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SORPTION OF FUMIGANTS BY CUT FLOWERS

GAYE L. WELLER AND J.E. VAN S. GRAVER
Stored Grain Research Laboratory, CSIRO Division of Entomology, GPO Box 1700, Canberra ACT 2601, Australia

ABSTRACT

Sorption of fumigants (carbonyl sulphide, methyl bromide and phosphine) by two flower species (*Dianthus* sp. and *Anigozanthos* sp.) was studied. Exposures were carried out in stainless steel chambers at concentrations suggested for insect disinfestation of cut flowers or similar commodities; carbonyl sulphide (COS), 15 mg L^{-1}; phosphine (PH_3), 0.25 mg L^{-1}; and methyl bromide (MB), 32 mg L^{-1}.

Sorption profiles differed for each of the fumigants but were relatively constant across the flower species. The greatest fumigant loss was observed with COS; after 7 h, no measurable levels of fumigant were detected, indicating that the sorption process is accompanied by a metabolic process in the flowers. Over the 12-h exposure period, PH_3 and MB displayed a 33% and 5% sorption of fumigant, respectively. Such levels of sorption may be easily accounted for in the development of a fumigation procedure. PH_3 may have potential as a replacement for MB as a fumigant for cut flowers.

INTRODUCTION

A need to identify new fumigants and fumigation regimes for a range of commodities became apparent following the identification of methyl bromide (MB) as a powerful ozone depletor (UNEP, 1994). MB has been routinely used to disinfest cut flowers, one of the commodities for which alternative fumigants are being sought. Cut flowers, which by their very nature attract insects, are not acceptable for either domestic or international markets if infested.

A recent study of the deleterious effects of five potential fumigants on flower quality identified phosphine (PH_3), carbonyl sulphide (COS) and hydrogen cyanide (HCN) as potential replacements for MB as a quarantine fumigant for cut flowers (Weller *et al.*, 1995).

Any successful fumigation requires that the concentration of fumigant be maintained at, or above, a given level long enough to kill all target organisms. Fumigant concentrations do not remain static during fumigation; they decline through leakage from the system and physical and chemical binding to the fumigation chamber and the commodity,

or they may be broken down through chemical reaction (Banks, 1986, 1990a). In developing fumigation regimes for any commodity, it is necessary to understand these interactions and compensate, where possible (Banks, 1990b). Sorption, the physical and chemical bonding of the fumigant to the fumigation chamber and to the commodity, is a predictable loss which can be overcome by using either a higher initial dose or by boosting the concentration during the fumigation (Stout, 1983).

In comparing the sorption response of durable commodities with that for cut flowers, very different responses might be expected because of the different properties of the commodities. The high moisture content of flowers and the presence of free water, whether associated with storage of cut flowers or condensation, will undoubtedly produce an effect due to the varying solubility of fumigants. Likewise, the more active metabolic state of cut flowers, compared with that of durable commodities, may effect the perceived sorption rates.

This paper reports on work undertaken to study sorption of three fumigants by cut flowers. Two of them have been identified as possible MB replacements: PH_3 and COS.

MATERIALS AND METHODS

The flowers used in this study were field carnations (*Dianthus* sp.) and kangaroo paw (*Anigozanthos* sp. hybrid).

Fumigations were carried out in stainless steel chambers (approximately 2.37 L) fitted with Swagelock-fittings to facilitate circulation of fumigants. A measured amount of concentrated source gas was introduced into the fumigation chamber through a septum (M-type, Alltech) insert to achieve the desired fumigation dose. Gases in the chamber were circulated using a diaphragm pump (5 L min^{-1}) for 5 min to ensure an even distribution of gas. Gas samples were taken from the chamber at regular intervals to measure any change in fumigant concentration during the exposure period.

Fresh flowers were purchased through a local wholesaler. Individual bunches of each flower type were mixed and sub-samples taken, weighed and placed in the fumigation chambers. The weight of flowers used in each experiment was 110–120 g. Following fumigation the dry weight of the flowers was determined by drying in a forced draught stainless steel lined oven at 70°C for 72 h.

Sorption profiles of COS, MB and PH_3 were determined for both carnations and kangaroo paw over a 12 h period. The initial dose applied for each fumigant was that suggested for cut flowers or similar commodities: MB 32 g m^{-3} (Stout, 1983), COS 15 g m^{-3} (Desmarchelier, 1994) and PH_3 0.25 g m^{-3} (Winks, 1986). All exposures were carried out at 21°C.

Controls consisting of sealed, empty fumigation chambers were also dosed as above to determine the "chamber effect", if any, on fumigant concentrations.

Concentrated sources of COS and PH_3 were generated in the laboratory. COS was produced by the addition of potassium thiocyanate to sulphuric acid, and the resultant gas

was passed through a lead acetate solution to remove associated hydrogen sulphide (Ferm, 1957). PH_3 was generated by the addition of aluminium phosphide tablets (Phostoxin, Degesch, Germany) to 5% (v/v) aqueous sulphuric acid (Anon., 1975).

The concentrations of the generated gases (COS and PH_3) were determined using a Gow Mac model 11-625 gas density detector on a Tracor MT150 gas chromatograph (GC) fitted with a Porapak Q 80/100 column. Fumigant loss was determined over the 12-h exposure period by analysis of gas concentrations in the head space of the chambers. Fumigant concentrations were measured in each chamber, during exposure, using gas chromatography techniques. MB was measured using a Shimadzu 6AM GC fitted with an FID and a 20% OV101 on Gas Chrom Q column run at 50°C isothermal. COS and PH_3 were both detected using a Tracor MT-220 GC fitted with a FPD (sulphur mode for COS and phosphorus mode for PH_3) and a Haye Sep Q 80/100 mesh column run at 110°C isothermal.

The effect on the rate and amount of sorption of the weight of flowers fumigated was studied for both PH_3 and COS using kangaroo paw. These experiments were carried out using the same methodology as above. The weight of flowers fumigated was varied by steps between 0 and 100 g. Tests were carried out using initial doses of 0.25 mg L^{-1} for PH_3 and 15 mg L^{-1} for COS. In calculating the amount of concentrated source to deliver to the chamber, the volume of the fumigation chamber was assumed to be that of the empty chamber (the reduction of headspace due to the mass of flowers was not taken into consideration).

RESULTS

Sorption of methyl bromide

Loss of MB observed over six replicates was averaged and is presented in Fig. 1. All plots are expressed as a fraction of the original concentration in the head space (C/C_0) against time (h). The lowest rate of loss occurred in the empty fumigation chamber

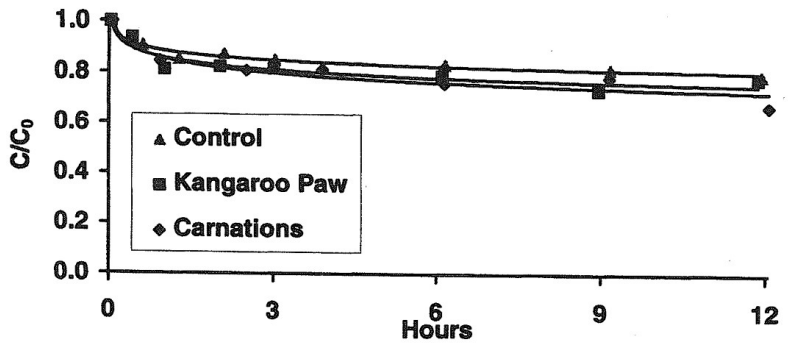

Fig. 1. Sorption of MB by cut flowers. Fraction of original head space concentration (C/C_0) vs time (h).

(control). The difference between the sorption profile of the control and the sorption profiles for the fumigation of kangaroo paw and carnations can be attributed to sorption by the flowers. It is apparent that the loss of a large proportion of the MB can be attributed to sorption by the fumigation chamber and a smaller proportion to sorption by the flowers.

All three tests followed a logarithmic curve which can be described thus:

— empty fumigation chamber: $y = -0.033 \ln(x) + 0.89$ (R^2 value 0.97);
— kangaroo paw: $y = -0.042 \ln(x) + 0.86$ (R^2 value 0.86);
— carnations: $y = -0.052 \ln(x) + 0.86$ (R^2 value 0.90).

Sorption of phosphine

Losses of PH_3 observed over five replicates were averaged and are presented in Fig. 2. The empty fumigation chamber displayed an initial loss of gas after which the concentration remained constant. The fraction of the original concentration in the head space (C/C_0) extrapolated to time zero (the intercept value) of 0.98 is indicative of a low level of adsorption to the chamber surface.

In the chambers containing flowers, the plots follow a logarithmic loss and are described thus:

— kangaroo paw: $y = -0.06 \ln(x) + 0.70$ (R^2 value 0.92);
— carnations: $y = -0.10 \ln(x) + 0.75$ (R^2 value 0.99).

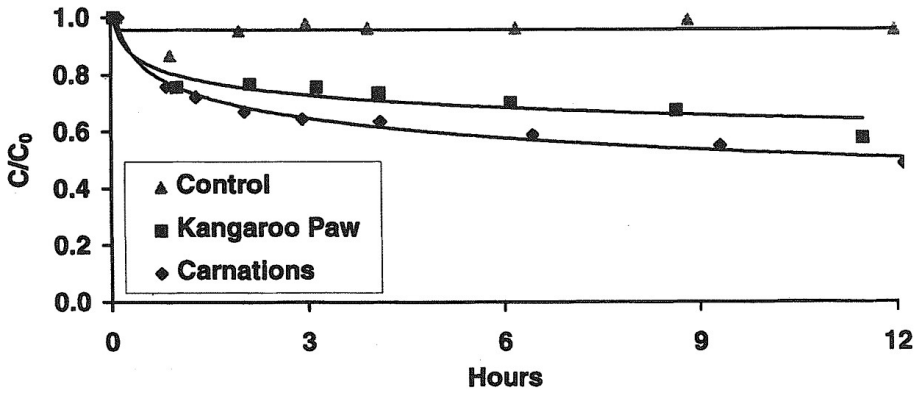

Fig. 2. Sorption of PH_3 by cut flowers. Fraction of original head space concentration (C/C_0) vs time (h).

Sorption of carbonyl sulphide

Losses of COS for six replicates were averaged and are presented in Fig. 3. The gas loss observed in the empty fumigation chamber was minimal. It can best be described as a straight line with a C/C_0 intercept value of 0.99.

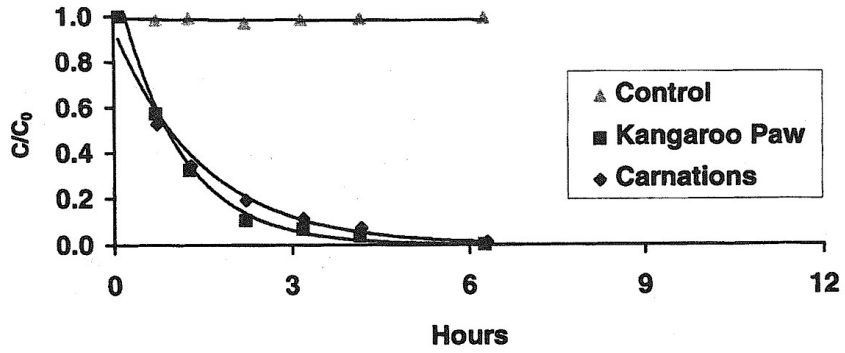

Fig. 3. Sorption of COS by cut flowers. Fraction of original head space concentration (C/C_0) vs time (h).

The loss of COS during the fumigation of flowers was so rapid that within 6 h of commencing fumigation there was no detectable COS. Hydrogen sulphide was detected in the chamber after 1 h and continued to increase in concentration over the duration of the fumigation. Fumigations were terminated when the concentration of COS fell below detectable levels.

In the chambers containing flowers the fumigant losses are described by logarithmic relationships thus:

— kangaroo paw: $y = -0.23 \ln(x) + 0.41$ (R^2 value of 0.99)

— carnations: $y = -0.25 \ln(x) + 0.40$ (R^2 value of 0.97).

Effect of fill ratio on sorption

Phosphine. Results where the weight of flowers being fumigated was varied are given in Fig. 4. The loss of PH_3 observed over the first hour increased with the increasing weight of flowers. Thereafter, the sorption profiles described by different masses of flowers were

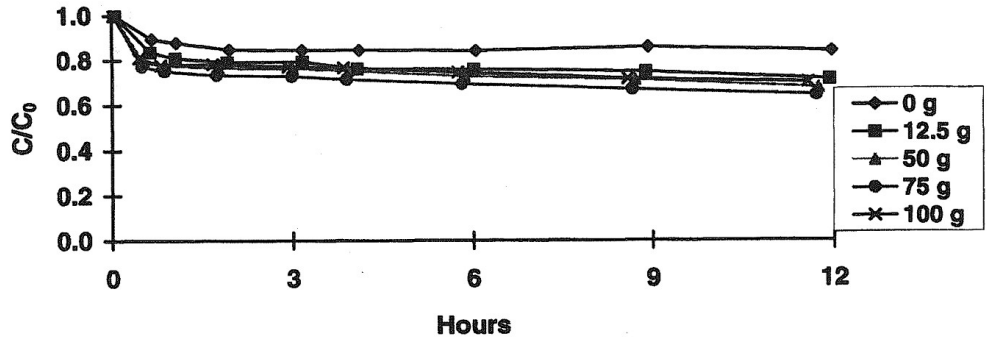

Fig. 4. Effect of weight of flowers (kangaroo paw) on sorption of PH_3 by cut flowers. Fraction of original head space concentration (C/C_0) vs time (h).

very similar. This could be explained by increased physical sorption due to the increasing surface area of the flowers.

Carbonyl sulphide. Results for the variation in weight of flowers for COS are given in Fig. 5. Uptake of COS was affected by the weight of flowers fumigated and can be plotted as a semi-logarithmic relationship (Fig. 6). Uptake of COS increased with increasing flower weight. Plotting the slopes from Fig. 6 (rate constant) against the weight of flowers fumigated gave a linear relationship (Fig. 7). This relationship enabled us to make predictions of the loss of COS that might be expected in a commercial scale fumigation facility at various fill levels. It may be noted that all of the fill ratios (even the lowest) used during this trial were significantly higher than those encountered in most commercial situations.

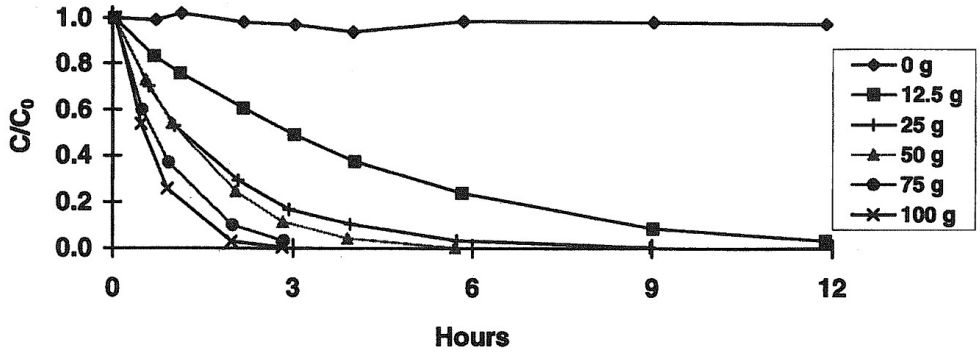

Fig. 5. Effect of weight of flowers (kangaroo paw) on sorption of COS by cut flowers. Fraction of original head space concentration (C/C_0) vs time (h).

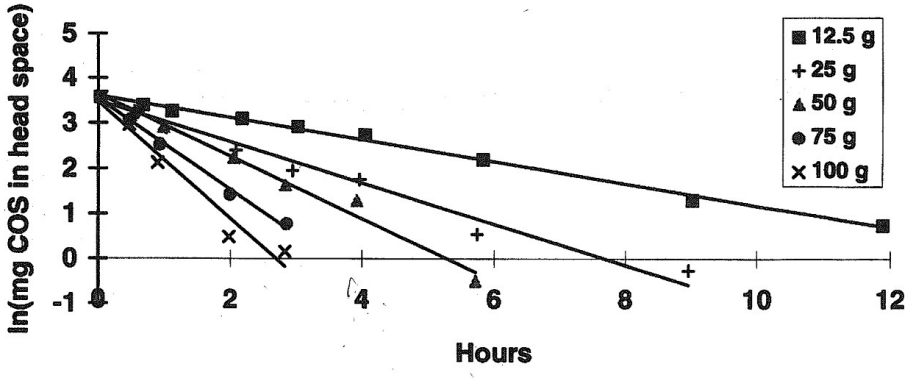

Fig. 6. Effect of weight of flowers (kangaroo paw) on sorption of COS by cut flowers (ln mg COS in the head space) vs time (h).

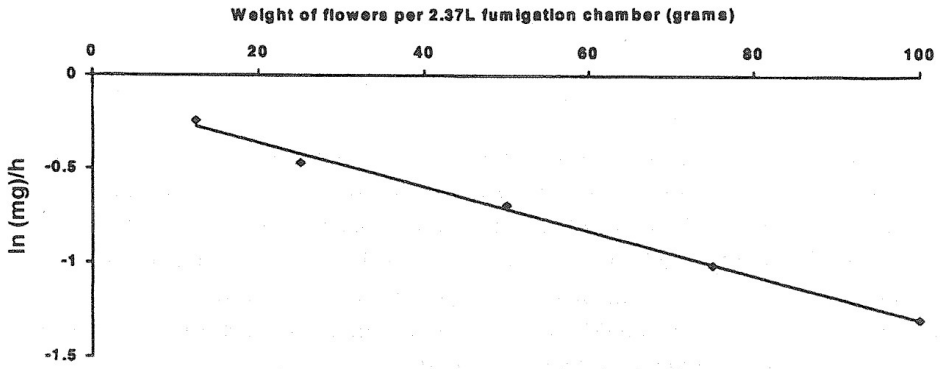

Fig. 7. Rate of COS sorption by cut flowers (kangaroo paw).

DISCUSSION

It is generally accepted that the mechanism of sorption incorporates two processes. The first is a rapid uptake of the fumigant, described as physical adsorption of the fumigant, whereby the gas molecules are loosely bound to the surfaces of the commodity and the fumigation enclosure. The second is a slower uptake of the fumigant, thought to be related to diffusion of the fumigant into the commodity, whereby the gas molecules are more tightly bound to them. In a gas tight system an equilibrium is reached between the "free gas" in the chamber and the sorbed or "bound gas". Gasses which have been sorbed by commodities can be recovered from the system.

Banks (1986) describes the diffusion/sorption process mathematically as a semi-logarithmic relationship, between concentration and time, which is dependent upon the commodity, the fumigant and the fill ratio.

Although there was no significant difference between the sorption of PH_3 and of MB by the two flower genera tested, carnations consistently sorbed more of both fumigants than kangaroo paw. This may be related to the different surface area and physical properties of the two flowers, and it may also correspond to their relative moisture content. The percentage weight lost through drying carnations at 70°C for 72 h was 83%, compared with an 81% loss in kangaroo paw.

Solubility of MB and PH_3 in the water component of flowers may, in part, account for the sorption observed. The solubility of both MB and PH_3 in water at 25°C is fairly low. MB has a solubility of 1.3 g/100 ml (Anon., 1979) and PH_3 0.03 g/100 ml (Weston, 1954).

COS fumigation of cut flowers followed a semi-logarithmic relationship. The fumigant concentration fell rapidly to levels which we were unable to detect. The production of hydrogen sulphide within the chamber indicated that, rather than being sorbed, the fumigant was reacting with the commodity or being metabolised. COS is only slightly soluble in water, 0.12 g/100 ml at 25°C (NIOSH, 1979) and it hydrolyses slowly to produce carbon dioxide and hydrogen sulphide. The reaction is catalysed by many substances and

ions, especially the hydroxyl ion (Thompson *et al.*, 1935). In higher plants metabolic pathways for the consumption of COS have been described, most significantly where carbonic anhydrase catalyses the hydrolysis of COS to produce H_2S and CO_2 (Protoschill-Krebbs and Kesselmeier, 1992).

In developing new fumigation procedures for cut flowers, PH_3 offers potential. The sorption properties of cut flowers with respect to PH_3 are measurable and may be easily accounted for in the development of a fumigation procedure. Unfortunately, the short exposure periods usually used for cut flowers do not kill the eggs and pupae of many insects and are also ineffective against many species of mites (Hole *et al.*, 1977). As a consequence PH_3 fumigation could form part of an integrated control program but is unlikely to offer a stand-alone treatment for all pests.

Despite the rapid consumption of COS by cut flowers, reducing the fill ratio to levels more akin to those experienced in commercial fumigation facilities would reduce the relative speed of decay. If the fill ratio is small enough, the concentration could be maintained at fumigation levels for a period long enough to achieve mortality; therefore, COS could be an effective fumigant for cut flowers.

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