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Transport Phenomena of Phosphine inside a Half Flower Box

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ABSTRACT. *Methyl bromide, currently used for insect disinfestation of cut flowers, will soon be restricted to the industry. The toxicity of a potential alternative fumigant, phosphine (2% PH_3 and 98% N_2), was tested in vitro on insects commonly found as pests on cut flowers. However, the efficacy of phosphine under commercial situations needs yet to be established.*

Preliminary studies based on numerical modelling indicates that in still conditions it may take over 700 min for phosphine to equilibrate at the center of an empty fiberboard box of 1.0 m × 0.3 m × 0.21 m. In a box full of proteas with large, tight bracts covering the flower, the time to reach equilibrium will be longer. Laboratory experiments were conducted by measuring the change in time - concentration relationship of phosphine diffusion in a box with or without flowers in still or moving air. The transport phenomena of phosphine into flower heads of the Protea 'Pink Ice' was also determined.

Phosphine took 240 min to attain equilibrium in still air as against 800 min under theoretical modelling. The equilibrium was reached in 35 min for an empty box when compared with a box packed with flowers where it took 60 min, whilst the diffusion of phosphine into Protea flower head took 75 min under moving air. The results also highlighted that a box full of Proteas cause resistivity to the free movement of phosphine. Accordingly, the time (130 min) required to attain equilibrium inside a flower head at the end of the box has observed to be a significantly (P=0.05) greater than the time taken to attain equilibrium (50 min) outside the flowerhead.

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INTRODUCTION

Fumigants have been widely used to control insects and other pest organisms in food and to disinfest material and commodities before they enter world market. Of these, methyl bromide and ethylene dibromide have been used to control post harvest insects since the early 1940 s. The Australian cut flower industry, worth $24 million in 1991, has expanded todate at a rate greater than 20% per annum (Anon, 1994). However, Japanese inspection results from 1986 have shown that diseases or pests were found in about 33% of imported flowers (Anon, 1987), of which 23% were fumigated with hydrogen cyanide and 77% with methyl bromide.

Current practice for insect control in export flowers involves good preharvest control of pests, followed either by fumigation or insecticide dips/aerosol treatments. Research on aerosol products such as dichlorovos, pyrethrins and permethrins has identified these as chemicals with significant toxicity on non target animals such as birds, bees, fish and aquatics (Brain and Cornor, 1988).

Further, aerosols consist of very small droplets (2-4 microns) which may not reach tiny crevasses within cutflowers and which may experience rapid deactivation when they deposit on solid surfaces with moisture. The difficulty to control some of the insects/pests may be due to the following factors:

a) Ability of insects to hide inside tiny crevasses of flower heads at the time of disinfestation, where fumigant concentration is too low to harm insects.

b) Restriction imposed on the diffusion of fumigants by different packing methods utilized in the industry.

c) Application of those concentrations of treatments recommended as suitable for attaining desired kill for certain insects/pests are based on laboratory evaluation.

Practical situations are often different to standard laboratory conditions, since the penetration of fumigant into localized areas inside a boxfull of flowers may be difficult, which eventually result in an inadequate exposure of insects to disinfestation treatments.

Methyl bromide has been identified as an ozone depleting gas at the 7th meeting of the parties to the Montreal Protocol in Vienna, Austria. It was

agreed in this meeting that for industrial nations, a 25% reduction of use should be achieved by 1st January 2001, a 50% reduction by 2005 and a complete phase out by 2010. However, for developing nations a freeze in 2002 not exceeding the average use for the years 1995-1998 was agreed to (UNEP, 1995), which will be re-visited in 1997. In a US Department of Agriculture study, it has estimated that the annual production losses for nursery and floral costs associated with restricting methyl bromide at $ 163 million (Anon, 1993). Hence, research and development of alternate fumigants and fumigation techniques as substitutes for methyl bromide are of prime focus.

Phosphine is a gas of high toxicity with small, highly mobile molecules capable of rapid penetration into a commodity (Bond, 1984). He showed that phosphine desorbs rapidly after fumigation, resulting in minute quantities of residues such as phosphites and phosphates. Experimental evidence so far has shown that phosphine treatment showed minimal phytotoxic effects, though it is rather slow in killing some insects. Earlier trials (Karunaratne *et al.*, 1995) showed that phosphine concentrations ranging from 300-6000 $\mu L.L^{-1}$ applied for durations upto 6 h resulted in a 100% kill of greenhouse thrips (*Heliothrips haemorrohidalis* Bouche'), adult aphids (*Myzus persicae* Sulzer) and light brown apple moth larvae (LBAM; *Epiphyas postvittana* Walker). It has also been shown that proteas (*Protea cynaroides*), wax flowers (*Chamelaucium uncinatum*) and tulips (*Tulipa* spp.) fumigated with 4000 $\mu L.L^{-1}$ phosphine for 6 h showed no significant loss of vase life when compared with untreated controls. For kangaroo paws (*Anigozanthos* spp.) phosphine concentrations up to 8000 $\mu L.L^{-1}$ for 6 h did not reduce vase life for any of the treatments (Karunaratne *et al.*, 1995).

It was evident by these observations that those phosphine concentrations identified as toxic to horticultural insects did not significantly ($P=0.05$) deplete the vase life of any of the flowers.

One of the objectives of the research outlined in this paper is to determine the time-concentration relationship of phosphine at various locations in a commercial flower box during the fumigation with or without turbulence. Further, the transporation of phosphine in a box packed with Protea 'Pink Ice' and into a Protea flower head is also investigated by this study. This information together with *in vitro* results can then be used to evaluate appropriate fumigation schedules for phosphine.

MATERIALS AND METHODS

The mathematical model

A mathematical model of the spread of fumigants in boxes used to transport flowers was simulated by computer. The mathematical modelling not only did facilitate to compare the time taken for attaining equilibrium, but also helped to get an overall estimate over the delay times. The information thus evaluated from the model was useful to plan out the frequency of phosphine sampling from the drum. The analysis assumed that the mass transfer of phosphine into a flower box of 1.0 m × 0.30 m × 0.21 m (length × width × height) takes place only by diffusion under steady state conditions. The following equation was used for the mathematical modelling.

$$\frac{\partial C}{\partial t} = D \nabla^2 C \qquad (1)$$

in which C is the concentration of the fumigant (kg/m^3), ∇^2 is the Laplacian operator in cartesian coordinates (1/m^2), t is time (seconds) and D is the binary diffusion coefficient of the species in the two component mixture (m^2/s).

Experimental set up

The set up drawn in Figure 1 was fabricated to measure the diffusion of phosphine into a flower box with or without flowers under still air or turbulence. A steel box with dimensions similar to half the length (0.5 × 0.3 × 0.2 m) of a commercial flower box was constructed and mounted on to a 66 liter plastic drum. Six ports along the center line of one side of the box were mounted for sampling of gas inside the box.

Port 4 had a 150 mm long needle fitted to it, such that the gas in the center of the box could be sampled. Four ports were mounted on the drum for dosing and sampling purposes. All the ports were sealed with removable rubber septa to maintain a gas tight seal in the box and to facilitate the sampling procedure. Further, the drum was fitted with a battery operated fan with an external switch to mix the atmosphere inside the drum, when required.

At the interface between the drum and box a removable template with elliptical holes of the same dimensions as a commercial flower box was placed.

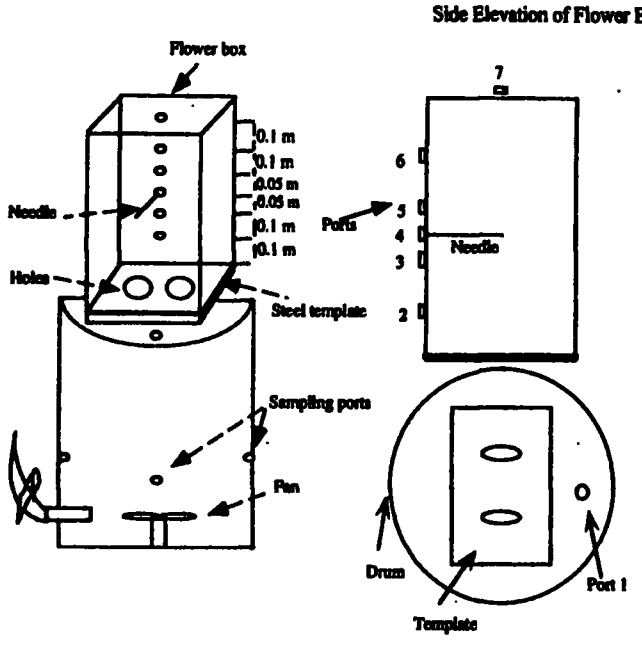

Figure 1. Chamber for measurement of phosphine diffusion.

Experimental trials

Trials were conducted at 24°C to determine the transport phenomena of phosphine in five different circumstances. In each case, the box was phosphine free and 240 ml of fumigant (2% PH_3, 98% N_2) was injected into the drum at time t = 0.

a) In Experiment 1 phosphine was allowed to diffuse into an empty flower box.

b) Experiment 2 was identical to Experiment 1 except that a small fan in the drum was used to mix the atmosphere in the drum. The fan was used in all subsequent experiments.

c) Protea 'Pink Ice' (20 stems) were packed into the box in Experiment 3 and the phosphine diffusion observed.

d) In Experiment 4, a single Protea flower head was suspended on the long needle on port "4" such that the entrance to the needle was deep inside the flower head. The template was removed to ensure rapid immersion of the Protea in fumigant.

e) Experiment 5 combined the effects of c and d. The box was packed with Protea. The needle was shifted to port "7" at the end of the box and a flower placed on the needle in a similar manner to d. It was surmised that an insect in this flower head would experience the greatest delay in being exposed to phosphine.

Measurement of phosphine

Phosphine concentrations were analyzed by gas liquid chromatography (Photovac 10A10, Ontario, Canada) after Bond (1982) using a 1.2 m × 3.2 mm (inside diameter) Teflon column packed with Porapack N with a mesh range of 80/100. The retention time of phosphine was 2.5 min.

Sampling of phosphine

Four syringes were used to simultaneously inject 240 ml of fumigant into the drum. Soon after the injection of gas into the drum, samples were taken from ports 1 to 7 until the desired equilibrium concentration of 5.24×10^{-5} g/litre was reached inside the box. At the start of the experimental trial, more samples were taken from ports 1 (0 m) and 2 (0.1 m) since there was a rapid rise of gas concentration adjacent to the entrance. Air tight glass vials of 4 ml were used to store the samples prior to analysis by gas chromatograph. All the analysis were done promptly inorder to prevent the possibility of gas leakage from the vials. Syringes were cleaned by stylet wires of appropriate sizes soon after each sampling. Acetone solution was also used to clean the syringes upon termination of each sampling session. In Experiments 1, 2, 3 and 5, sampling ports 1, 2, 4, 6 and 7 were used. Sampling ports 3 (0.2 m) and 4 (0.25 m) were used for Experiment 4.

Statistical analysis

The variance of the time series taken to attain equilibrium at different ports under respective experimental trials was compared by Bartlett's test (Walpole *et al.*, 1978). This test is applicable to statistics whose sampling distribution is approximated very closely by the chi-square distribution when the k random samples are drawn from independent normal populations. The test is normally applied if the sample sizes per treatment are unequal or if one variance is much larger than the others. The hypothesis (H_1) was to check whether there is no significant difference between the variance of the sampling curves for concentration *vs* time, when compared with the alternative hypothesis (H_0), where the variances between sampling curves were not all equal.

RESULTS AND DISCUSSION

The Equation (1) was numerically solved subject to boundary conditions that reflect the impermeability of the wall of the flower box to the fumigant, save at the holes provided specifically for fumigant ingress and a plane of symmetry mid way along the length of the box. A constant concentration was assumed to exist outside the box. Preliminary numerical modelling demonstrated that phosphine takes approximately 800 min to attain 90% equilibrium concentration inside the far end of the flower box (0.5 m) under still air conditions. The two holes in each end of box required were 3 cm wide and 5.5 cm high.

The delay times obtained by preliminary mathematical modelling in relation to Equation 1 assume that mass transfer takes place only by diffusion. These conditions rarely occur in practice. Under our experimental conditions, diffusion may be subject to the formation of 'eddy' currents, arising from injection of the fumigant, sampling, thermal inequilibria and movement of the apparatus. These eddy currents result from chaotic fluctuations of gas velocities at different points throughout the flow area. The size of eddies or depth of their penetration before collapsing is directly proportional to the rate of turbulence (Azbel *et al.*, 1983).

Their fluctuations also may produce particle displacements in a direction normal to the axis of flow resulting in an increase in the diffusivity of the fumigant (Azbel *et al.*, 1983). The relative increases in temperature which may have occurred during the experimentation could also have affected the diffusion of phosphine, resulting in a much lower actual delay time (240 min)

at port 7 compared to numerical modelling (330 min). Hence, in Experiment 1, when there was ostensibly still air in the drum and box, small eddy currents resulted in significantly faster transport than is predicted in theory.

In addition, numerical modelling was done based on the diffusivity coefficient of 1.9×10^{-5} m^2/s (phosphine nitrogen mixture), calculated by the equation developed from Chapman and Enskog theory, which itself had an average difference in accuracy of about 8%. Hence, this also would have contributed to the decrease in time to reach equilibrium in modelled condition by approximately 550 minutes as against the experimental value (240 min).

As explained earlier, a small fan having an air flow of 10 m/min was used to mix the fumigant in the drum. With the fan turned on, the movement of phosphine (Experiment 2) was comparatively rapid and equilibrium was attained after 35 min at port 7 compared with the fan turned off (240 min). It should be noted that this reduction is due to small fluctuations in air currents near the opening of the box. At the macro scale the pressure at the two openings was identical so there was no mass flow through the box.

In a box packed with proteas (Experiment 3), although the delay time taken to attain equilibrium may be negligible in the first two ports (35 min for 0.1 m and 40 min for 0.25 m), it took 60 min to attain equilibrium at the back of the box (port 7) compared with 35 min when the box was empty. Here, 20 stems of proteas with the stems cut short were packed into the box in three different layers. Packing was based on actual packing regimes and some long stems of proteas were cut short before being fumigated under turbulence. Packing the box with flowers has two effects on phosphine transport. They reduce the cross-sectional area through which the fumigant must travel to diffuse through the box and they dampen any pressure fluctuations generated by the fan. The combination of these two effects have been demonstrated in Experiment 2 and 3, where the time to reach equilibrium almost doubled to 60 minutes.

When first picked the bracts of Protea, which consist of a tight compact flower head, typically cover all of the florets. However, at the time of maturity the bracts and florets normally tend to get more loosened. The Protea head used in the experiment had approximately 80 mm long florets. The bracts around the florets had commenced to open such that the diameter of the circle formed by the bract tips was approximately 30 mm, which represented a more mature stage than would normally be fumigated.

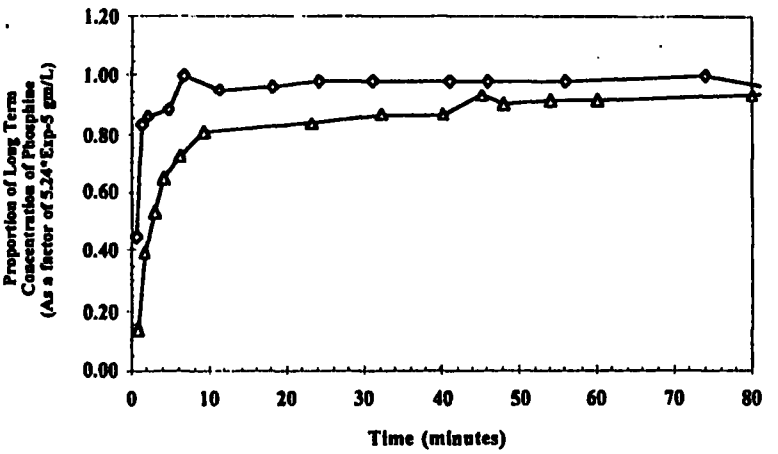

Figure 2. Diffusion of phosphine into a single protea flowerhead. (Δ = Exp 4, concentration of phosphine inside the protea flower head located inside the box at port 4; ◊ = Exp 4, concentration outside the flower head at port 3)

In Experiment 4, the efficiency of movement of phosphine into the mature flower head of an individual protea was evaluated. Despite the maturity of the head, a considerable time was taken to diffuse phosphine in to the base of the florets when the head was immersed in a phosphine atmosphere (Figure 2). Although the equilibrium was reached in about 10 min outside the Protea flowerhead (port 3), the time taken to attain equilibrium inside the flower head was about 75 min.

It was also observed that around 85% of equilibrium concentration was reached inside a flower head more rapidly (30 min) and that a considerable time was needed to attain the balance 15% (45 min). This also signified that the fumigant movement into a compact flowerhead was a slow phenomena when compared with the equilibrium time outside a flowerhead. One can consider phosphine transport to the base of florets in a flower box being a two stage process where firstly the phosphine has to diffuse into the flower box around the flowers and then diffuse into the flower structure at a reduced concentration gradient.

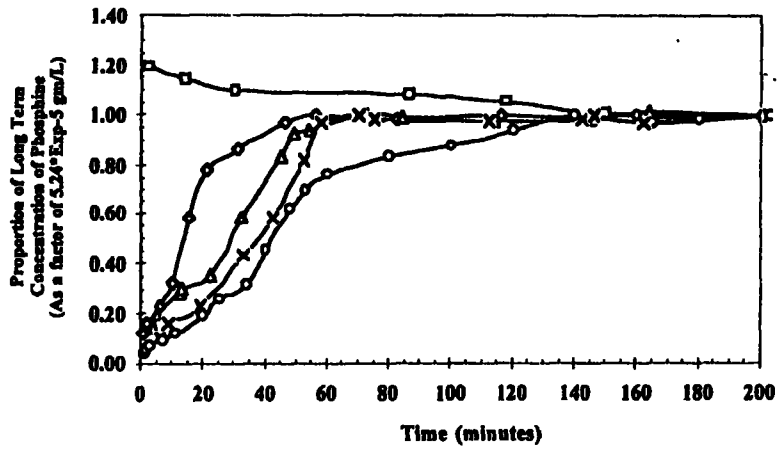

Figure 3. **Diffusion of phosphine in flower box packed with Protea 'Pink Ice' (Exp. 5).**
(□ = Drum, port 1; ◇ = Near entrance at port 2; Δ = Middle of box at port 4; 5 = Port 6; o = Inside the flower head at port 7).

The total time taken for an insect to die inside a flower head is directly proportional to its exposure time to the fumigant. The exposure time in this instance is the summation of the fumigation time and the time taken for the movement of fumigant into the flower head. As a result, reducing the time taken for the transport of fumigant into the structure of flowers like Proteas has become commercially important to design better fumigation techniques. This was further investigated (Experiment 5) by measuring the movement of phosphine into the flower head of a Protea located at port 7 (0.5 m), in a tightly packed box. The results for Experiment 5 are graphed in Figure 3. The sampling within a flower at port 7 indicates a steady rise in concentration to about 80% of equilibrium after 50 min. A further 80 min lapsed before final equilibrium was attained. However, the atmosphere around the flowers reached equilibrium in about 50 min. Experiment 5 also showed that the total time taken to reach equilibrium within the flower is about 150 minutes. This is a considerable proportion of the fumigation duration of 360 min (6 h) found necessary to achieve death *in vitro* for some common insects of cut flowers.

This slow rise in concentration has two implications for fumigation of floriculture produce.

The duration of fumigation must be significantly longer than that determined by *in vitro* experiments where an immediate increase in concentration is usually achieved. Secondly, the slow rise in concentration of phosphine may result in a different toxicological response of the insects. In our early experiments on insect kill narcosis was observed under elevated phosphine concentrations. It is not known whether the rate of increase of concentration of phosphine effects the onset of narcosis.

The statistical analysis (Table 1) shows that the variance of the sampling curve (σ_2^1) at port 2, is significantly different (P=0.05) to the variance of time taken to reach equilibrium (σ_A^{23}) in empty box and a box full of Proteas under turbulence (σ_B^{234}). This also highlights the fact that time taken to attain equilibrium in an empty box without turbulence is much slower than that under turbulence. However, there is no significant difference between any of the sampling curves under turbulence (P=0.05).

Table 1. Comparison of time variance in models observed under different experimental trials (rows compared for significance).

Port Number	Empty box (no turbulence)*	Empty box (under turbulence)*	Box full of Proteas (under turbulence)*	Inside the flower head (0.25 m)#	Box full of Proteas (under turbulence)*
0.1 m - port 2	σ_2^1	σ_A^{23}	σ_B^{234}		σ_D^{134}
0.25 m - port 4	σ_4^1	σ_E^{23}	σ_F^{234}	σ_C^1	σ_G^{234}
0.4 m - port 6	σ_6^1	σ_H^{23}	σ_i^{234}		σ_j^{234}
0.5 m - port 7	σ_7^1	σ_k^{23}	σ_l^{235}		σ_m^{45}

Superscripts: (*) = Flower box mounted with the template;
(#) = Flower box without the template.
σ_l^{235} = Sampling outside the flower heads;
σ_m^{45} = Sampling inside a flower head.
H_o = Values of variance in a row with same superscripts are non significantly different (P = 0.05).

At 0.25 m, the variance (σ_4^1) in diffusion of phosphine (empty box) is significantly different without turbulence to that of an empty box (σ_E^{23}) or a box full of proteas (σ_F^{234}) under turbulence (P=0.05). However, there is no significant difference (P=0.05) between variance of phosphine diffusion into a protea flower head under turbulence (σ_C^1) as against non turbulence (σ_4^1). This may have occurred since movement of phosphine into a flower head has observed to be a slow process, especially during the latter part of the fumigation. There has been no significant difference (P=0.05) in reaching equilibrium in any of the experiments at 0.4 m under turbulence.

However, the empty box with the fan turned off (σ_6^1) recorded a significantly higher time variance than others (P=0.05). The variance (σ_m^{45}) in time taken to attain equilibrium inside a flower head located at 0.5 m is non significant (P=0.05) only to the time variance (σ_l^{235}) at 0.5 m of a box full of proteas. In both instances, the boxes were full of 20 stems of proteas assorted in each, but under turbulence. Further, the diffusion of phosphine into a flower head located at 0.5 m is supposed to encounter the longest delay in reaching equilibrium. There was also no significant difference (P=0.05) between the empty box (σ_k^{23})and the box full of proteas under turbulence in any of the conditions (port 7). A number of parameters were not varied in this experiment that are known to influence diffusion. The main ones being the area of the holes at the end of the box and the manner in which the flowers are packed. The rate of diffusion is proportional to the cross sectional area normal to the direction of transport. Therefore smaller holes, tighter packing of flowers and paper or cellophane liners in boxes will all decrease the ingress of the fumigant. The transport of fumigant could be increased by several means. The 50 minute delay in the box reaching equilibrium could be reduced to a very short time if the fumigant atmosphere was forced through the box. A set of manifolds that could easily be clamped to the ends of a pallet load of boxes could be devised to facilitate this in the first few minutes of disinfestation. Such a system could also be used for initial cooling of the product. The additional delay in transport into the flower head could be reduced by enhancing the effect of pressure fluctuations near the flower. It was evident that the small fluctuations near the box opening in this experiment markedly reduced transport times into the empty box. Similar fluctuations superimposed on the flow from a manifold system would reduce transport times into the flower.

CONCLUSIONS

Fumigation by diffusion is a slow process even under turbulence with times in excess of 120 min being required for fumigant to reach equilibrium within the structure of some flowers when packed in standard flower boxes.

The time taken to attain equilibrium inside a flower head consists of a major factor out of the total fumigation time. This delay is of the same order of magnitude as the duration of fumigation required to kill the insects.

The experimental evidence suggests the need to be cautioned at the time of applying *in vitro* exposure times concluded as sufficient to attain desired kill of insects when scheduling commercial fumigation techniques.

Alternative designs of equipment to deliver the fumigant to the insects could substantially reduce the observed delays in attaining desired kill by improving the transport phenomena of fumigant.

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