued desorption has practical workplace health and safety benefits. On the other hand, sorbed SF appears irreversibly bound to the commodity matrix indicating the need to be alert to the possibility of excessive residues, particularly in longer term fumigations.

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1. Introduction

Effective control of insect pests with fumigants depends on maintaining the fumigant gas at the desired concentration for sufficient time for the chemical to exert its full toxicity. In practice, several factors influence the performance of fumigants. These include gas-tightness of the fumigation container (or storage structure, e.g. silo), the physical properties of the fumigant in

relation to environmental factors such as temperature and atmospheric pressure, and the physical and chemical interaction between the fumigant and the commodity. The terms sorption and desorption are used to describe the uptake and release of fumigant gases by commodities, respectively, and these phenomena can have a significant impact on fumigant concentrations in sealed storages (Banks, 1989). Not only can sorption reduce fumigant effectiveness, the uptake of fumigant by commodities may also result in chemical reaction with the commodity leaving unwanted residues (Banks, 1993).

Sorption of fumigants into cereal grains usually occurs in two phases (Banks, 1986; Bond, 1984; Darby, 2008). There is an initial rapid diffusion of gas into the grain, which is believed to be a

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reversible physical process. This is followed by a slower phase in which the fumigant may react with components in the grain to give fixed residues or be bound by physical processes. This dual-phase pattern has been observed to varying degrees with several fumigants including hydrogen cyanide (Lubatti and Harrison, 1944), methyl bromide (Winteringham and Harrison, 1946), phosphine (Daglish and Pavic, 2009) and ethyl formate (Darby et al., 2009). The amount and rate of loss of a particular fumigant through sorption in a sealed system is determined by several factors. The most important of these are the innate properties of the commodity and its state of subdivision, commodity temperature and moisture content, and fumigant concentration and exposure period (Banks, 1993; Braby, 1992; Daglish and Pavic, 2008). Depending on the reactivity of the fumigant, sorption can be partially reversible. Initially in the desorption process, fumigant rapidly diffuses from the commodity (Dumas, 1980), and this is followed by gradual release of “physically-bound” material (Banks, 1986), which may be accelerated by increasing the temperature (Banks, 1986) or grinding the grain into flour (Lindgren et al., 1962).

The fumigant, sulfuryl fluoride (SF) was originally developed to control termites in structures (Stewart, 1957). During the past decade, SF has also been registered internationally for control of stored-product pests in food handling facilities (grain processing, mills, warehouses etc.) and stored grain (Prabhakaran, 2006). In Australia, SF has been registered for disinfestation of bulk cereal grain and is a key component in the management of phosphine resistance in some insect pest populations (Nayak et al., 2010). Information on sorption of SF into wheat and wheat products is quite limited. It has been reported to be low for wheat and medium for whole wheat flour (Sriranjini and Rajendran, 2008), however, these data relate to 24 h exposure periods only. To achieve complete control of pest populations in bulk grain in Australia, it has been found that longer fumigation times, 7–15 days, are required (R. Kaur and M.K. Nayak, personal communication). Concentrations of SF applied for longer fumigation times are lower as the concentration \times time (CT) protocols must not exceed the maximum allowable CT of 1500 mg/h/L. The sorption and desorption behaviour of SF in these longer term fumigations is unknown. Given the potential risk of fluoride residues (APVMA, 2007; EPA, 2011) and the possible effect on insect control, it is imperative that we understand this behaviour under various storage conditions.

In these experiments we exposed whole wheat and durum grain, flour and semolina to a range of SF applications. Our aim was to quantify the process of sorption and desorption of SF in these commodities under a range of storage conditions that might typically be encountered in bulk storage facilities, flour mills and other processing facilities used in many countries.

2. Materials and methods

2.1. Experimental design

The experimental design consisted of a randomized complete block with three replicates. Four different factors were tested: commodity (hard wheat kernels, durum wheat kernels, flour made from hard wheat and semolina made from durum wheat); storage temperature (15, 25 and 35 °C); commodity moisture content (m.c., 12 and 15%), and fumigant concentration \times exposure time (CT product). Three CT products were tested that represent the likely range of fumigations (4.167 mg/L \times 360 h, 8.928 mg/L \times 168 h and 31.25 mg/L \times 48 h) each of which gives a total CT product of 1500 mg/h/L, the maximum CT registered for this fumigant in Australia. The temperature and moisture contents represent the range of these conditions likely to occur in a typical grain storage system or flour mill.

2.2. Preparation of test samples

Wheat and flour (hard white, cultivar Gregory) were purchased from a certified organic producer on the Darling Downs, southeast Queensland, Australia and stored in 20 kg bags at –20 °C. Durum wheat (cultivar EGA Bellaroi) was a gift from Weston Milling, Brisbane, Australia; and the durum semolina, ground at the same mill, was purchased locally.

Before conditioning the commodity to the desired moisture content and temperature, one bag of the commodity was brought from the freezer and left unopened at room temperature (22 °C) for 2 d for equilibration with laboratory temperature. The moisture content of each commodity was determined using AACC recommended Air-Oven Method 44-15.02 (AACC, 2010) and adjusted to the required m.c. using distilled water. Samples of wheat grains were ground using a manual grinder (Spong and Co Ltd, No. 2) to avoid changing the moisture content during the grinding process.

2.3. Experimental units

Each treatment replicate consisted of a glass Erlenmeyer flask of ~2.4 L containing the commodity at the required temperature and moisture content. After achieving the desired moisture content for the commodity, each flask was filled with the commodity to 50% flask volume (filling ratio of 0.50). Flasks were then held at 15, 25 or 35 °C for two days to attain equilibrium temperature.

Each flask was sealed with a glass stopper containing a silicone rubber septum for addition of fumigant and gas sampling. The exact volume of each experimental flask was pre-determined by filling with water to the base of the stopper then weighed. Flasks were then placed in a glassware cabinet at 60 °C for 24 h for complete drying.

2.4. Fumigation process

SF purity of 99.8% in a 3 L cylinder was a gift from SA Rural Agencies Pty Ltd (Wingfield, South Australia). Before fumigation, the SF was decanted from the cylinder into a Flex foil gas sampling bag for sulfuryl compounds and low molecular weight gases (SKC, www.skcin.com). A range of volumes of gas were then taken from the bag using a gas tight syringe to construct a standard curve for gas concentration. SF concentration was measured using a gas chromatograph (Perkin Elmer, Claris 500) fitted with a thermal conductivity detector (TCD) and type SS Column Porapak N 50/80, column size was 3.66 m \times 3.2 mm OD. The injection port temperature was 200 °C, and the carrier gas was helium at 124.1 kPa and 20 mL/min flow rate. The oven temperature was 100 °C and the detector was 250 °C.

At the commencement of each experiment, the appropriate amount of SF to be added to each experimental unit was calculated based on the volume of each flask. Volumes of SF were then taken from the gas bags using a gas tight syringe and injected through the septum into each flask. Flask stoppers were coated with silicone grease to prevent leakage of gas. Flasks were then moved to storage rooms set at the test temperature. To ensure that there was no loss of gas from test flasks, control flasks injected with SF but without grain were included in all experiments.

2.5. Measuring sorption

Gas samples (5 μ L) were removed at intervals from the head-space of each experimental flask using a gas tight syringe. Experiments at 4.6 mg/L \times 360 h and 8.9 \times 168 h were sampled at 4, 24 and then every 24 h to 360 or 168 h, respectively, while experiments at 31 mg/L for 48 h were sampled at 4, 8, 12, 24, 28, 32, 36

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