Gas leakage and distribution characteristics of methyl bromide and sulfuryl fluoride during fumigations in a pilot flour mill

Watcharapol Chayaprasert, Dirk E. Maier, Bhadriraju Subramanyam, Michelle Hartzer

How to cite this manuscript

If you make reference to this version of the manuscript, use the following information:

Chayaprasert, W., Maier, D. E., Subramanyam, B., & Hartzer, M. (2012). Gas leakage and distribution characteristics of methyl bromide and sulfuryl fluoride during fumigations in a pilot flour mill. Retrieved from http://krex.ksu.edu

Published Version Information

Citation: Chayaprasert, W., Maier, D. E., Subramanyam, B., & Hartzer, M. (2012). Gas leakage and distribution characteristics of methyl bromide and sulfuryl fluoride during fumigations in a pilot flour mill. Journal of Stored Products Research, 50, 1-7.

Digital Object Identifier (DOI): doi:10.1016/j.jspr.2012.03.002

Publisher’s Link:
http://www.sciencedirect.com/science/article/pii/S0022474X12000197

Highlights

- The half-loss times (HLTs) during three methyl bromide (MB) and three sulfuryl fluoride (SF) fumigations were monitored.
- Concentrations of both fumigants within the mill ranged from 2 to 7 g/m^3.
- The observed HLTs for the MB and SF fumigations were in the range of 3.61 to 28.64 h and 9.97 to 31.65 h, respectively.
- HLTs were inversely related only to wind speeds.

Revised version

Gas leakage and distribution characteristics of methyl bromide and sulfuryl fluoride during fumigations in a pilot flour mill

Watcharapol Chayaprasert[1,2], Dirk E. Maier[1], Bhadriraju Subramanyam[1,*], and Michelle Hartzer[1]

[1]Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas, 66506, USA

[2]Department of Agricultural Engineering, Faculty of Engineering at Kamphaengsaen, Kasetsart University - Kamphaengsaen Campus, Nakhon Pathom, 73140, Thailand

---

*Corresponding author: Tel: +1 785-532-7010, E-mail: sbhadrir@k-state.edu

Abstract

The half-loss time (HLT) is used as an indicator to quantify gas leakage rates during methyl bromide (MB) and sulfuryl fluoride (SF) fumigations. Comparisons of HLTs between three MB and three SF fumigations were quantified in the Hal Ross pilot flour mill, Department of Grain Science and Industry, Kansas State University, USA. The sealing quality or gas tightness of the mill before each fumigation was verified by a pressurization test. Fumigant concentrations during the six fumigations were monitored continuously at 30 locations among the five mill floors during the 24 h fumigation period. A weather station on the mill roof monitored barometric pressure, wind speed and direction, temperature, and relative humidity. A data logger on each mill floor recorded temperature and relative humidity. The pressurization test showed that the relationship between airflow rate and building static pressure varied among the fumigations despite the same areas being sealed by two separate fumigation service providers due to environmental conditions not being identical among the fumigations. Concentrations of both fumigants within the mill ranged from 2 to 7 g/m^3. The observed HLTs for the MB and SF fumigations were in the range of 3.61 to 28.64 h and 9.97 to 31.65 h, respectively, and were inversely related only to wind speeds during fumigation and not any other environmental conditions recorded. In our study, the fumigant leakage rate was found to be predominantly a function of wind speed rather than inherent gas characteristics of MB and SF.

Keywords: Structural fumigation, Sealing quality, Leakage rates, Gas dynamics, Half-loss time, Wind speed

1. Introduction

A structural fumigation is considered successful when the target dosage for an effective kill of all insect life stages is achieved. The dosage is a cumulative product of the fumigant concentration (C) over the exposure time (t), and is referred as the Ct product (Kenaga, 1961; Gandy and Chanter, 1976; Annis, 1999; Bell et al., 1999). The Ct product is a function of the amount of released fumigant, exposure time, and fumigant leakage rate. Fumigant leakage rate is quantified by the half-loss time (HLT), which is the time taken in hours (h) for 50% loss of the total fumigant concentration from the structure being fumigated. The gas leakage rate and HLTs are inversely related. In commercial fumigations, an ideal HLT should be >15 h, but realistic HLTs may range from 5 to 22 h (Chayaprasert, 2007).

Methyl bromide (MB) has been the primary fumigant used for structural fumigation in food-processing facilities such as flour mills (Taylor, 1994). Sulfuryl fluoride (SF) was registered in the United States for use in food-processing facilities in January 2004 under the trade name ProFume® by Dow AgroSciences LLC, Indianapolis, Indiana, USA. It is a viable replacement for MB, which was phased out in the United States in 2005 due to its adverse effects on stratospheric ozone, but continues to be available through the critical use exemption (CUE) process (US-EPA, 2010).

A majority of fumigation experiments conducted in commercial food-processing facilities focused on efficacy against insects and/or on insect population rebounds following the treatment (Drinkall et al., 2003; Reichmuth et al., 2003; Bell et al., 2004; Campbell and Arbogast, 2004; Drinkall et al., 2004; Small, 2007). Chayaprasert (2007) reported that fumigant concentrations, indoor temperature and relative humidity, and outside weather conditions alone cannot explain fumigant leakage rates without taking sealing quality into consideration. Chayaprasert and Maier (2010) used experimental building pressurization tests and computational fluid dynamics (CFD) model simulations to evaluate the effect of building sealing quality or gas-tightness and weather conditions on SF leakage rates. They concluded that sealing quality and environmental factors should be considered when comparing structural fumigants. Cryer (2008) used CFD simulations to compare leakage characteristics between MB and SF from two flour mills subjected to various hypothetical fixed wind speeds, and found that under similar environmental conditions the HLTs for MB and SF were nearly identical. A computer simulation study by Chayaprasert et al. (2009) also supported this view.

Typically when HLTs during commercial structural fumigations are compared, environmental conditions are not taken into consideration by fumigators. Additionally, sealing quality effectiveness is rarely quantified whenever fumigation is done making it difficult to interpret effectiveness of practical structural treatments. Therefore, the current study objectives were to validate computer simulation results with empirical measurements of gas leakage and distribution in a pilot flour mill subjected to MB and SF fumigations and to relate gas leakage rates to environmental conditions.

2. Materials and methods

2.1. Mill fumigation treatments

The state-of-the art Hal Ross pilot flour mill belonging to the Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas, USA, was used for the present study. The mill has five floors that occupy a total volume of ~9,628 m^3, and Fig. 1 shows the mill exterior and generic floor plan which is essentially similar across the floors. All mill floors have interconnected air supply vents, in addition to openings between floors to accommodate equipment. Three MB and three SF fumigations were conducted during 2009 and 2010. Each pair of MB and SF fumigations was carried out within a three-week time span to ensure comparisons under approximately similar environmental conditions. The fumigations were split between two separate professional fumigation service providers following label directions and safety precautions. The mill was cleaned and sealed prior to all fumigations. We did not compare the sealing material and sealants used by these two service providers. Two 0.51-m diameter fans were placed on each floor to facilitate gas distribution. These fans were in operation during the entire 24 h exposure period. One fumigant introduction point was selected on every floor. All of the stairwell doors were open with some exceptions. The first and second floor doors were closed during the second SF fumigation, and the doors on every floor were closed during the third SF fumigation to reduce fumigant leakage. These decisions were made by the fumigators. The date of fumigation, amount introduced on each floor, and the introduction time are shown in Table 1.

Six gas monitoring lines of different colors, made of nylon tubes with 4.3-mm internal diameter, were placed on each mill floor. One line was placed on the mill floor at the southwest corner and another line was placed near the ceiling at the northeast corner. The other four monitoring lines were evenly distributed throughout each floor both inside and outside of milling equipment, where there were bioassay boxes with different life stages of the red flour beetle. Two or three of these lines were inserted into different machines where bioassay boxes were located. The bioassay results are being reported elsewhere and are not relevant to the objectives of this paper. The equipment was closed after placement of the monitoring lines. Fumigant concentrations at 10 locations (2 per floor) were monitored automatically every 20 minutes by the Spectros Single Point Monitor (Spectros Instruments, Hopedale, Massachusetts, USA). The remaining 20 locations was monitored manually on an hourly basis by using either the Spectros Instruments Single Point Monitor or Fumiscope (Key Chemical and Equipment, Clearwater, Florid, USA) throughout the 24 h exposure period.

The environmental conditions during each fumigation were monitored using a HOBO® U30 weather station (Onset Computer Corporation, Bourne, Massachusetts, USA), which was installed on the mill roof to record barometric pressure, wind speed and direction, temperature, and relative humidity at one-minuet intervals. A HOBO® H8 data logger (Onset Computer Corporation) on each mill monitored temperature and relative humidity at one-minute intervals. During the third MB fumigation the weather station failed to record wind speed, and wind speed data for this particular fumigation were obtained from the weather station installed on the ground at the Agronomy Farm located about 500 m to the west of the mill.

2.2. Pressurization test

One to two hours before each fumigation, the building sealing quality or gas tightness was quantitatively evaluated by a pressurization test. The pressurization test was conducted using the E3 blower door fan (Infiltec, Waynesboro, Virginia, USA). The fan is capable of delivering a maximum airflow rate of 2.57 m^3/s. The fan was attached to one of the exit doors on either the east or west side. During each pressurization test, the building was subjected to different pressure levels between 10 and 140 Pa by increasing the fan airflow rate. At each pressure level, the flow rate through the fan and the static pressure difference across the blower door were measured by the DM4 micro-manometer (Infiltec, Waynesboro, Virginia, USA).

2.3. Data analysis

The gas-tightness characteristic of the mill was determined by fitting a nonlinear regression model (Equation 1) to the relationship between the flow rate across the pressurization fan (Q, m^3/s) and the static pressure difference across the blower door (p, Pa) (ASHRAE, 2001):

$$Q = bp^n \tag{1}$$

where, b is the flow coefficient ($m^3/s\text{-}Pa^n$) and n is a dimensionless pressure exponent. All possible pair-wise combinations based on three pressurization tests for MB and three for SF fumigations were compared by testing the deviation of individual models (Equation 1) fit to the flow rate and pressure data to a pooled model (Draper and Smith, 1981). A significant difference ($P < 0.05$) between pooled and individual models indicated that the relationship between flow rate and pressure was significantly different between the two pressurization tests being compared. The six fumigations between MB and SF resulted in 15 pair-wise comparisons.

The HLTs observed from the fumigations were estimated by a first-order kinetic equation (Equation 2) of gas concentration readings over time (Banks et al., 1983; Chayaprasert et al., 2008; Cryer, 2008):

$$C_t = \frac{C_i}{2^{\frac{t}{HLT}}} \qquad (2)$$

where, C_t is the current concentration (g/m^3) at the elapsed time t (h) and C_i is the initial concentration (g/m^3).

A direct comparison of the resulting HLTs between the MB and SF fumigations could not be made without taking into account all of the weather conditions. Banks and Annis (1984) showed that the overall ventilation rate (d^{-1}), which is defined as the total volume of the enclosure divided by the volumetric gas loss rate during fumigation in grain storages, is a summation of individual ventilation rates associated with barometric pressure, buoyancy, and wind forces. One common method used to calculate air infiltration rates, q (m^3/s), in buildings is the superposition method (Equation 3) in which the wind and stack effects are determined separately and then combined together based on a predefined correlation (ASHRAE, 2001):

$$q = \frac{A_L}{1000}\sqrt{c_s \Delta T + c_w U^2} \qquad (3)$$

where, A_L is the effective leakage area (cm^2), c_s is the stack coefficient ((L/s)^2/cm^4-K), c_w is the wind coefficient ((L/s)^2/cm^4-(m/s)^2), ΔT is the average indoor-outdoor temperature difference (K), and U is the average local wind speed (m/s). HLT and q are related as shown in Equation 4 (Banks et al., 1983; Chayaprasert, 2007):

$$HLT = \frac{V}{q}\frac{\ln(2)}{3600} \qquad (4)$$

where, V is the volume of the fumigated building (m^3). Equations 3 and 4 were used to establish any correlations between the HLTs calculated from Equation 2 and the measured indoor-outdoor temperature differences and prevailing wind speeds.

Barometric pressure was not taken into account in the superposition calculations because of lack of relationship between fumigant concentration and barometric pressure. Wind direction can affect the fumigant leakage rate when tall structures are neighboring fumigated structures (e.g., grain silos nearby a fumigated flour mill) or when areas of leakage within fumigated structures are not evenly distributed on all sides (Cryer, 2008; Chayaprasert et al., 2009). At the Hal Ross flour mill there were no structures within a 200-m radius taller than half of the mill's height to alter wind direction and influence gas leakage rates. Wind direction was, therefore, neglected in the analysis of gas leakage rates.

3. Results and discussion

The plots of the pressure-airflow rate curves representing sealing effectiveness of all fumigation experiments are shown in Figure 2. Equation 1 satisfactorily described the pressure and airflow data ($r^2 = 0.819$ to 0.995) (Table 2). The coefficients b ranged from 0.098 to 0.279 while the coefficient n ranged from 0.445 to 0.655. The gas-tightness was similar only for the first MB and first SF fumigations ($F = 1.06$; df = 2, 68; $P = 0.351$). The gas-tightness was significantly different for the remaining 14 pair-wise comparisons (F, range = 8.49 – 273.63; df, range = 2, 68 - 2, 145; $P < 0.0005$). This could be attributed to differences in environmental conditions (see below) during each of the fumigations, because data used in Equation 1 could not be corrected for differences in environmental conditions. The result of the pressurization test for the second SF fumigation was adversely affected by strong prevailing winds (6 to 8 m/s) during the test resulting in more scattered data points. However, the lower boundary of the scattered data points, which indicates the highest building gas-tightness, coincided with similar pressure-airflow rate curves for the five other fumigations. In general, the pressurization test results suggested that the differences in the HLTs were not caused by variations in sealing quality but by the outside environmental conditions.

Substantial variations in barometric pressure, outside temperature, and outside relative humidity were observed among fumigations (Figure 3A-C). The barometric pressure curves in Figure 3A were adjusted for the barometric pressure reduction due to the difference in height between the weather station on the mill roof and the ground. The average values of barometric pressure, outside temperature, and relative humidity between the fumigations ranged from 971 to 984 mbar, 13 to 26°C, and 63 to 84%, respectively. Within each fumigation the differences between the highest and lowest values of barometric pressure, outside temperature, and relative humidity were approximately 3 to 9 mbar, 5 to 15°C and 30 to 60%, respectively. The inside temperature and relative humidity were, however, stable during the fumigations (Table 3). On each floor the inside temperature and relative humidity generally varied by less than 1°C and 10%, respectively, and the differences in the inside temperature and relative humidity among floors were less than 4°C and 20%, respectively. The inside temperatures were either equal to or higher than the outside temperatures with a maximum difference of at least 10°C, except for the first and second MB fumigations, where for a few hours, the opposite occurred. These findings suggested that at the gas-tightness level achieved in this study air infiltration did not have an effect on the thermal changes inside the flour mill. In addition to preventing rapid gas loss, good sealing quality helps increase fumigation efficacy against insects and helps maintain stable temperatures inside a fumigated building irrespective of outside temperature changes.

The fumigant concentrations over time near the ceiling across the five mill floors for each of the fumigations are illustrated in Figure 4. For the MB and SF fumigations, differences in fumigant concentrations within each floor were less than 3 and 5 g/m^3, respectively (data not shown). Initially, the fumigant concentrations increased rapidly and distributed well among the mill floors, after which the concentrations gradually decreased over time. However, gas concentrations at one monitoring location in an ingredient mixing drum on the third floor was an exception to this general observation. During the first MB and all SF fumigations, the gas concentrations inside the mixing drum did not decrease as fast as the other locations because of restricted gas movement. The sudden peaks in gas concentrations 15 h after the initial fumigant introduction in the first and third MB fumigations were due to adding more gas (Table 1). SF gas was also added during the third fumigation at 14.5 h into the fumigation, but gas monitoring data did not show any sudden peaks. The concentration differences within the entire mill were between 2 and 7 g/m^3. Even gas distribution was established throughout the mill within the first 4 h, except for the second and third SF fumigations in which it took at least 10 h. The longer time for gas to equilibrate within the structure may be due to the stairwell doors being closed during these two fumigations, making it more difficult for the fumigant to circulate quickly among mill floors. In some structures, partitioning very leaky areas as separate fumigated volumes can be beneficial in preventing excessive fumigant loss.

In this particular study the observed HLTs correlated well with the outside wind speeds regardless of whether or not the stairwell doors were closed. The even gas distributions observed with MB and SF fumigations showed that these two fumigants have similar gas distribution characteristics. In structures where commodities are present distribution of MB and SF gases could be different due to different rates of sorption by the commodities. However, this effect was nonexistent because the mill was free of any stored commodity.

The hourly-average outside wind speeds during the fumigations were superimposed on the corresponding concentration plots in Figure 4. While wind speeds varied mostly within a range of 0 to 5 m/s, the rapid hour-by-hour wind fluctuations were not reflected in the gas concentration curves. Except for the third MB fumigation, HLTs for each fumigation shown in Figure 4 were calculated by dividing the gas concentration curves over time into sections in which wind speeds were either above or below 5 m/s. During the third MB fumigation at 8 h the gas concentration curves indicated a sudden drop (Figure 4E), and thus the concentration curves after this time were divided separately. For each divided section, the five concentration curves were first averaged and Equation 2 was fitted to the average concentration over time data. The exposure periods immediately after fumigant releases when concentration differences were greater than 5 g/m^3 were excluded from the HLT calculations. The average estimated HLTs (and SE), average wind speeds, average absolute inside-outside temperature differences, and corresponding elapsed exposure periods are summarized in Table 4. The HLTs for the MB and SF fumigations were in range of 3.61 to 28.64 h and 9.97 to 31.65 h, respectively. Williams et al. (2000) suggested HLTs above 24 h as desirable and any values below 10 h as undesirable for structural fumigations. They reported HLTs of 8 to 15 h to be common in food-processing facilities subjected to fumigation. The range of HLTs observed reflects variation among structures in gas tightness despite effective sealing, since all of the building gaps cannot be accurately identified or sealed. Based on the pressurization test, the Hal Ross flour mill had nearly identical sealing quality based on visual inspection, but the differences in HLTs were observed across the six fumigations. Of all the weather variables observed, only wind speeds predominantly affected HLTs, and HLTs were inversely related to wind speeds (Figure 5A).

Except for the last two HLTs of the third MB fumigation, when the average wind speeds were not greater than 5 m/s, the HLTs were longer than 10 h, regardless of the type of fumigant used. The last two HLTs of the third MB fumigation were 3.61 and 9.71 h while the corresponding average wind speeds were less than 5 m/s. These two unexpectedly short HLTs were observed after the sudden drop in the fumigant concentration during the third MB fumigation probably due to some seal damage which we could not firmly identify. From Equations 3 and 4, if the stack effect was neglected, it can be seen that:

$$HLT = \frac{x_1}{U} \quad (5)$$

where, x_1 is a constant. Discarding the last two short HLTs of the third MB fumigation, fitting Equation 5 to the data in Figure 5A resulted in the mean ± SE (no. observations = 8) x_1 value of 68.52 ± 2.85 and a r^2 value of 0.922. Similarly, combining Equations 3 and 4 with the wind effect neglected yields Equation 6:

$$HLT = \frac{x_2}{\sqrt{\Delta T}} \quad (6)$$

where x_2 is a constant. However, such correlation in Equation 6 could not be established as indicated by the scattered data points of the HLTs plotted against the square roots of the average absolute inside-outside temperature differences in Figure

5B. This was likely attributed to the strong wind effect overshadowing the buoyancy force. Chayaprasert and Maier (2010) found that as the wind speed doubled the HLT decreased by half (Equation 5). Cryer (2008) neglected stack effect in his simulated fumigations and the results indicated that the HLTs for MB and SF were interchangeable. This finding was corroborated by a similar simulation study by Chayaprasert et al. (2009) in which both the wind and stack effects were included in the simulations. The high r^2 value of the curve fitting result (Equation 5) in the present study indicated a strong correlation between the HLTs and wind speeds rather than the type of fumigant used. In addition, when wind is the dominant force of gas leakage, HLT were inversely proportional to the prevailing wind speed. These empirical findings provide a quantitative basis to support the fact that HLTs are influenced by environmental conditions, which should be taken into consideration during structural fumigations.

4. Conclusions

This study provided a quantitative side-by-side comparison between MB and SF fumigations in the same flour mill. The pressurization test showed that sealing effectiveness can be quantitatively determined ahead of a fumigation to quantify gas tightness of a structure. The concentrations of both fumigants varied within a range of 2 to 7 g/m^3, which implied similar gas distributions with the mill. The observed HLTs decreased with increasing wind speeds regardless of the type of fumigant used. Our results suggest that for a given level of gas tightness of a structure, fumigant leakage rate is a function of the driving forces such as wind speeds rather than inherent gas characteristics of MB and SF.

Acknowledgements

This study was funded by a 2008 grant from USDA-CSREES Methyl Bromide Transitions Program under agreement number 2008-51102-04583. The authors thank The Industrial Fumigant Company, Olathe, KS, USA, and Presto-X, Omaha, NE, USA, for providing fumigation services. The cooperation of Dow AgroSciences, Indianapolis, Indiana, USA, and Chemtura, West Lafayette, Indiana, USA, is also acknowledged. We thank Sam Hanni, Sara Savoldelli, Lakshmikantha Channaiah, Johnselvakumar Lawrence, Moses Khamis, Monika Brijwani, Xue Meng, James Weaver, Roshan Chetry, Adrian Martinez-Kawas, Carlos Campabadal, and Anne Rigdon for help in monitoring gas concentrations during the six fumigations. This paper is contribution number 12-325-J of the Kansas State University Agricultural Experiment Station.

References

Annis, P.C., 1999. The relative effects of concentration, time, temperature and other factors in fumigant treatments. In: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., Lianghua, G. (Eds), *Proceedings of the Seventh International Working Conference on Stored Product Protection*, 14-19 October 1998, Beijing, China, Sichuan Publishing House of Science and Technology, Chengdu, China, pp. 331-337.

ASHRAE, 2001. ASHRAE Handbook - Fundamentals. American Society of Heating, Refrigerating and Air-Conditioning Engineers Inc., Atlanta, GA.

Banks, H.J., Annis, P.C., 1984. The importance of processes of natural ventilation to fumigation and controlled atmosphere storage. In: Ripp, B.E., Banks, H.J., Bond, E.J., Calverley, D.J., Jay, E.G., Navarro, S. (Eds), *Controlled Atmosphere and Fumigation in Grain Storages: Proceedings of an International Symposium "Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages"*, 11-22 April 1983, Perth, Australia, Elsevier, Amsterdam, Netherlands, pp. 299-323.

Banks, H.J., Longstaff, R.A., Raupach, M.R., Finnigan, J.J., 1983. Wind-induced pressure distribution on a large grain storage shed: Prediction of wind-driven ventilation rates. Journal of Stored Products Research 19, 181-188.

Bell, C.H., Savvidou, N., Wontner-Smith, T.J., 1999. The toxicity of sulfuryl fluoride (Vikane®) to eggs of insect pests of flour mills. In: Zuxun, J., Quan, L., Yongsheng, L., Xianchang, T., Lianghua, G. (Eds), *Proceedings of the Seventh International Working Conference on Stored Product Protection*, 14-19 October 1998, Beijing, China, Sichuan Publishing House of Science and Technology, Chengdu, China, pp. 345-350.

Bell, C.H., Savvidou, N., Wontner-Smith, T.J., Cardwell, S.K., Bodle, C., 2004. Development of sulfuryl fluoride as a fumigant for the milling industry. HGCA Project Report No. 333. London, UK: Home-Grown Cereals Authority.

Campbell, J.F., Arbogast, R.T., 2004. Stored-product insects in a flour mill: Population dynamics and response to fumigation treatments. Entomologia Experimentalis et Applicata 112, 217-225.

Chayaprasert, W., 2007. Development of CFD models and an automatic monitoring and decision support system for precision structural fumigation. Ph.D. Thesis. West Lafayette, IN: Purdue University, Department of Agricultural and Biological Engineering.

Chayaprasert, W., Maier, D.E., 2010. Evaluating the effects of sealing quality on gas leakage rates during structural fumigation by pressurization testing and Computational Fluid Dynamics simulations.pdf. Transactions of the ASABE 53, 853-861.

Chayaprasert, W., Maier, D.E., Ileleji, K.E., Murthy, J.Y., 2008. Development and validation of Computational Fluid Dynamics models for precision structural fumigation. Journal of Stored Products Research 44, 11-20.

Chayaprasert, W., Maier, D.E., Ileleji, K.E., Murthy, J.Y., 2009. Effects of weather conditions on sulfuryl fluoride and methyl bromide leakage during structural fumigation in a flour mill. Journal of Stored Products Research 45, 1-9.

Cryer, S.A., 2008. Predicted gas loss of sulfuryl fluoride and methyl bromide during structural fumigation. Journal of Stored Products Research 44, 1-10.

Draper, N., Smith, H., 1981. Applied regression analysis, 2nd Ed. John Wiley and Sons, New York.

Drinkall, M.J., Pye, C.D., Bell, C.H., Braithwaite, M., Clack, S.R., Ive, J., Kershaw, S., 2004. The practical use of the fumigant sulfuryl fluoride to replace methyl bromide in UK flour mills. In: Cauvain, S.P., Salmon, S.S., Young, L.S. (Eds), *Proceedings of the Twelfth International ICC Cereal and Bread Congress*, 23-26 May 2004, Harrogate, UK, Woodhead Publishing, Cambridge, UK, pp. 245-249.

Drinkall, M.J., Zaffagnini, V., Süss, L., Locatelli, D.P., 2003. Efficacy of sulfuryl fluoride on stored-product insects in a semolina mill trial in Italy. In: Credland, P.F., Armitage, D.M., Bell, C.H., Cogan, P.M., Highley, E. (Eds), *Proceedings of the Eighth International Working Conference on Stored Product Protection*, 22-26 July 2002, York, UK, CAB International, Wallingford, UK, pp. 884-887.

Gandy, D.G., Chanter, D.O., 1976. Some effects of time, temperature of treatment and fumigant concentration on the fungicidal properties of methyl bromide. Annals of Applied Biology 82, 279-290.

Kenaga, E.E., 1961. Time, temperature and dosage relationships of several insecticidal fumigants. Journal of Economic Entomology 54, 537-542.

Reichmuth, C., Rassmann, W., Binker, G., Fröba, G., Drinkall, M.J., 2003. Disinfestation of rust-red flour beetle (*Tribolium castaneum*), saw-toothed grain beetle (*Oryzaephilus surinamensis*), yellow meal worm (*Tenebrio molitor*), Mediterranean flour moth and Indian meal moth (*Plodia interpunctella*) with sulfuryl fluoride in flour mills. In: Credland, P.F., Armitage, D.M., Bell, C.H., Cogan, P.M., Highley, E. (Eds), *Proceedings of the Eighth International Working Conference on Stored Product Protection*, 22-26 July 2002, York, UK, CAB International, Wallingford, UK, pp. 736-738.

Small, G.J., 2007. A comparison between the impact of sulfuryl fluoride and methyl bromide fumigations on stored-product insect populations in UK flour mills. Journal of Stored Products Research 43, 410-416.

Taylor, R.W.D., 1994. Methyl bromide - Is there any future for this noteworthy fumigant? Journal of Stored Products Research 30, 253-260.

U.S.-EPA, 2010. Critical Use Exemption Information. Available at: http://www.epa.gov/ozone/mbr/cueinfo.html. Accessed 17 August 2010.

Williams, R.E., Prabhakaran, S., Schneider, B.M., 2000. Monitoring for precision fumigant application in food-processing plants. In, *2000 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions*, 6-9 November 2000, Orlando, FL.

Figure Captions

Figure 1. Hal Ross flour mill and a generic mill floor plan. Note that only one gas introduction point was selected from one of the two points shown in the figure. Only the southwest and northeast gas monitoring locations are represented in the figure out of the six locations.

Figure 2. Results of the building pressurization test for each of the six fumigations.

Figure 3. Barometric pressures (A), temperatures (B), and relative humidities (C) recorded by the weather station on the mill roof during each of the six fumigations.

Figure 4. Fumigant concentrations over time (solid lines) near the ceiling among all five mill floors and hourly-average outside wind speeds outside the mill (open circles) during the first MB (A) and SF (B), second MB (C) and SF (D), and third MB (E) and SF (F) fumigations.

Figure 5. Relationship between HLT values (Table 4) and average wind speeds (A) and HLT values and the square roots of the average absolute inside and outside temperature differences (B). The data points for MB and SF fumigations were plotted as closed circles and closed squares, respectively. The dashed line in A shows Equation 5 fitted to the data. Note that the last two HLT values of the third MB fumigation (open circles) were not included in the curve-fitting calculations (see text for details).

Table 1. Quantities of MB and SF fumigants used and gas introduction times.

Fumigation	Fumigant introduction		Exposure period (h)	Introduced amount (kg) on mill floor					
	Date	Time		First	Second	Third	Fourth	Fifth	Total
MB1	6 May 2009	6:40 pm	24	22.7 +22.7[a]	22.7	22.7	45.4	45.4	181.6
SF1	27 May 2009	6:00 pm	24.5	113.6	113.6	113.6	113.6	113.6	568.0
MB2	11 Aug 2009	2:50 pm	24	22.7	22.7	22.7	45.4	45.4	158.9
SF2	19 Aug 2009	2:45 pm	24	113.6	56.8	113.6	113.6	113.6	511.2
MB3	11 May 2010	5:00 pm	24.3	+22.7[b] +18.1[c]	22.7	22.7	45.4	45.4	199.6
SF3	25 May 2010	5:10 pm	25	113.6	113.6	113.6	113.6 +28.3[d]	113.6 +28.3[d]	623.7

[a] Top-up (additional gas) release at 9:50 am on 7 May 2009.

[b] Top-up release at 8:15 am on 12 May 2010.

[c] Top-up release at 9:45 am on 12 May 2010.

[d] Top-up release at 7:50 am on 26 May 2010.

Table 2. Coefficients (mean ± SE) from Equation 1 fitted to pressure-airflow rate data.

Fumigation	No. observations	b	n	r^2
MB1	34	0.102 ± 0.007	0.655 ± 0.017	0.982
SF1	38	0.112 ± 0.007	0.630 ± 0.016	0.978
MB2	38	0.105 ± 0.004	0.639 ± 0.009	0.993
SF2	70	0.279 ± 0.031	0.445 ± 0.027	0.819
MB3	72	0.105 ± 0.009	0.603 ± 0.021	0.916
SF3	77	0.098 ± 0.002	0.634 ± 0.005	0.995

Table 3. Mean ± SE values for temperature and relative humidity observed inside the flour mill during fumigations.

Fumigation	Floor				
	First	Second	Third	Fourth	Fifth
			Temperature (°C)		
MB1	21.9 ± 0.009	22.2 ± 0.010	22.3 ± 0.014	23.0 ± 0.014	23.0 ± 0.008
SF1	23.3 ± 0.006	24.4 ± 0.004	25.2 ± 0.003	25.7 ± 0.009	25.6 ± 0.000
MB2	26.7 ± 0.013	28.6 ± 0.011	30.0 ± 0.010	30.9 ± 0.010	31.1 ± 0.005
SF2	27.9 ± 0.005	29.7 ± 0.009	31.1 ± 0.002	31.9 ± 0.001	31.1 ± 0.000
MB3	23.6 ± 0.007	23.8 ± 0.008	24.4 ± 0.000	24.7 ± 0.007	25.4 ± 0.009
SF3	27.6 ± 0.009	28.3 ± 0.010	28.4 ± 0.015	28.9 ± 0.014	29.3 ± 0.009
			Relative humidity (%)		
MB1	46.3 ± 0.097	45.2 ± 0.088	44.3 ± 0.056	42.7 ± 0.064	40.9 ± 0.080
SF1	43.2 ± 0.030	40.1 ± 0.028	37.6 ± 0.025	36.7 ± 0.025	34.8 ± 0.028
MB2	57.6 ± 0.049	50.6 ± 0.043	46.0 ± 0.031	43.5 ± 0.029	41.3 ± 0.018
SF2	54.2 ± 0.027	46.5 ± 0.064	43.0 ± 0.023	41.1 ± 0.031	41.1 ± 0.031
MB3	34.7 ± 0.043	33.4 ± 0.035	32.1 ± 0.026	31.1 ± 0.021	29.2 ± 0.022
SF3	49.8 ± 0.122	46.5 ± 0.047	46.0 ± 0.036	43.1 ± 0.037	42.1 ± 0.066

Table 4. Mean and SE estimated half-loss times (HLT) and average wind speeds and corresponding elapsed time periods in which these two values were calculated.

Fumigation	Elapsed exposure period (h)	Absolute average temperature difference (°C)	Average wind speed (m/s)	HLT (h)			
				No. observations	Mean	SE	r^2[a]
MB1	5-15	5.96	2.45	28	28.76	0.001	0.962
	17-24	4.03	7.12	19	9.65	0.002	0.971
SF1	5-24	8.00	3.67	55	19.75	0.000	0.992
MB2	5-24	5.35	2.16	41	28.64	0.000	0.976
SF2	11-21	12.25	3.00	24	28.29	0.000	0.986
	21-24	6.01	6.90	8	9.97	0.002	0.981
MB3	4-8	10.95	5.04	9	10.80	0.003	0.917
	8-15	12.50	4.93	18	3.61	0.004	0.983
	20-24	10.67	3.11	10	9.71	0.003	0.967
SF3	13-25	4.36	2.10	26	31.65	0.001	0.955

[a] The r^2 values were based on linear regression of hourly fumigant concentration (y) versus elapsed time (x). In an hour, there were 2 to 3 points of average fumigant concentration data. The curve generated from Equation 2 intercepts y-axis at $y = C_i$ (i.e., the average concentration at the beginning of each fumigant concentration

curve section). Plotting Equation 2 on a semi-log scale gives a straight line, the slope of which is essentially the HLT.

Figure 1

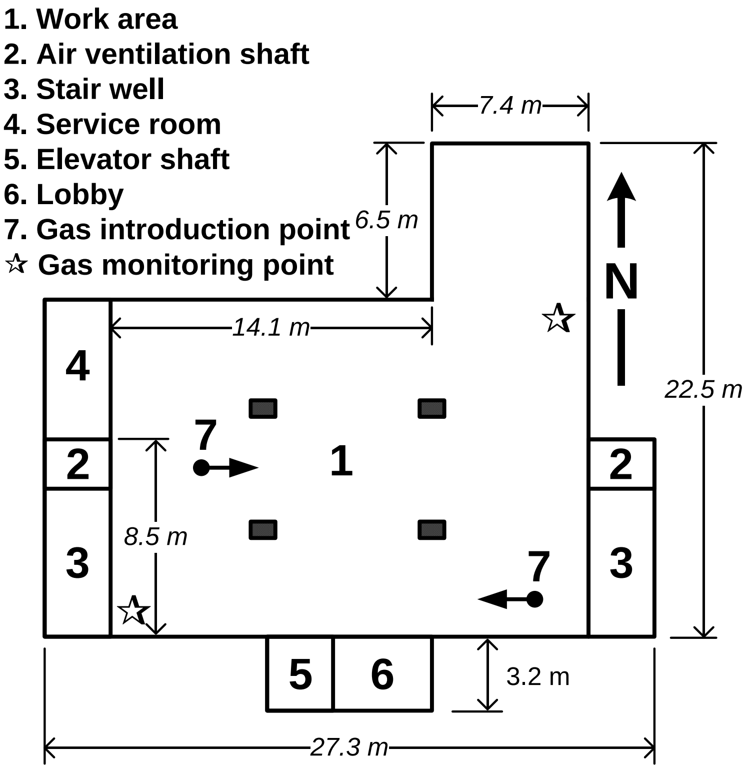

1. Work area
2. Air ventilation shaft
3. Stair well
4. Service room
5. Elevator shaft
6. Lobby
7. Gas introduction point
☆ Gas monitoring point
7.4 m
6.5 m
22.5 m
N
14.1 m
4
2
7
1
2
8.5 m
3
7
3
☆
☆
5
6
3.2 m
27.3 m

Figure 2

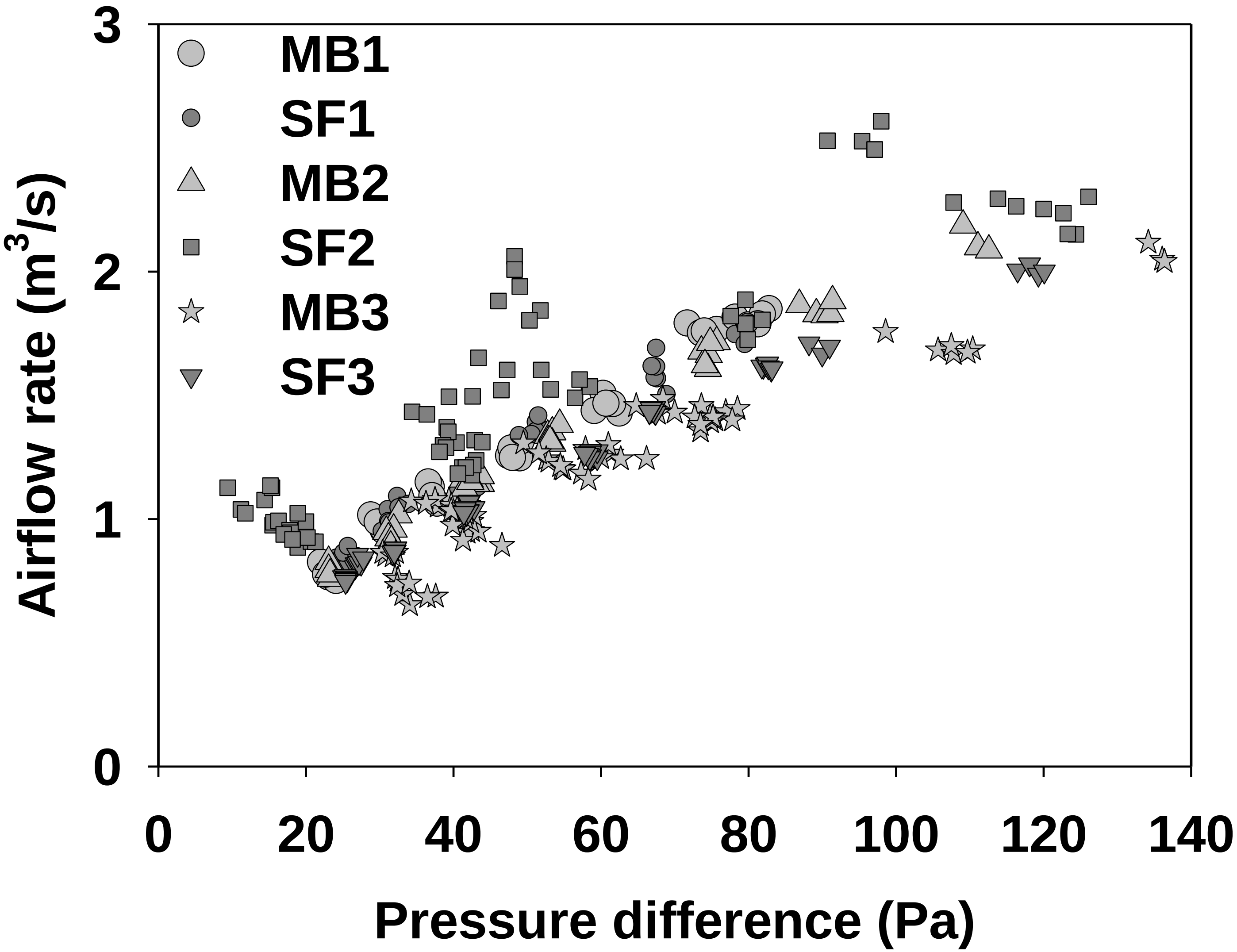

MB1
SF1
MB2
SF2
MB3
SF3
3
2
1
0
Airflow rate (m^3/s)
0
20
40
60
80
100
120
140
Pressure difference (Pa)

Figure 3

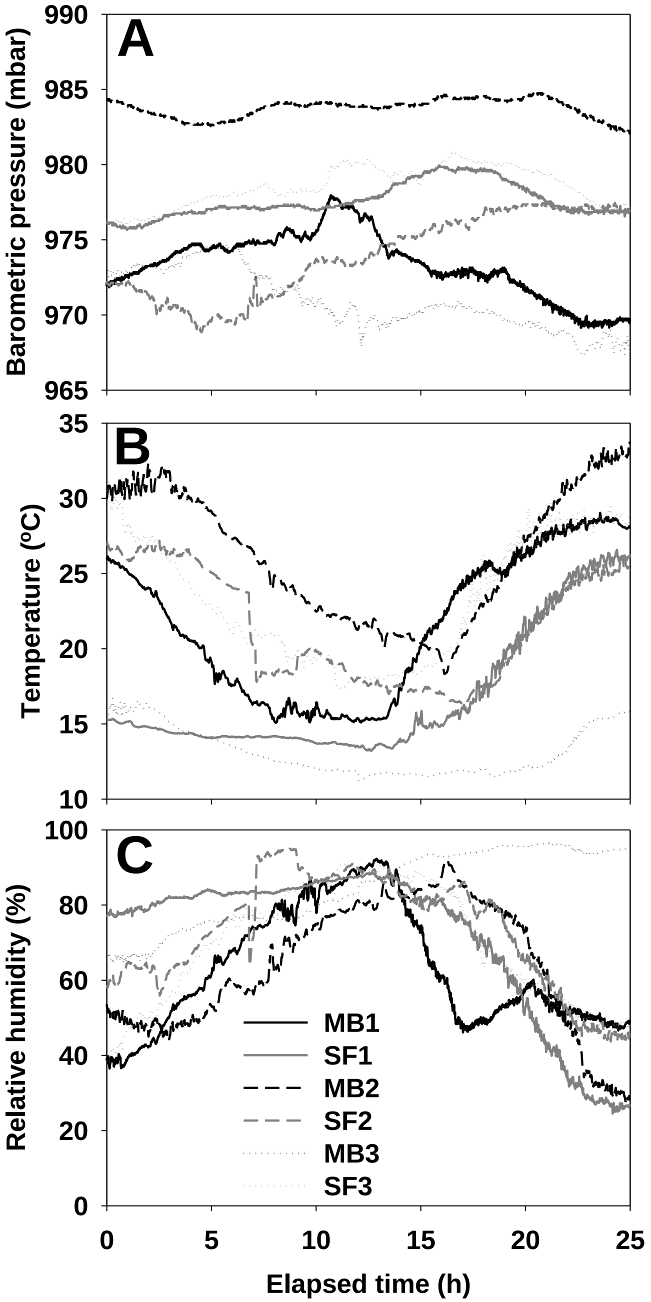

A
B
C
Barometric pressure (mbar)
990
985
980
975
970
965
Temperature (ºC)
35
30
25
20
15
10
Relative humidity (%)
100
80
60
40
20
0
MB1
SF1
MB2
SF2
MB3
SF3
0
5
10
15
20
25
Elapsed time (h)

Figure 4

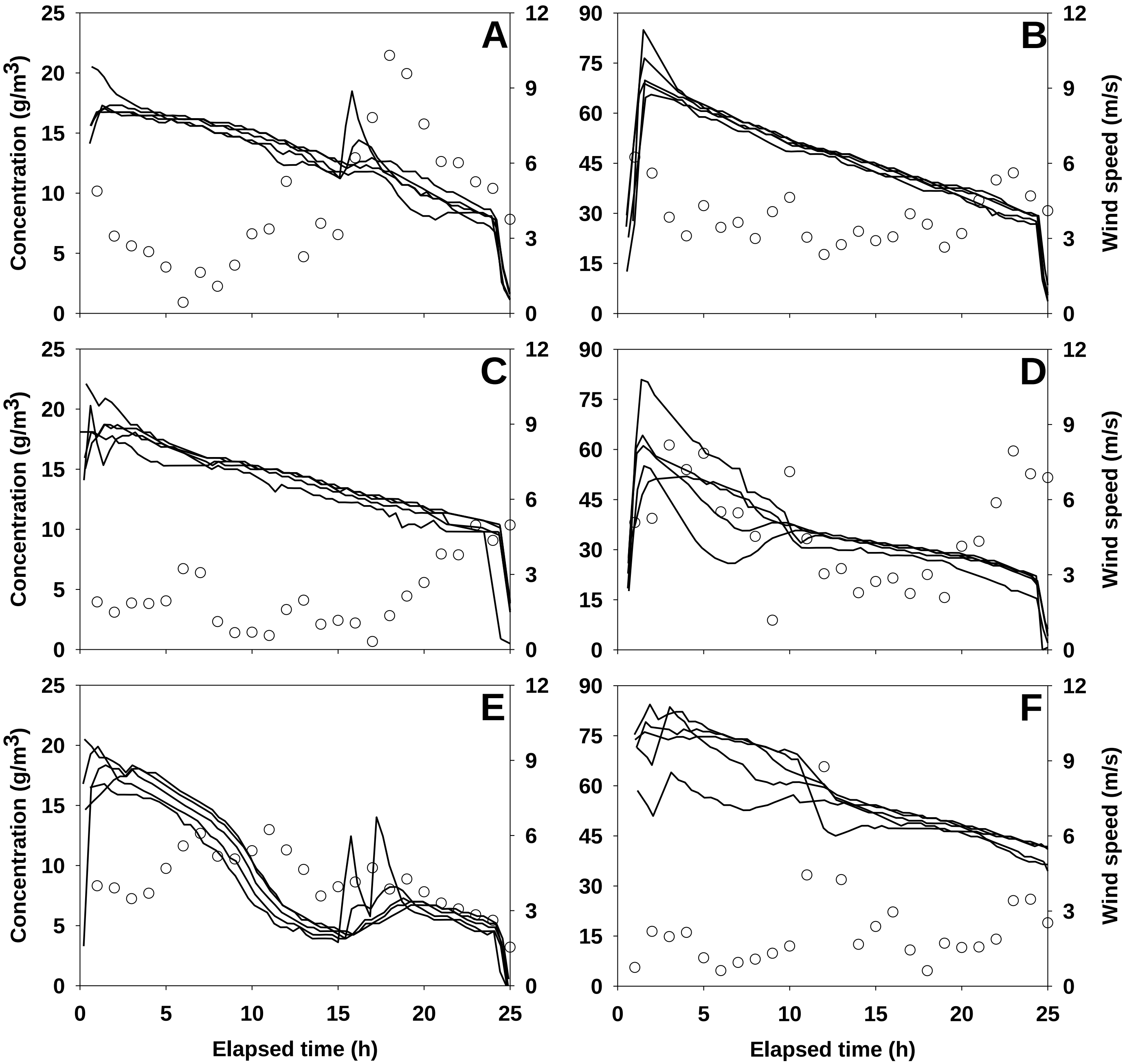
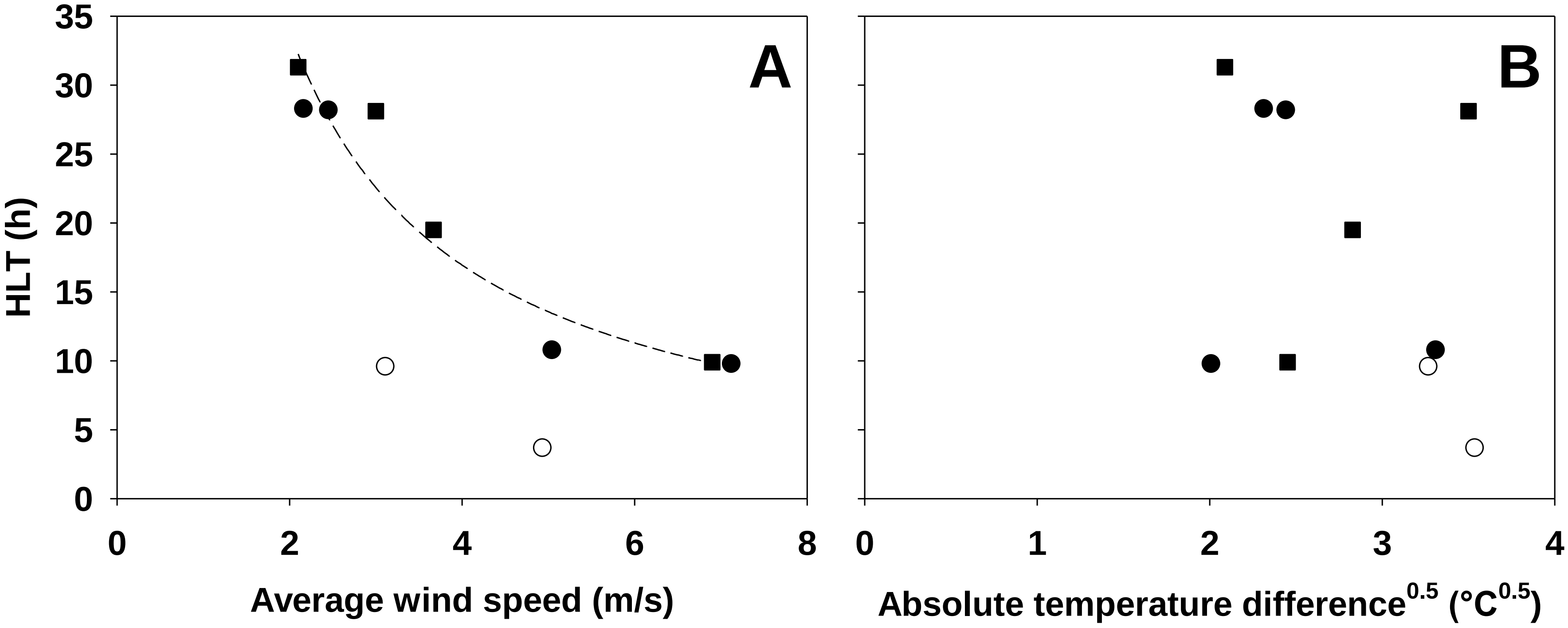

A
B
C
D
E
F
Concentration (g/m^3)
Wind speed (m/s)
Elapsed time (h)
0
5
10
15
20
25
0
15
30
45
60
75
90
0
3
6
9
12

Figure 5



A
B
HLT (h)
0
5
10
15
20
25
30
35
0
2
4
6
8
Average wind speed (m/s)
0
1
2
3
4
Absolute temperature difference$^{0.5}$ (°C$^{0.5}$)