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Does sorption of sulfuryl fluoride by wheat reduce its efficacy against adults and eggs of *Rhyzopertha dominica*?

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ABSTRACT

Despite its growing importance as a fumigant for grain, there is no information on the impact of sorption on the efficacy of sulfuryl fluoride (SF) against target insect pests. Eggs and adults of a major grain pest, *Rhyzopertha dominica*, living in wheat (12% m.c.), were fumigated with SF at 0.5, 1, and 2 mg/L for 168 h at 25 °C. Sorption of the fumigant by the grain followed an exponential decay and reduced the mortality rates of both adults and eggs. The partition ratio (K), a measure of physical sorption, had a strong impact on mortality of both adults and eggs. The quadratic model showed the best fit to the data and turning points in the relationship indicated that although mortality increased as concentration increased, physical sorption removed fumigant resulting in a decrease in the mortality rate. There was a linear relationship between mortality and the rate of sorption (k) of SF by the wheat. At each concentration, mortality rate increased as k increased despite sorption continuing, indicating that the chemical sorption rate had little impact on mortality. Sorption of SF into the commodity has the potential to reduce the biological efficacy of the fumigant resulting in potential control failures. Concentration x time protocols may need to be revised to account for this phenomenon.

1. Introduction

Sulfuryl fluoride (SF) has been registered in the USA for more than 50 years and was originally used primarily as a treatment for pests of buildings, particularly termites (Osbrink et al., 1987). Its use expanded to replace methyl bromide in several applications when the latter began to be phased out of broad use under the Montreal Protocol Agreement (UNEP, 1994; Bell et al., 2003; Drinkall et al., 2004; Ducom, 2012). These applications included use in flour mills and food handling facilities, disinfestation of food commodities including cereal grains (Ducom, 2012), and dried fruit and nuts (Drinkall et al., 2004) in several countries.

Information on the efficacy of SF against insect pests is generally limited to fumigation times of 48 h or less, matching the usual application protocol for methyl bromide. Laboratory bioassays indicate that insect eggs are generally 5–30 fold more tolerant to SF than other life stages. This has been demonstrated in beetle pests of museums (Su and Scheffrhan, 1990), wood boring beetles (Williams and Sprenkel, 1990), as well as beetle (Bell et al., 2003; Ciesla and Ducom, 2009; Jagadeesan and Nayak, 2016), moth (Baltaci et al., 2009; Bell and Savvidou, 1999) and psocid (Athanassiou et al., 2012) pests of stored products. Older eggs appear to be more tolerant than younger eggs (Baltaci et al., 2009; Williams and Sprenkel, 1990).

The lesser grain borer, *Rhyzopertha dominica* (Fab.), is a serious pest of stored wheat, barley and sorghum in Australia (Collins et al., 2017) and a major pest of stored cereals in warm temperate to tropical regions of the world (Edde, 2012). If left uncontrolled, it is capable of severely damaging or destroying grain stocks. In Australia and internationally, the fumigant phosphine is by far the preferred treatment for controlling infestations of *R. dominica*. However, serious levels of resistance in this pest to phosphine have been documented in several regions (Collins et al., 2017; Duong et al., 2016; Edde, 2012; Kaur et al., 2015; Opit et al., 2012) threatening the viability of phosphine. In Australia, SF has been adopted as an alternative treatment for control of phosphine-resistant *R. dominica* and other pest species (Nayak et al., 2015).

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An important factor to consider in the practical application of fumigants is the impact of sorption of the gas into the commodity during fumigation. Sorption may reduce the biological activity of a fumigant by reducing the concentration of gas available to target insects (Banks, 1993). As demonstrated previously (Hwaidi et al., 2015), sorption of SF into commodities is significant, therefore, we reasoned that sorption may reduce the biological efficacy of this fumigant against target pests. The aim of our research was to determine the impact of sorption on the biological activity of SF against a major target pest, *R. dominica*.

2. Materials and methods

2.1. Experimental design

Eggs and adults of a phosphine resistant strain of *R. dominica* were fumigated with three different concentrations of SF: 0.5, 1.0 and 2.0 mg/L at exposure times ranging from 24 to 168 h. The design was a randomized complete block with three replicates. Each replicate consisted of a glass Erlenmeyer flask (LabDirect, http://www.labdirect.com.au) of approximately 2.4 L capacity containing hard wheat grains (12% m.c.) filled to 50% flask volume (filling ratio of 0.50) and equilibrated for 2 days at 25 °C. Flasks were sealed with a glass stopper containing a silicone rubber septum to facilitate addition of fumigant and gas sampling.

2.2. Insects and commodity

R. dominica strain QRD569 was used for all experiments. This strain had been maintained in the laboratory since 1997 when it was collected from a phosphine fumigation control failure. QRD569 is classified as strongly resistant to phosphine (Collins et al., 2002) and was cultured on organic whole wheat at 30 °C and 60% rh. The wheat, *Triticum aestivum*, (hard white, cultivar Gregory) used in these experiments was purchased from a certified organic producer on the Darling Downs, southeast Queensland, Australia and stored in 20 kg bags at −20 °C. The wheat was brought to laboratory temperature and allowed to equilibrate for 2 days before conditioning to 25 °C and 12% moisture content (AACC, 2010).

2.3. Fumigations

Fumigations were undertaken as described by Hwaidi et al. (2015). Briefly, SF (99.8% purity) was decanted from a 3 L cylinder into a Flex foil gas-sampling bag (SKC, www.skcinc.com) from which various volumes of SF could be withdrawn using gas-tight syringes (Hamilton, Grace Discovery Sciences, Epping, VIC., Australia) for bioassay. SF concentration was measured using a gas chromatograph (Perkin Elmer, Claris 500) fitted with a thermal conductivity detector (TCD).

Glass Erlenmeyer flasks of known volume (about 2.4 L) were filled to 50% volume with wheat of 12% m.c., and 100 adult *R. dominica* (a mixture of males and females, 2–4 weeks post-eclosion) were placed in each flask. The insects were left for 4 days prior to fumigation to allow the adults time to lay eggs. The desired concentration of SF was added to each flask using a gas-tight syringe. The flasks were placed in a controlled environment room for up to 168 h at 25 °C and 60% rh. Gas samples (5 μL) were removed from the headspace of each experimental flask using a gas tight syringe at 24 h intervals. For each replicate, three samples were taken at each time interval and the average used as the reading. As the experimental SF concentrations were much lower than the range measured by a TCD, a more sensitive flame photometric detector was used (Hwaidi et al., 2015).

After completion of the fumigation, flasks were removed from the controlled environment room, opened and aerated under a fume hood for 2 h to disperse the gas. The wheat and insects were gently sieved using a 2 mm mesh sieve to separate all adults from the grain. The grain was carefully inspected to ensure that all adults had been removed. After making sure that 100 adults were retrieved, the adults were allowed a 7-day recovery period then scored for mortality and destroyed.

The grain, which now contained eggs laid by the adults before the fumigation, was transferred to 2 L plastic jars (Atlas Plastics, Minto NSW, Australia). A hole (50 mm) was drilled into the lid of each plastic jar and a white filter paper circle (110 mm, Advantec, Toyo Roshi Kaisha, Japan) and a piece of gauze were placed across the neck of the jar before screwing on the lid, to facilitate gaseous exchange. The jars were stored at 25 °C and 60% relative humidity for 8 weeks to allow all eggs sufficient time to develop into adults. After the 8 weeks, the 2 L plastic jars were opened to count the number of adults remaining.

2.4. Controls

2.4.1. Fumigant

A set of control flasks, containing SF in air only, were monitored during the experiment to detect possible loss of fumigant. There were 9 flasks, three for each test concentration. The control flasks were also used as the reference for creating calibration curves before measuring sulfuryl fluoride concentration in the headspace of bioassay flasks. To facilitate this, one of the three flasks had the desired test concentration and the other two had a concentration either higher or lower than the test concentration. For example, for 2 mg/L SF, there was one flask with 1.8 mg/L, a second containing, 2.0 mg/L and a third containing 2.2 mg/L.

2.4.2. Insects

Control flasks consisted of wheat and adult insects subjected to the same conditions as the SF treated flasks but not fumigated. There were three flasks (replicates) for each of the eight time points during the study.

2.5. Calculating initial fumigant concentration and commodity volume

As described previously (Hwaidi et al., 2015) the initial concentration of SF at zero time (C_0) was calculated by multiplying the volume to be added by the source concentration divided by the total space (after adding the commodity):

$$C_0 = C_f * C_s / V \quad (1)$$

where

$$C_f = C_d * V / C_s \quad (2)$$

C_d = desired concentration.V = the volume of the fumigation flask.C_s = gas concentration of the source.$C_d = C_0$, in this case.

The space remaining in each flask after adding the commodity was calculated by dividing the bulk density (ρ_{bulk}) by the true density (ρ_{true}).

$$S = 1 - \rho_{bulk} / \rho_{true} \quad (3)$$

2.6. Statistical analysis

Data were analysed using SAS software (SAS, 1999). The decay of gas concentrations and egg and adult numbers were fitted to mathematical models described below:

The decrease in gas concentration was best described as the exponential relationship:

$$C_t = C_0 e^{-k*t} \quad (4)$$

where C_t is the gas concentration C at time t. C_0 is the gas concentration C at time zero ($t=t_0=0$). At $t = 0$ the sorption rate constant $k = 0$ because when substituting zero into equation number (4) and multiplying the zero by k, gives zero sorption. In this case $C_t = C_0$.

Adult (parent) mortality was described as:

$$M_t = M_0 e^{-R*t} \quad (5)$$

Where M_t was the number of adults M at any time t and R is the rate constant for adult mortality. M_0 was adult number M at time zero ($t=t_0=0$).

Egg survival was described as:

$$N_t = N_0 e^{-E*t} \quad (6)$$

where (N_t) is the number of adult progeny (N) at a given time (t). (N_0) is the number of progeny at time zero ($t=t_0=0$). E is the rate constant of adult progeny hatched from fumigated eggs. When substituting (t) for zero in equation (6) and multiplying by (E), the result would be zero. In this case $N_t = N_0$.

The sorption rate for a full container, k_f, and the tendency to take up fumigant by physical sorption, known as the partition ratio (or co-efficient) of physical sorption, K, were each calculated following the methods of Hilton and Banks (1997). The partition ratio gives a dimensionless measure of the tendency of the commodity to take up fumigant by physical sorption (Hilton and Banks, 1997).

$$k_f = k/f \quad (7)$$

where k was sorption rate constant from equation (4), and f was the experimental filling ratio.

$$K = (C_a - C_i)*V_g \,/\, C_i*V_f \quad (8)$$

where C_a was the applied concentration, C_i was the predicted concentration, V_g was the gas volume and V_f was the volume occupied by the commodity.

The relationships between the partition ratio, K, and the egg survival rate constant, E, and the adult mortality rate constant, R, were fitted using a polynomial quadratic regression.

$$E = B_0 + B_1 K + B_2 K^2 \quad (9)$$

$$R = B_0 + B_1 K + B_2 K^{\mathbf{2}} \quad (10)$$

Where B_0 was the intercept, B_1 was the linear coefficient and B_2 was the quadratic coefficient.

The turning point of the standard polynomial quadratic regression line was calculated using the following equation.

$$K = -B_1 \,/\, 2\,B_2 \quad (11)$$

The turning point of the fitted line is the point at which the line turns back toward zero. Therefore, it is considered to be the point of maximum partition of physical sorption (K). This gives the maximum egg survival (E) or adult mortality (R) rate constant. After calculating K, equations (9) and (10) were used to calculate the maximum rate of mortality by substituting the derived values of K into each equation.

A linear regression formula was used to describe the relationship between both the egg survival rate (E) and the adult mortality rate (R) with the sorption rate (k).

$$E = B_0 + B_1(k) \quad (12)$$

$$R = B_0 + B_1(k) \quad (13)$$

In addition, the same linear equation was used to describe the relationship between egg survival (E_g) and exposure time (t) when the fumigant was not present.

$$E_g = B_0 + B_1(t) \quad (14)$$

The percentage of gas loss, egg survival and adult mortality per h were calculated using the following equation:

$$\text{Percentage} = 100\,(1\text{-e}^{i}) \quad (15)$$

where (i) was (k, E or R).

Finally, time to 50 (equation (9)) and 99% (equation (10)) loss of the gas, and egg survival and adult mortality were calculated according to the following:

$$1/2L_0 = L_0\, e^{-i*t}/L_0,\ 1/2 = e^{-i*t},\ t = \ln(1/2)/\text{-}i. \quad (16)$$

$$0.01L_0 = L_0\, e^{-i*t}/L_0,\ 0.01 = e^{-i*t},\ t = \ln(0.01)/\text{-}i. \quad (17)$$

where, L_0 was C_0, N_0 or M_0, i was k, E or R and ln was the natural logarithm.

3. Results

3.1. Sorption

SF concentration was very stable in the control flasks over the period of the study, indicating negligible leakage and providing confidence in the calibration curves used for measuring SF at each time interval. The mean readings and standard deviations for SF concentrations at 0.5, 1.0 and 2.0 mg/L across all time intervals were 0.48 ± 0.02, 0.98 ± 0.017 and 1.94 ± 0.21, respectively.

The concentration of SF in the headspace of fumigated flasks containing wheat with *R. dominica* adults and eggs present declined with time in each treatment (Fig. 1). This decline indicates that the fumigant was sorbed into the wheat, otherwise the concentration would have remained stable, as occurred in the controls. Sorption was initially rapid followed by a slowing of the rate. The rate of decline differed between the three SF concentrations and were compared by fitting an exponential model, which provided a highly significant fit to the data with all treatments (Table 1). The decline in SF concentration over time was fastest at 0.5 and slowest at 2.0 mg/L. The calculated (from equations (9) and (10)) time to 50 and 99% loss of SF increased with increasing applied SF concentration (Table 1).

3.2. Adult mortality

Fumigating with SF resulted in an exponential decline in numbers of adult *R. dominica* over time (Fig. 2). The mortality rate constant for adults (R) increased with increasing SF concentration. However, complete control of adults was not achieved in the presence of wheat even at the highest concentration (2 mg/L) of SF tested (Fig. 2). The exposure period required at 2 mg/L for complete

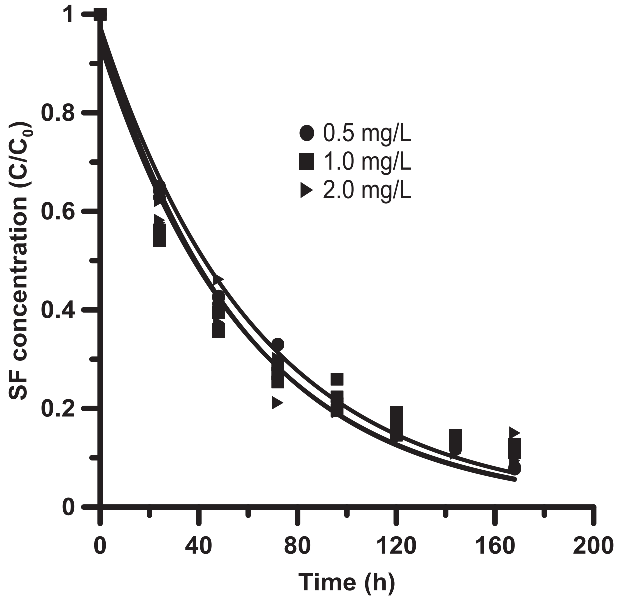

Fig. 1. Sulfuryl fluoride concentration in the head space of flasks containing wheat (12% mc) and *Rhyzopertha dominica* adults and eggs fumigated with 0.5, 1.0 or 2.0 mg/L at 25 °C and 60% rh for 168 h.

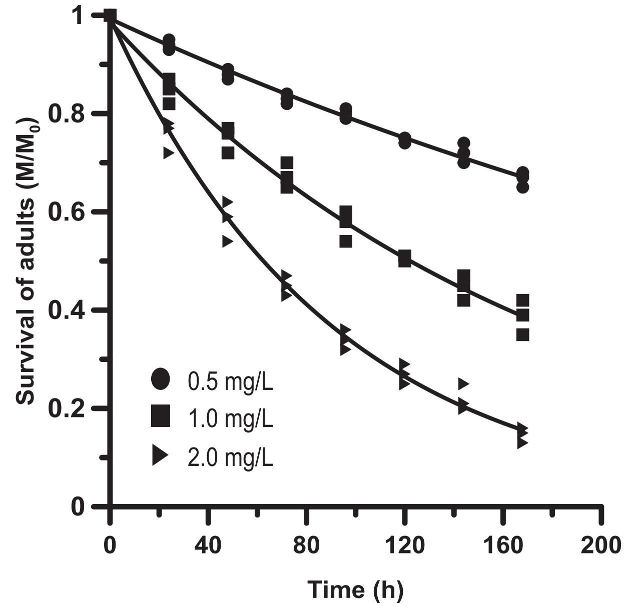

Fig. 2. Survival of adults of *Rhyzopertha dominica* relative to controls in wheat (12% mc) fumigated with 0.5, 1 or 2 mg/L sulfuryl fluoride at 25 °C and 60% rh.

control can be predicted from the regression equation (Table 2). Thus, the exposure time would need to be extended to 422 h to achieve 100% mortality of adults with 2 mg/L SF, while 99% of the fumigant would be lost after 820 h (Table 1).

The partition ratio (K) had a strong impact on the adult mortality rate, R, and this effect was stronger at the lower SF concentrations, that is, K and R were larger in magnitude at 0.5 than at 2 mg/L (Fig. 3). The quadratic model provided the best fit for this relationship with high R^2 values of 0.94–0.97 (Table 3). The relationship between K and R showed turning points at which the rate of adult mortality R began to decrease as K values increased (Fig. 3, Table 3).

Adult survival rate (R) increased as sorption rate (k) increased in absolute value. A linear model, with excellent fit of the data (Table 4), best described the relationship between R and k. At each concentration, R continued to increase as k increased despite sorption continuing, indicating that the chemical sorption rate had little impact on adult mortality and that the greatest impact was due to loss of fumigant through physical sorption. For example, increasing k by one unit leads to an increase in R by 0.142, 0.731 and 1.930 at 0.5, 1 and 2 mg/L, respectively (Table 4).

3.3. Egg survival

Number of adult progeny and therefore egg survival decreased with increasing concentrations and as fumigation time increased at each concentration. Egg survival occurred in all treatments, even at the highest concentration tested, 2 mg/L for 168 h (Table 2). The rate constant of egg mortality (E) closely fitted the exponential model, explaining 98–99% variation in the data (Table 2). Egg mortality was strongly affected by sorption of the fumigant into the commodity. However, in the control, the numbers of adult progeny emerging from the grain (non-fumigated treatment) increased rapidly with time (Fig. 4). In contrast to the situation with adults, these curves predict that, at 2 mg/L, 99% of the fumigant would be lost before 99% control of eggs could be achieved.

The relationship between egg mortality rate (E) and the partition ratio of physical sorption (K) was curvilinear at the three concentrations tested. This relationship was best explained by the quadratic model, which was an excellent fit for the data ($R^2 = 0.95$–0.99) (Table 3). The turning points of the fitted lines (Table 3) revealed an increase of E values with increasing applied SF concentration, but showed a decrease in K values. Thus, although egg mortality rate initially increased as concentration increased, physical sorption removed fumigant resulting in a decrease in the rate of mortality until it reached zero, and then the numbers of eggs surviving began to increase. As expected, maximum or turning point K values obtained for adult and eggs were identical as they are derived from the same fumigation (Table 3). However, E values were lower than R values reflecting the higher sensitivity of adults to the fumigant (Table 3).

The relationship between sorption rate (k) and egg mortality rate (E) was linear at each concentration tested (Fig. 5, Table 4). For example, when SF was 0.5 mg/L, mortality increased to about 0.061 with an increase in k of one unit, and when SF was 2 mg/L, mortality increased by about 0.76 with each increase in k of one unit.

Table 1
Modelling the change in sorption rate constant (k) (equation (4)) of sulfuryl fluoride (SF) over time in flasks containing wheat (12% mc) and *Rhyzopertha dominica* adults and eggs fumigated with sulfuryl fluoride at 0.5, 1 or 2 mg/L at 25 °C, 60% rh. Constant rate of reaction of SF with wheat (k_f), percentage loss per h, time to 50 and 99% loss of the fumigant at a filling ratio 0.5.

SF mg/L	Regression	Significance	R^2	% loss SF per h	Time (h) to 50% loss of SF	Time (h) to 99% loss of SF	kf
0.5	$C_t = 0.4547e^{-0.016t}$	$F_{2,22} = 366.91$; $P < 0.0001$	0.92	1.610	43.04	286.03	0.0322
1	$C_t = 0.9584e^{-0.007t}$	$F_{2,22} = 994.11$; $P < 0.0001$	0.93	0.749	92.52	614.16	0.0149
2	$C_t = 1.9823e^{-0.005t}$	$F_{2,22} = 1191.65$; $P < 0.0001$	0.90	0.561	123.52	820.08	0.0112

Table 2
Adult mortality rate constant (R) (equation (5)) and egg mortality rate constant (E) (equation (6)), % mortality per h, and time to 50 and 99% mortality of *Rhyzopertha dominica* adults and eggs in wheat (12% mc) fumigated with sulfuryl fluoride (SF) at 0.5, 1 or 2 mg/L at 25 °C and 60% rh at filling ratio 0.5.

SF mg/L	Regression	Significance	R^2	% Mortality per h	Time (h) to 50% mortality	Time (h) to 99% mortality
Adult mortality						
0.5	$M_t = 98.87e^{-0.002t}$	$F_{2,22} = 595$; $P < 0.0001$	0.96	0.229	301.30	2002.24
1	$M_t = 98.19e^{-0.005t}$	$F_{2,22} = 109$; $P < 0.0001$	0.93	0.550	125.54	834.26
2	$M_t = 98.74e^{-0.010t}$	$F_{2,22} = 715$; $P < 0.0001$	0.98	1.084	63.57	422.49
Egg mortality						
0.5	$N_t = 2.543e^{-0.001t}$	$F_{2,19} = 223.92$; $P < 0.0001$	0.99	0.099	693.00	4605.17
1	$N_t = 2.392e^{-0.002t}$	$F_{2,19} = 343.18$; $P < 0.0001$	0.98	0.209	330.01	2192.93
2	$N_t = 2.3475e^{-0.004t}$	$F_{2,19} = 151.20$; $P < 0.0001$	0.99	0.439	157.50	1047.02

The egg mortality rate constant (E) was lower than the adult mortality rate (R) at all concentrations tested, demonstrating that eggs were more tolerant than adults to SF (Table 2). Thus, the time required to control adults was much shorter than needed to control eggs. For example, at 2 mg/L, R was 0.01 per h, whereas E was 0.004 per h. The adult mortality rate constant (R) increased significantly with increasing fumigant concentration (Table 2) and time to 50 and 99% mortality decreased with increasing SF concentration. The increase in E was much slower than the increase in R with fumigant concentration (Table 2).

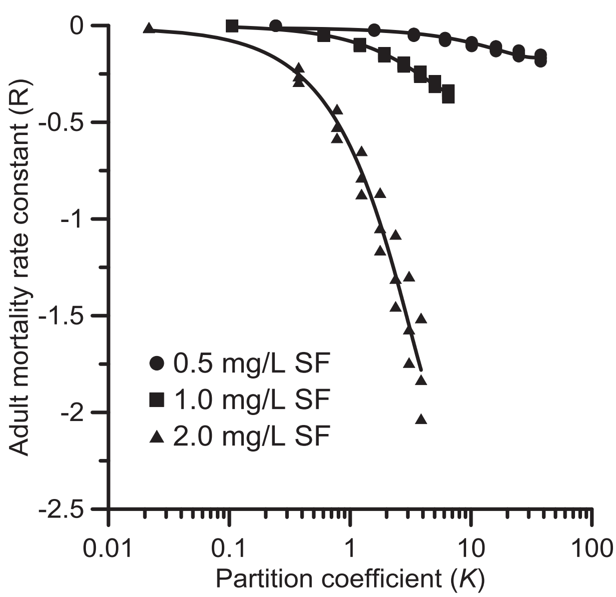

Fig. 3. Relationship between the partition coefficient for physical sorption (K) of wheat (12% mc) fumigated at three concentrations of sulfuryl fluoride (SF) and the adult mortality rate constant (R) for *Rhyzopertha dominica*.

4. Discussion

The aim of this study was to test the hypothesis that sorption into the commodity during fumigation would reduce the efficacy of SF against *R. dominica*, a major pest of stored grain. Sorption was characterised using the partition ratio (K) sorption rate constant (k) of the chemical reaction between SF and grain. These factors were compared with the mortality rate constants for the egg (E) and adult (R) life stages.

The results of these experiments indicate that sorption into wheat led to a decrease in the efficacy of SF against eggs and adults of *R. dominica.* Wheat grains sorbed SF in an exponential manner and the data closely fitted first order exponential decay equations describing the relationship between fumigant sorption and exposure time as discussed in detail previously (Hwaidi et al., 2015). There was a rapid initial (first 24 h) decline in headspace concentration of SF (Fig. 1), which is typical of fumigant sorption behaviour (Banks, 1993; Daglish and Pavic, 2008; Hilton and Banks, 1997). The sorption rate constant (k) was independent of the applied

Table 4
Fit of the model for the relationship between the constant rate of reaction (k) and the mortality rate constant for adults (R) and eggs (E) in wheat (12% m.c., filling ratio 50%) fumigated with sulfuryl fluoride (SF) at three different concentrations at 25 °C and 60% r.h. *Eg* is the model for population growth rate constant for insects in control (non-fumigated) wheat.

SF mg/L	Linear regression	Significance	R^2
Adult mortality			
0.5	$R = (-0.00171)+(0.14278)(k)$	$F_{1,22} = 247$; $P < 0.0001$	0.98
1	$R = (-0.00359)+(0.73187)(k)$	$F_{1,22} = 281$; $P < 0.0001$	0.96
2	$R = (-0.00583)+(1.93060)(k)$	$F_{1,22} = 243$; $P < 0.0001$	0.95
Egg mortality			
0.5	$E = (-0.00191)+(0.06121)(k)$	$F_{1,22} = 360.64$; $P < 0.0001$	0.94
1	$E = (-0.00247)+(0.27768)(k)$	$F_{1,22} = 852.77$; $P < 0.0001$	0.97
2	$E = (-0.00180)+(0.76267)(k)$	$F_{1,22} = 4565$; $P < 0.0001$	0.99
Control			
0	$Eg = (0.011)+(2.307)(t)$	$F_{1,22} = 815.33$; $P < 0.0001$	0.97

Table 3
Fit of the model for the relationship between the partition coefficient of physical sorption (K) and the mortality rate constant for adults (R) and eggs (E) in wheat (12% m.c., filling ratio 50%) fumigated with sulfuryl fluoride at three different concentrations at 25 °C and 60% r.h. Maximum R, Maximum E and Maximum K are the turning points of the fitted equation.

SF mg/L	Orthogonal polynomial regression	Significance	R^2	Maximum R	Maximum E	Maximum K
Adult mortality						
0.5	$R = (-0.02692)+(-0.02084)^*(K)+(0.00030670)^*(K)^2$	$F_{2,21} = 499$; $P < 0.0001$	0.97	−0.381		33.970
1	$R = (0.00359)+(-0.22799)^*(K)+(0.01334)^*(K)^2$	$F_{2,21} = 855$; $P < 0.0001$	0.99	−0.972		8.545
2	$R = (-0.01067)+(-0.68295)^*(K)+(0.05554)^*(K)^2$	$F_{2,21} = 292$; $P < 0.0001$	0.94	−3.867		6.148
Egg mortality						
0.5	$E = (-0.01171)+(-0.00906)^*(K)+(0.00013335)^*(K)^2$	$F_{2,21} = 239.29$; $P < 0.0001$	0.95		−0.167	33.971
1	$E = (0.00132)+(-0.08705)^*(K)+(0.00509)^*(K)^2$	$F_{2,21} = 1664$; $P < 0.0001$	0.99		−0.371	8.551
2	$E = (-0.00421)+(-0.26942)^*(K)+(0.022191)^*(K)^2$	$F_{2,21} = 6688$; $P < 0.0001$	0.99		−0.832	6.148

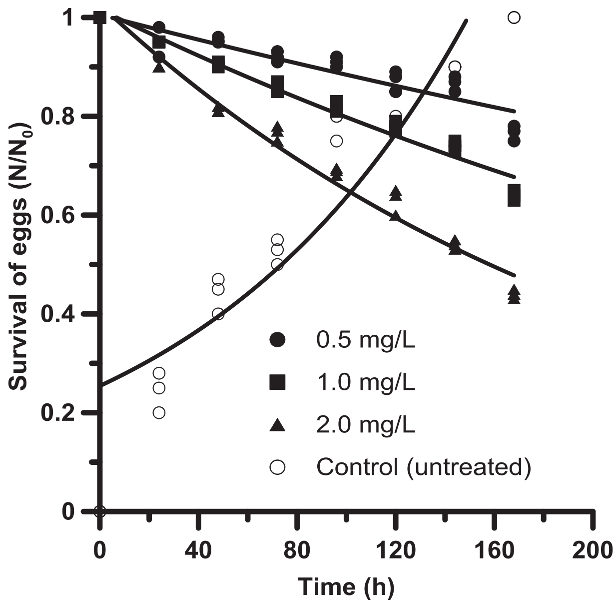

Fig. 4. Survival of eggs, measured as adult progeny, of *Rhyzopertha dominica* relative to controls in wheat (12% mc) fumigated with sulfuryl fluoride at 0 (control), 0.5, 1.0 or 2.0 mg/L at 25 °C and 60% rh.

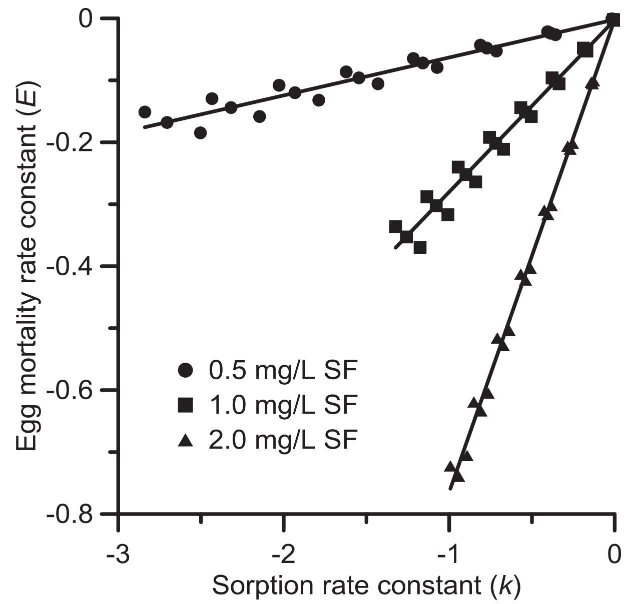

Fig. 5. Relationship between egg mortality rate constant (*E*) for *Rhyzopertha dominica*, and the sorption rate constant (*k*) of wheat (12% m.c.) fumigated at three concentrations of sulfuryl fluoride (SF).

concentration, consistent with previous results with this fumigant (Hwaidi et al., 2015).

The relationship between SF concentration and both adult and egg mortality rates, *E* and *R*, respectively, were described by first order equations (Tables 2 and 3) indicating the potential impact of sorption on the toxicity of SF during commodity fumigation. It has been demonstrated with several fumigants that increasing fumigant concentration (Aung et al., 2001; Baltaci et al., 2009; Daglish et al., 2002) increases mortality in the egg and other life stages. However, a decline in the efficacy of the applied concentration against eggs and adults over time due to sorption was demonstrated in this study (Tables 1–3). Although it may occur, a reduction of efficacy against insects due to sorption has not been quantified for other fumigants.

Sorption caused a decline in the effective SF concentration during the fumigations, resulting in an increase in the estimated time required for control of *R. dominica* adults and eggs. For example, the time estimated for 99% control of adults fumigated with 2 mg/L SF at 25 °C, was ~18 d at filling ratio 0.5 and for eggs was ~44 d. However, under these conditions, 99% of the fumigant would be sorbed after only 34 d making it impossible to obtain complete kill of eggs. The results of this study indicate the effect of sorption on the exposure time, that is, a longer time of exposure combined with a higher concentration would be required for complete control of the insect eggs and adults.

The dosages of SF used in these experiments, 0.5, 1, and 2 mg/L for 168 h, were lower than the application rates recommended for field fumigations (Agas, 2017). This was done deliberately to allow some survival of insects so that the effect of sorption of SF into grain on insect survival could be quantified. The current maximum application rate in Australia is 1500 mgh/L. Although little information is available, recent research has indicated that current commercial rates are unnecessarily very high (Nayak et al., 2015). Current rates were developed for 24–48 h fumigations, but by increasing the exposure period, the concentration of SF can be reduced markedly below the maximum application rate. It is likely that lower rates will be adopted by industry because of the saving in costs. Thus, rates used in these experiments are relevant to future commercial use patterns.

Both the egg and adult mortality rates (*E* and *R*) were strongly influenced by the partition ratio of physical sorption (*K*) (Table 3, Fig. 3), which had an inverse quadratic relationship with *E*. An increase in *E* was expected to occur due to the toxic effect of the gas over time. However, the continued physical sorption with time resulted in a reversal of the toxic effect and after reaching a turning point, *E* began to decrease resulting in an increase in survival of insects when the fumigant was sorbed completely. Dumas (1980) reported that physical sorption of phosphine increased with increasing exposure time, and a similar effect was very clear in the results of the present study. Time had a strong impact on the toxicity of SF to eggs and adults, as sorption resulted in a decrease in the gas concentration to below the toxic level.

Unlike the relationship between *K* and both *R* and *E*, the relationship between the rate of sorption of the fumigant by the commodity (*k*) and the mortality rate for eggs (*E*) was linear (Fig. 5). The reaction of the fumigant with the commodity is a one directional, irreversible chemical reaction, but the rate of that reaction did not impact on *E* under the conditions of this study. The linear relationship indicated an increase in the mortality rate, even though the reaction rate for the fumigant and the commodity increased (Table 4). It appears that although rapid physical sorption occurred in the first 24 h (Fig. 1), much of this SF was still biologically active as it had not undergone chemical reaction. The latter occurred gradually with time. These results also predict that the relationship between the sorption rate of the fumigant by the commodity (*k*) and the mortality rate for eggs (*E*) would become nonlinear as continuing chemical sorption with time decreases the available gas then *E* decreases and a quadratic directional relationship with *k* follows. That is, the chemical reaction between the gas and the commodity would continue until all the gas is sorbed completely, and the relationship would become quadratic. Further experiments are required to assess to what extent the relationship will continue to be linear, and how sorption affects the relationship between the reaction rate and the toxicity of the fumigant. Other factors that should be considered are the effects of applying higher concentrations and shorter exposure periods. The possibility of resorption of fumigant during longer exposure periods should also be investigated.

These results demonstrate that sorption is a key process that should be considered when developing fumigation protocols for SF. This is particularly important, as under-dosing due to loss of fumigant is an important factor in the development of resistance to fumigants in insect pests of stored products (Opit et al., 2012).

5. Conclusion

These experiments demonstrate that sorption of SF by wheat reduces the efficacy of SF against eggs and adults of *R. dominica* by removing biologically active fumigant from the system. Extending exposure time without ensuring adequate dosage or increasing concentration with an inadequate exposure time may not be sufficient to control infestations due to the phenomenon of sorption of the fumigant by the commodity. Therefore, sorption should be considered as a fundamental factor in designing SF fumigation protocols.

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