

Sorption and desorption of sulfuryl fluoride into wheat and flour

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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 and flour at typical industrial grain storage temperatures (15, 25 and 35°C), moisture contents (m.c.) (12% and 15%), and concentration x time combinations at CT=1500 mg/L (4.167 mg/L x 360 h, 8.928 mg/L x 168 h and 31.25 mg/L x 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% MC, 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, $C_t = C_0 e^{-k \cdot t}$, 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 other common fumigants such as phosphine and methyl bromide. 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.

Keywords: sulfuryl fluoride, sorption, wheat, flour, semolina

1. Introduction

During the past decade, the fumigant sulfuryl fluoride (SF) has been registered internationally for control of stored-product pests in stored grain and food handling facilities (Prabhakaran, 2006). In Australia, SF is used to disinfest bulk cereal grain and is a key component in the management of phosphine resistance in some insect pest populations (Nayak et al., 2010). An important factor influencing the performance of fumigants, in practice, is their uptake and release by commodities. This process, known as sorption and desorption, respectively, can have a significant impact on fumigant concentrations (Banks, 1989) and potentially, on the presence of unwanted chemical residues (Banks, 1993). The amount and rate of loss of a particular fumigant through sorption is determined by several factors including, 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; Daghilish and Pavic, 2008).

Data on sorption of SF into cereals and cereal products is limited to a brief report of %loss under 24 h exposure periods (Sriranjini and Rajendran, 2008). However, it has been found in Australia that longer fumigation times, 7-15 days, are required for control of pest populations (Kaur and Nayak, personal communication). Concentrations of SF applied for longer fumigation times are lower as the concentration x time (CT) protocols must not exceed the maximum allowable CT of 1500 mgh/L. The sorption and desorption behaviour of sulphuryl fluoride 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 flour to a range of SF applications. Our aim was to observe and 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

Each treatment replicate consisted of a glass Erlenmeyer flask of ~2.4 L containing the commodity (wheat or flour) at the required temperature and moisture content. 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. The moisture content of each commodity was determined using AACC recommended Air-Oven Method 44-15.02 (AACC, 2010). Each flask was sealed with a glass stopper containing a silicone rubber septum for addition of fumigant and gas sampling.

2.1. 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.skcinc.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).

2.2. Measuring sorption

Gas samples (5 µL) were removed at intervals from the headspace of each experimental flask using a gas tight syringe. The experimental SF concentrations were measured using a flame photometric detector (FPD).

2.3. Measuring desorption

At the end of the experimental exposure period the stoppers were removed from the flasks and the commodities were transferred from the flasks onto flat trays (200 x 350 mm) and kept in a fume hood for 10 min. This was to allow any unbound gas to be removed from the sample. The samples were then returned to their original flasks and sealed with gas-tight stoppers. The flasks were stored at 25°C and samples of gas were removed from the headspace, initially daily for 3 weeks, and then monthly for 18 months. SF concentration was measured using a gas chromatograph fitted with FPD.

2.4. Statistical analysis

The data were analysed using SAS program version 6 for windows and the NLIN procedure was used to quantify the exponential decay of the fumigant with time (Freund and Littell, 2000).

3. Results

At time zero (0 h), there were no significant differences among all the treatments in initial gas concentrations. The SF concentration in the flask head space declined significantly for each treatment over time and this loss was best described by an exponential relationship between concentration and time, $C_t = C_0 e^{-k*t}$, with R^2 values for fit ranging between 0.91 and 0.99. In these equations, the rate constant of sorption, k , indicates the loss of fumigant over the specific storage period.

3.1. Sorption of SF into commodities

Sorption of SF into flour was much greater than into whole grain at the three concentrations tested. For example, at the lowest concentration, 4.167 mg/L (25°C, 12% m.c.) at 0 h, SF concentrations in wheat and flour treatments were 5.880 and 5.353 mg/L, respectively but by the end of the experiment (360 h), these concentrations fell to 2.64 mg/L for wheat and to undetectable level at 96 h for flour (Fig. 1). Similarly, at the highest concentration, 31.25 mg/L (25°C, 12% m.c.), the initial concentrations (0 h) for wheat and flour were 44.097 and 40.144 mg/L, respectively, however these had decreased to 28.50 mg/L and 9.059 mg/L, respectively, by the end of the fumigation (48 h).

Rate of sorption, k , was much higher in flour than whole wheat, at each SF concentration. For example, at 4.167 mg/L, sorption rate, k , of flour was 0.0400 and 0.00658 for wheat. This shows about 6-fold greater sorption by flour than wheat (Fig. 1). Under typical Australian grain storage conditions of 25°C and 12% grain MC, the rate of sorption in flour was about 4.7-fold greater than that of wheat at the dosage of 8.928 mg/L for 168 h.

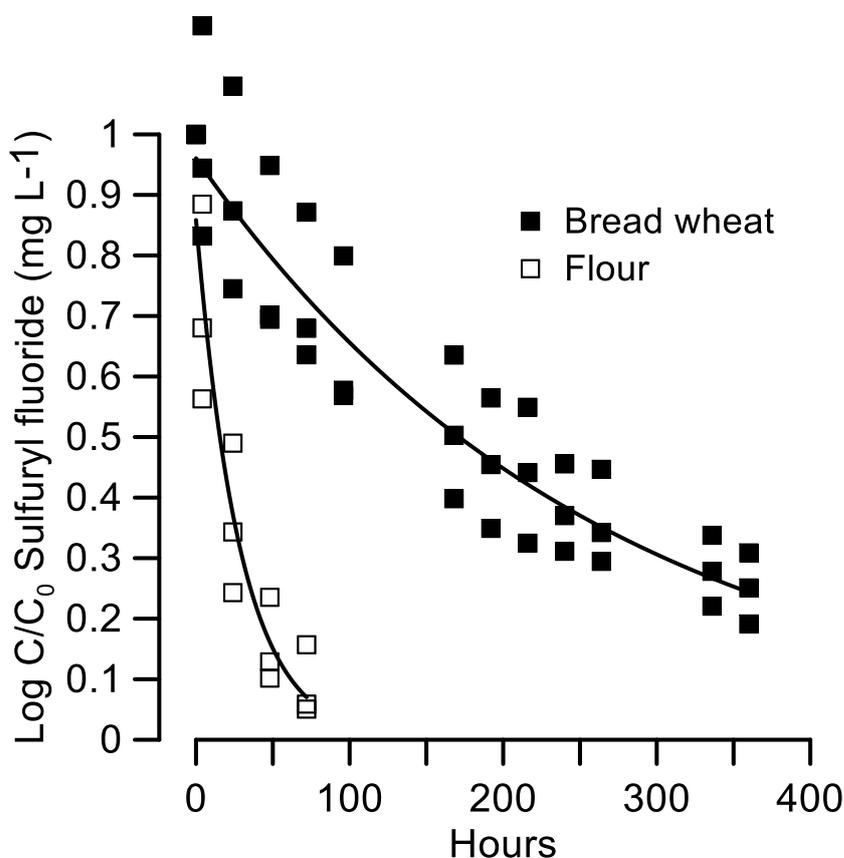


Figure 1 Sorption of sulfuryl fluoride into wheat and flour at 25°C and 12% moisture content. Sulfuryl fluoride was applied at 4.167 mg/L.

3.2. Effect of temperature on sorption of SF

Sorption of SF was significantly higher at 35°C than at the lower temperatures and higher at 25°C than at 15°C at every fumigation CT/m.c. combination for both commodities. For example, at 4.167 mg/L, concentrations at the completion of the fumigations (360 h) were 0.943, 0.359 and 0.048 mg/L for 15, 25 and 35°C, respectively, while at 8.928 mg/L (168 h), final SF concentrations were 8.96, 5.24 and 1.62 mg/L for 15, 25 and 35°C, respectively. At the three concentrations tested, the rate of sorption, k , increased substantially with increase in temperature at both 12 and 15% MC with both commodities. For wheat and flour fumigated at 4.167 mg/L for 360 h at 12% m.c., k was 2.8 and 2.7 times higher, respectively, at 25°C than at 15°C, and 7.6 and 5.4 times higher, respectively, at 35°C than at 15°C (Fig. 2).

3.3. Effect of moisture content on sorption of SF

SF concentration decreased significantly with increase in m.c. from 12 to 15% for each commodity and all temperature/CT combinations as %loss/h was always greater at 15% m.c. Rate of sorption, k , increased with m.c. across all temperatures and both commodities (Fig. 2).

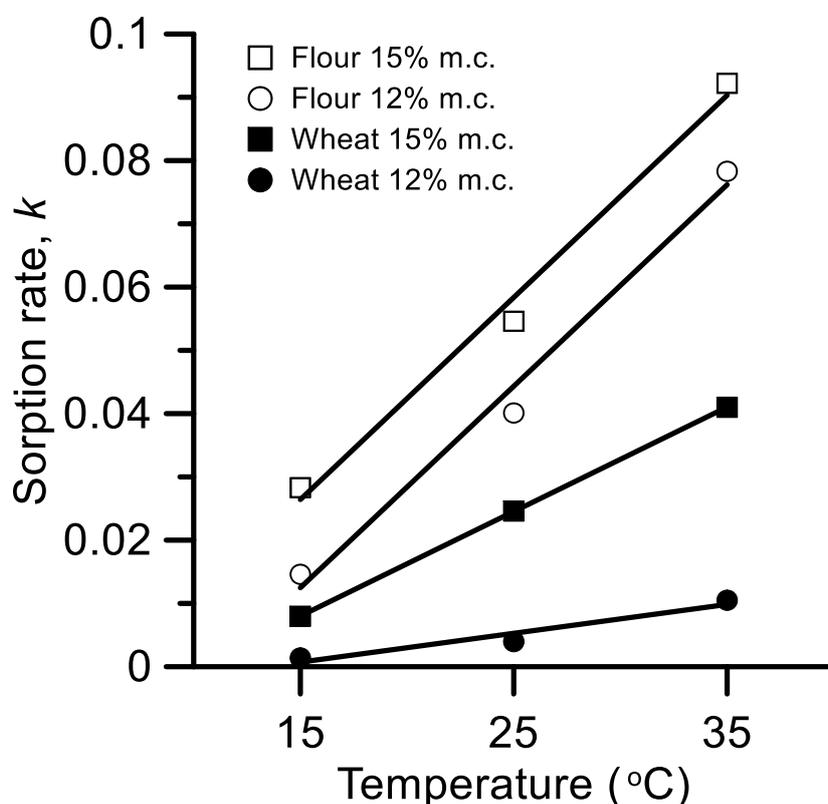


Figure 2 Rate of sorption, k , of sulfur dioxide into flour and wheat at two moisture contents and three temperatures. Sulfur dioxide was applied at 4.167 mg/L for a fumigation period of 360 h.

3.4. Desorption of SF from commodities

Flasks containing fumigated commodity were stored for 18 months after the 10 min aeration period and the headspace was sampled initially daily, then monthly. Throughout this period, SF concentrations were below detectable levels (data not shown) indicating that there was no significant desorption of SF from grain or flour.

4. Discussion

The rate of sorption of SF increased with temperature and MC in both commodities and it was most strongly sorbed at the highest temperature-moisture content regime. In addition, rate of sorption was higher flour than in wheat. However, initial concentration did not appear to influence sorption rate. The most striking result of this work was the failure to detect desorption of SF from any of the tested commodities. Exponential decline in SF concentration was observed with both commodities and storage conditions tested with very good fit (R^2) of the data to the model $C_t = C_0 e^{-k^*t}$. Other reports of SF decay are not available, however, a first order model of sorption has also been reported for other fumigants including methyl bromide (Hilton and Banks, 1997a), phosphine (Daglish and Pavic, 2008), ethyl formate (Hilton and Banks, 1997b; Weller, 2003) and dichloromethane (Banks, 1993). Other more complex models, based on exponential decay, have also been developed (Darby 2008; Darby et al., 2009). The high goodness of fit of our model indicates that sorption, in general, occurs at a constant rate, k , under the given conditions. This provides a basis for analysis of SF sorption under various conditions and for comparison with other fumigants (Banks, 1993). We used the method of Banks (Banks, 1986; Hilton and Banks, 1997a) to adjust for filling ratio when calculating k values.

Limited published information concludes that sorption of SF into food commodities is generally low or moderate compared with other fumigants such as methyl bromide (Bell, 2006; Sriranjini and Rajendran, 2008). Sorption rates in our experiments for flour were considerably higher than those reported by Sriranjini and Rajendran (2008), which may be due to their use of relatively dry commodity (their moistures were 2-4% lower than ours) and short fumigation periods (20-24 h). We have demonstrated that m.c. is an important factor governing sorption rate (Fig. 2). Published information is limited. Nevertheless, studies of sorption into wheat have been reported for other fumigants including phosphine (Daglish and Pavic, 2008; 2009), methyl bromide (Banks, 1986), and carbonyl sulphide (Weller, 2003). Under experimental conditions close to those used here (25°C and 55-60% relative humidity), adjusted k values reported for phosphine, methyl bromide and carbonyl sulphide applied to wheat were 0.1031 – 0.0466 (Daglish and Pavic, 2008), 0.0237-0.0253 (Banks, 1986) and 0.013 (Weller, 2003), respectively. Adjusted k values derived with SF in these experiments for wheat at 25°C and 12% m.c. (equivalent to 55% r.h.) were 0.00792, 0.00912 and 0.00816 indicating that SF is sorbed at a lower rate than other fumigants.

Under all combinations of CT, temperature and m.c. in these experiments rate of sorption of SF was higher in flour than in the whole wheat grains. SF is believed to bind with proteins and amino acids in the commodity (Meikle, 1964) and is converted to sulphate and fluoride ions. Most protein in wheat grain is located in the endosperm which is surrounded by several bran layers. SF must penetrate these layers before significant binding to protein can commence. Thus it appears that grinding grains to flour facilitates sorption rate by exposing protein molecules to the fumigant.

The rate of sorption into the various commodities was strongly influenced by temperature and grain moisture content. Within the biological range tested here, higher temperatures would be expected to increase SF sorption rates both because as temperature increases the kinetic energy of gases and therefore gas diffusion rates increase, and because the biological activity of SF increases with temperature (Bell and Savvidou, 1999). Although not previously reported with SF, increases in sorption rates with temperature increase have been observed with phosphine (Berck, 1968; Banks, 1993) and methyl bromide (Banks, 1993) applied to wheat, and methyl bromide (Hilton and Banks, 1997a) and ethyl formate (Hilton and Banks, 1997b) applied to sultanas. Increasing temperature from 15 to 35°C increased methyl bromide

sorption rate, k , into unprocessed sultanas 3.3 times (Hilton and Banks, 1997a) and ethyl formate sorption by 1.9 fold (Hilton and Banks, 1997b). Irreversible phosphine sorption into wheat increased 1.8 times when temperature was increased from 24 to 35°C (Berck, 1968). With methyl bromide, an increase in temperature of 9.8°C degrees provided a doubling of k , while an increase of 6°C degrees gave a doubling of k with phosphine (Banks, 1993). Compared with these fumigants, SF is quite responsive to changes in temperature. In our experiments at 12% m.c., there was 4.6 to 7.6 fold increase in k for wheat and a 5.4 to 6.6 times increase in k for flour.

There are few data available on the influence of moisture content or relative humidity on sorption of fumigants. In our experiments, k increased by about 1.5 to 3 fold when MC was increased from 12 to 15% under a range of conditions (Fig. 2). Increase in sorption of methyl bromide and ethyl formate in unprocessed sultanas has been reported as 1.4 (Hilton and Banks, 1997a) and 1.8 times (Hilton and Banks, 1997b), respectively, when relative humidity was increased from 50% to 70%. Similarly, permanent sorption of phosphine increased 1.7 fold at 15% MC compared with 12.5% (Berck, 1968). Both phosphine and SF are only slightly soluble in water (Bond, 1984) so improved solubility at higher MC does not necessarily explain increased sorption rates. The reason could be a generalised increase in metabolic activity when more water is available resulting in more rapid sorption.

Rate of sorption of SF was independent of initial concentration supporting the conclusion that the sorption process with these commodities followed first order kinetics (Banks, 1993). Sorption rates independent of concentration were also observed by Hilton and Banks (1997a, 1997b) in sultanas fumigated with methyl bromide and ethyl formate. However, the influence of initial concentration may vary with commodity as sorption of phosphine into wheat (Daglish, 2008) and rice (Banks 1993) and methyl bromide into wheat (Banks 1993) was found to be higher at lower fumigant concentrations.

The lack of detection of SF soon after aeration of the experimental commodity samples suggests that any unbound SF was removed from the experimental containers, while the continued failure to detect SF for 18 months indicates that any sorbed fumigant was permanently bound into the commodity. Even grinding the grains did not result in any detection of desorption. It is not unusual that a reaction with the commodity would occur resulting in irreversible sorption but complete lack of desorption was not expected. Extremely rapid loss of SF from experimental flasks soon after aeration has been noted previously (Osbrink et al., 1988). Scheffrahn et al. (1989) reported that aeration interval had no effect on fluoride or sulphate residue levels in a range of foods indicating formation of permanent metabolites. This suggests that no further parent SF remained in the food commodity. Desorption of methyl bromide and phosphine from commodities is regularly observed in industry, however, little quantitative data are available.

Compared with other common fumigants, sorption of SF into cereals is relatively slow. However, the results of our experiments indicate that as SF penetrates the commodity it is rapidly and apparently irreversibly bound into the matrix of the commodity, presumably undergoing metabolism. The two phase sorption behaviour observed with many fumigants, in particular those with high boiling points such as methyl bromide (Bond, 1984), which includes a rapid initial phase, was not apparent with SF (Fig. 1). Diffusion into commodities, particularly whole grains, appears to be relatively slow. The practical consequence of this is that short fumigation periods, up to 24 h, result in little sorption of fumigant and low risk of adverse levels of residue. However, extended fumigation times result in significant sorption and the likelihood of residues. On the other hand, the relatively slow rate of sorption suggests that residues may be within safe limits. In addition, the lack of continued desorption once a

commodity has been aerated at the completion of a fumigation has practical workplace health and safety benefits for the safe handling and transport of the fumigated commodity.

Our results indicate that SF possesses a number of characteristics that recommend it as a dry commodity fumigant. It is sorbed slowly by wheat grains and their processed products relative to other common fumigants. Furthermore, unbound SF is rapidly lost from the commodity upon aeration with no further desorption detected. The latter, however, also indicates that sorbed SF is irreversibly bound to the commodity matrix. This may indicate the need to be alert to the possibility of excessive residues.

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