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THE USE OF ETHYL FORMATE FOR SPACE FUMIGATION OF DRIED VINE FRUIT

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ABSTRACT

Research seeking alternative fumigants to methyl bromide for dried vine fruit has involved studies with ethyl formate as a space fumigant. The practicalities and effects on insect pests of space fumigation with ethyl formate are described here. In 2000 and 2001, 4.5 tonnes (t) of unprocessed dried sultana raisins were fumigated in shipping containers using ethyl formate and an ethyl formate/CO_2 mixture respectively. In the first trial, the fruit was treated with 60 g m^{-3} of ethyl formate, added as a liquid and treated for 44 hours at an average commodity temperature of 9.2ºC. Gas concentrations were slightly lower within the fruit compared to the headspace. Insect bioassays of *Oryzaephilus surinamensis* (L.) and *Tribolium confusum* (J. du Val) placed within fruit and headspaces produced 100% mortality with the exception of *T. confusum* pupae placed within the fruit, which had 99.7% mortality. In the second trial, fruit was treated with 34g m^{-3} of ethyl formate and 40-50% CO_2, for 48 hours at an average commodity temperature of 19.8ºC. CO_2 was added as a co-fumigant, carrier gas and fire retardant. Gas concentrations were similar throughout the load and insect bioassays of *T. confusum* and *Plodia interpunctella* (Hübner) recorded 100% mortality after treatment. Both fumigations demonstrated the effectiveness of ethyl formate as a fumigant for dried vine fruit. The second combined ethyl formate/CO_2 fumigation showed enhanced penetration of ethyl formate when carried by CO_2. The combined effect of ethyl formate and CO_2 resulted in high mortalities with low dosages of both chemicals.

INTRODUCTION

Research seeking alternative fumigants to methyl bromide for dried vine fruit has involved studies with ethyl formate as a space fumigant. To date stack fumigation with methyl bromide has been the preferred pest control option for unprocessed fruit in 0.5 t bins. However, with the pending phasing-out of methyl bromide, alternatives such as ethyl formate need investigation. The practicalities and effects of space fumigation with ethyl formate are described here.

Ethyl formate is a highly attractive option for bulk disinfestation of unprocessed dried fruit during warehousing. Ethyl formate has been registered for application to dried fruit where it has been used as a post processing disinfestation treatment since 1927 (Simmons and Fisher, 1945) and has proven to be effective on the major insects present in the Australian industry (Tarr and Clingeleffer, 1993; Hilton and Banks, 1997). Vincent and Lindgren, (1972), found that of the insects they tested on dried dates, *Carpophilus hemipterus* (L.) and *O. surinamensis*, were less susceptible to ethyl formate treatment than *P. interpunctella* and *Ephestia figulilella* (Gregson). All of these insects have been reported as pests of dried vine fruit (Hamlin *et al.*, 1931; Howe, 1956; Buchanan *et al.*, 1984; Johnson *et al.*, 1995) although *C. hemipterus* is not usually present in the stored fruit due to it's preference for moister substrates. Surveys of Australian dried fruit processing facilities have confirmed the presence of these insects plus the occurrence of *T. confusum* and *Tribolium castaneum* (Herbst.) (Myers, 1928; Tarr *et al.*, 1994; Hilton and Banks, 1997). Muthu *et al.*, (1983) and Hilton and Banks, (1997), found *Tribolium* species to be more tolerant to ethyl formate over longer treatment exposures than *O. surinamensis*. Recent studies prior to these trials also showed *T. confusum* and *T. castaneum* to be less susceptible to ethyl formate than *O. surinamensis*, *P. interpunctella* and other dried vine fruit pests. In these cases, a dosage of at least 40 g m^{-3} was needed to cause 100% mortality of both adults and larvae of both *Tribolium* species (Tarr and Reuss unpublished data). As a result, *T. confusum* was deliberately selected as a difficult target to be used as a bioassay in these trials.

Natural levels of ethyl formate in a range of products and its environmental fate have been reviewed by Desmarchelier (1999) along with the methodology of residue analysis in dried vine fruit and grains (Desmarchelier *et al.*, 1999). Hilton and Banks, (1997) and more recently Reuss and Annis, (2003), investigated the fate of ethyl formate in stored products including dried vine fruit, where they reported low levels of sorption into dried fruits. A review of acute toxicological studies of ethyl formate has been published by Haritos *et al.* (2003). Ethyl formate has low mammalian toxicity while producing high insect mortalities. It has a threshold limit value (TLV, i.e. occupational exposure limit) of 100ppm in Australia and holds a generally regarded as safe "GRAS" status for food flavourings in the United States.

Research on ethyl formate's explosive nature was conducted by Pearson and Apte (1998). They confirmed a lower explosive limit of 84-91 g m^{-3} of ethyl formate and an upper explosive limit of > 586 g m^{-3} at 25ºC if a source of combustion was

provided. Below these limits safe application to larger enclosures was considered possible. Desmarchelier *et al*. (1998) demonstrated in initial experimentation that ethyl formate, like ethanol, was not flammable when mixed with water and could be used effectively in this way. The option of using CO_2 as a fire retardant was also discussed. In 2000 and 2001, two trials were carried out to demonstrate and refine fumigation technologies in dried vine fruit. The first fumigation used liquid ethyl formate to treat a shipping container loaded with unprocessed dried sultanas in June 2000 and the second used a combined ethyl formate and CO_2 fumigation to treat a shipping container of unprocessed dried sultanas in April 2001.

TRIAL 1. ETHYL FORMATE FUMIGATION OF A SHIPPING CONTAINER LOAD OF UNPROCESSED DRIED SULTANAS IN JUNE 2000

Methodology

The trial commenced on 29th June 2000 on site at the premises of a commercial storage and processing facility in Irymple, Victoria. Approximately 4.5 t of unprocessed dried sultanas in nine 0.5 t bulk bins were placed in a 6m shipping container and treated with 60 g m^{-3} of ethyl formate vapour for 44 hours (h).

The container was in good condition, with plywood flooring and good door seals. All joins in the floor were sealed using an acetic cure silicone sealant and an initial pressure test using a Contestor pressure decay monitor (Sharp and Cousins, 1982) showed the container had a good seal. After in-loading fruit and installation of gas monitoring lines (Figure 1a) further sealing around the doors was carried out and a successful pressure test achieved prior to addition of the ethyl formate.

Figure 1. Shipping container with 0.5t bins and sample lines prior to addition of ethyl formate

Gas addition: The fumigant was applied in the afternoon in liquid form by gravity feed under a light gas blanket of 10% by volume of CO_2 which was directed above the liquid to act as a flame retardant. Ethyl formate was left to vaporise from a section of guttering within the container. All fittings were carefully earthed prior to fumigation. The fumigation was terminated 44 h after application and the remaining ethyl formate vapour removed from the container by natural ventilation.

Temperatures within the container and ambient conditions were monitored throughout the fumigation.

Throughout the fumigation process ethyl formate concentrations were monitored with a portable GC-PID (Photovac gas chromatograph with photo-ionisation detector). Samples were taken from 7 points in the container by the instrument's sample pump via copper sample lines; gas was drawn through to the GC-PID after the lines had been flushed manually using a 1 litre syringe. Concentrations were calculated based on the area under the peak compared to standards. During the coldest sample periods some problems with condensation were found to occur and peak readings for these times were discarded.

Bioassays: Cultures of local insect populations were established by collecting insects from Sunraysia dried vine fruit packing establishments during the 1999 season and breeding up populations of these insects prior to exposing them to ethyl formate. The insects captured and cultured included, the beetles, *O. surinamensis* (saw-toothed grain beetle), *T. confusum* (confused flour beetle), *Tribolium castaneum* (Herbst.) (red flour beetle), *Oryzaephilus mercator* (Fauvel) (merchant grain beetle) and the moths, *P. interpunctella* (Indian meal moth) and *E. figulilella* (raisin moth).

The *Tribolium* species were raised on a mixture of wholemeal stone ground flour, unprocessed sultanas and yeast. The rest of the insects were raised on unprocessed sultanas. All food substrates were sterilised by freezing for 3 months prior to use to eliminate mite infestation and cross infestation of the cultures. All insects were cultured in a controlled temperature (ct) room at 25ºC with 14:10 hours light: dark regime. The chamber had no humidity control, this was modified by the addition of steam from a steam humidifier (Eucybear brand).

Caged bioassays of *O. surinamensis* and *T. confusum* sourced from the above cultures were placed in the headspace and buried amongst the fruit in the shipping container. Several cages were buried about 35cm under the fruit surface in the centre of the bin to assay the worst case scenario for ethyl formate penetration. Laboratory and field controls were maintained for comparison. Both bioassays included all lifecycle stages including eggs, larvae, pupae and adults. A mixed culture was produced by adding adult beetles to the food medium (as above) and removing them 1 week later. This was repeated weekly to produce weekly cohorts until the initial samples produced adults (8 weeks). The weekly cohort samples were mixed together

and divided equally amongst the desired number of sample bottles (12 *T. confusum* and 4 *O. surinamensis*) prior to placing amongst the dried sultanas before fumigation.

After fumigation the bioassays were removed, all dead and alive insects counted and the remaining food substrate incubated in the ct room for 14 days after which pupal survival was assessed and then incubated for a further 14 days to account for eggs and very small larvae. Mortality figures were adjusted using Abbott's formula (1925).

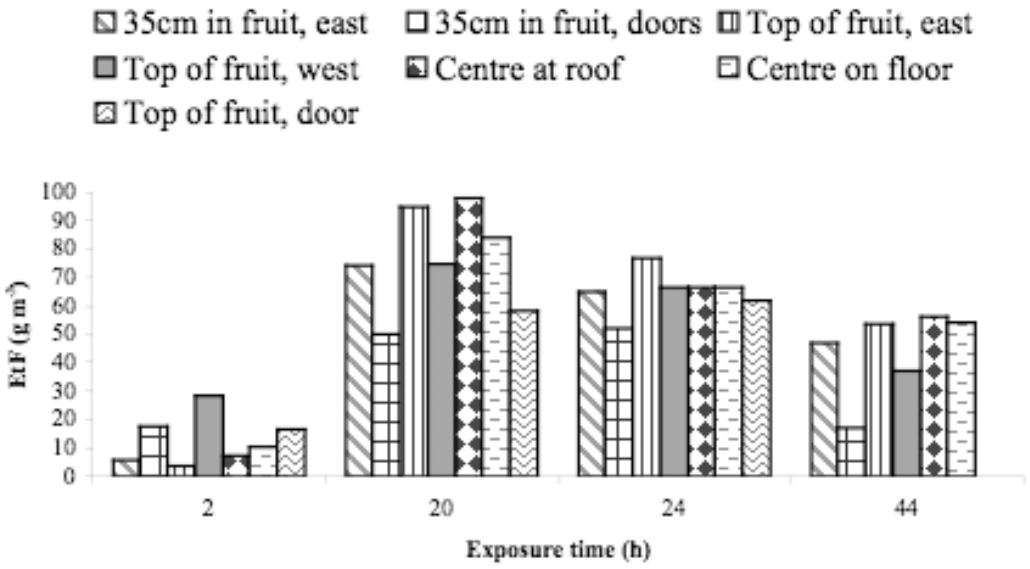

Figure 2. Ethyl formate (EtF) concentrations in headspace and within sultana fruit bins during a 44 hour fumigation in June 2000

RESULTS

Ethyl formate concentrations in the headspace reached 5-10 g m^{-3} shortly after application. Concentrations rose slowly approaching 30 g m^{-3} within 4 h after application (Figure 2). Over the next 3 h, concentrations varied from 30-50 g m^{-3} and reached 65 g m^{-3} eight hours after application, indicating the end of the vaporisation phase. After 24 h fumigant levels in the container were between 30-65 g m^{-3} throughout the container. Higher concentrations were found in the headspace while lower concentrations were measured inside the bins of fruit, although generally fumigant distribution was fairly even. After 44 h headspace concentrations were maintained above 50 g m^{-3}. Airing off was easily achieved by natural ventilation with concentrations quickly reduced to below the TLV of 100 ppm when measured with an adapted Dräger detector tube technique (Allen and Desmarchelier 2000). Headspace temperatures within the container during the fumigation averaged 8.5°C

(min.: 3.7°C, max: 14.2°C). Within the commodity, temperatures averaged 9.2°C (min:6.6°C, max: 10.7°C). Relative humidity averaged 61% (min: 51.9%, max: 72.5%). In summary, target concentrations were easily reached after a prolonged vaporisation phase. This was possibly due to the low headspace and commodity fumigation temperatures (8.5ºC and 9.2ºC respectively).

Bioassay results of *O. surinamensis* and *T. confusum* placed in the headspace and buried inside the bins of fruit showed 100% control of all adults, larvae and eggs. Complete control of *O. surinamensis* pupae was also recorded, but some survival of *T. confusum* pupae, the more resistant life stage was noted. After incubation of samples there were 2 surviving pupae from 3135 treated insects. This equates to 100% mortality for eggs, larvae and adults and 99.7% mortality for pupae. The survivors were from samples buried within the fruit.

TRIAL 2. A COMBINED ETHYL FORMATE AND CO_2 FUMIGATION OF A SHIPPING CONTAINER OF UNPROCESSED DRIED SULTANAS IN APRIL 2001

Methodology

The trial commenced on 2nd April 2001 on site at the premises of a commercial storage and processing facility in Irymple, Victoria. A shipping container was loaded with approximately 4 t of unprocessed dried sultanas in 0.5 t open crates (Figure 3). The fruit was naturally infested with *Oryzaephilus* sp., *Tribolium* sp. and *Plodia interpunctella*.

Figure 3. Refrigerated container and bulk bins set up prior to ethyl formate/ CO_2 gas fumigation.

The container (a refrigerated type, with volume of 27.3 m^3) was in good condition and after the rear refrigeration ports and doors were sealed, passed a pressure test using a Contestor pressure decay monitor (Sharp and Cousins, 1982) prior to in-gassing. On 4th April, 48 h after commencement of the fumigation, the remaining ethyl formate vapour was removed from the container by natural ventilation.

Temperatures within the container and ambient conditions were monitored throughout the fumigation. During fumigation, the average ambient temperature was 20.8°C (min.: 10.6°C, max.: 27.0°C). Within the commodity, temperatures averaged 20.1°C (min.: 19.8°C, max.: 20.2°C). Relative humidity averaged 51.1% (min.: 49.8%, max.: 51.5%).

***Gas addition**:* In this fumigation a gaseous combination of ethyl formate and CO_2 was added. The combination was proposed to control the potential flammability risk which could occur with ethyl formate addition. The ethyl formate/CO_2 fumigant mix was produced by directing gaseous CO_2 from a gas cylinder through a flow meter into a sealed dosing vessel that contained liquid ethyl formate. To facilitate evaporation of ethyl formate, the chamber was kept at 35-40°C by immersion in a water bath. After bubbling through the liquid fumigant, a mixture of ethyl formate and CO_2 gas left the vessel through an outlet attached directly to the shipping container (Figures 4 a, b). The fumigant gas was applied to the commodity through the rear port of the sealed container, at a constant flow rate adjusted by the in-line flow meter.

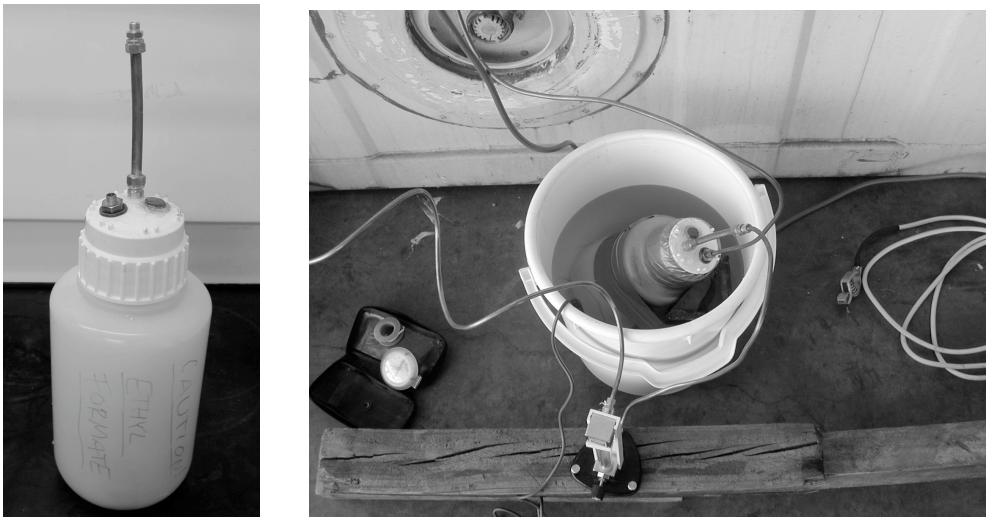

Figure 4. **a (left)**: Experimental ethyl formate dosing vessel, **b (right)**: ethyl formate dosing vessel attached to CO_2 gas flow via copper lines and kept warm in water bath during gas addition.

CO_2 concentrations were measured with a portable GC-TCD (Gas chromatograph with thermal conductivity detector) fitted with a sample pump. Ethyl formate concentrations were monitored with a portable GC-PID (Gas chromatograph with photo-ionisation detector) as described above.

The mixed fumigant was applied in two stages. The first stage began immediately after sealing. CO_2 was passed through the sealed dosing vessel containing 1600 mL of ethyl formate at a flow rate of 60 mL min^{-1} for a period of 3 h. Measurements of ethyl formate concentrations during this time showed that the flow rate may have been too high and that ethyl formate was being vented from the system, meaning that a peak concentration above 50 g m^{-3} was unlikely to occur (the aim was 60 g m^{-3}). The second stage began 21 h after sealing. CO_2 was passed through the dosing vessel containing 1000 mL of ethyl formate at a flow rate of 30 mL min^{-1} for a period of 5 h. This additional ethyl formate allowed test insects to be exposed to dosage levels expected to cause 100% mortality.

Bioassays: Caged bioassays of *P. interpunctella* and *T. confusum* sourced from populations collected in 1999 and raised under identical conditions to trial 1 were placed in the headspace and buried inside the fruit bins and counted as described above. The *T. confusum* bioassay included all lifecycle stages including eggs, larvae, pupae and adults (14 cages). The *P. interpunctella* bioassay included larvae, pupae and adults in smaller numbers only. A mixed culture was produced by adding adult beetles/moths to the food medium as described above. The bulk fruit also had an active infestation of *O. surinamensis*, *Tribolium* species and *P. interpunctella.*

After fumigation the bioassays were removed, all dead and alive insects counted and the remaining food substrate incubated in the ct room. Assessment of pupal survival was carried out once a week for 4 weeks and then incubated for a further 7 days to account for eggs and very small larvae. Mortality figures were adjusted using Abbott's formula (1925).

RESULTS

The ethyl formate concentration averaged over the whole 48 h treatment period was 34.2 g m^{-3}. The average CO_2 concentration was 41% (Figure 5.). In the first hour of the first stage of application, ethyl formate concentration reached 27 g m^{-3} while CO_2 rose above 30%. When addition of gas was stopped after three hours, ethyl formate concentrations were above 45 g m^{-3} and CO_2 at 42%. The average pressure in the container during application was 152 Pa. For the next 18 hours, the CO_2 concentration remained constant, while the ethyl formate concentration declined to below 30 g m^{-3}. When application was resumed for 5 h at a lower flow rate, ethyl formate concentrations were restored to 40 g m^{-3} while CO_2 concentrations reached

50%. The container was pressurised to 37 Pa. Over the next 20 hours CO_2 levels were relatively constant while ethyl formate concentrations declined gradually with readings fluctuating around 30-40 g m^{-3} (Figure 5 & 6). Airing off was easily achieved by natural ventilation with concentrations reduced below the TLV of 100 ppm within less than an hour after opening the container doors.

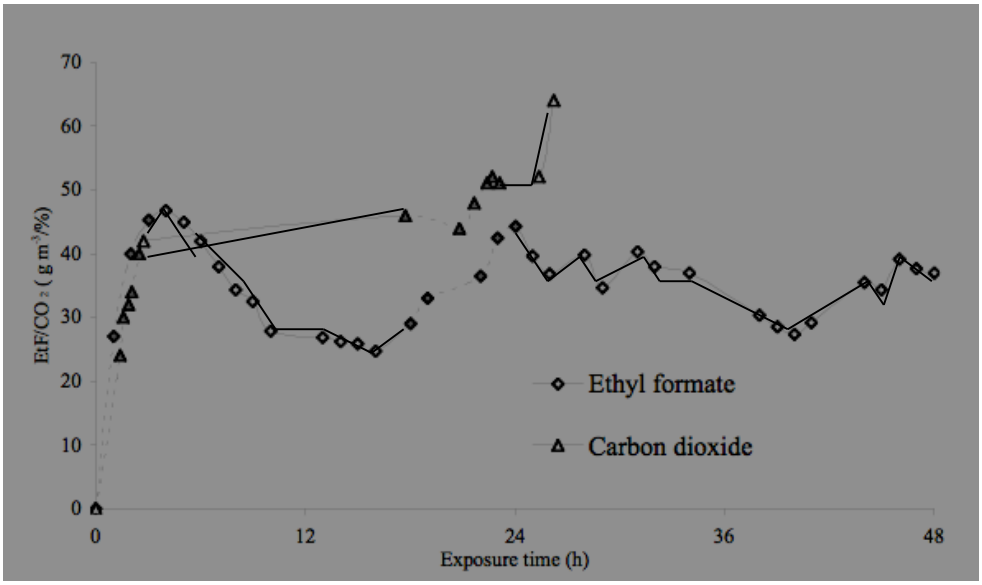

Figure 5. Ethyl formate(EtF) and carbon dioxide concentration during fumigation of a shipping container filled with dried fruit in bulk bins.

* Empty markers and full lines show container sealed and under gas, dotted line and filled markers show periods when gas was added to the container.

Fruit samples collected after the fumigation and incubated with bioassays in the ct room produced no viable offspring, showing complete control of all dried fruit insects found infesting the fruit prior to treatment. Bioassays placed in the container of *T. confusum* and *P. interpunctella* recorded 100% mortality of all insects exposed to the treatment. A total of 3,900 *T. confusum* adults, pupa and larvae were exposed and killed along with an estimated 480 eggs (calculated from the field controls). It should be noted that for *P. interpunctella* the bioassay consisted of only the pupa and last stage larva, which were available in limited numbers.

DISCUSSION

The successful fumigation of dried vine fruit with ethyl formate in the first experiment demonstrated the efficacy of ethyl formate at very low fumigation temperatures upon the pests *T. confusum* and *O. surinamensis*. The average

commodity temperature was 9.2ºC, a temperature not recommended for fumigation with methyl bromide or many fumigants. However, at this temperature the ethyl formate performed creditably with 100% mortality of *O. surinamensis* and 99.7% mortality of *T. confusum* from an estimated dosage of less than 60 g m^{-3} (when sorption onto the commodity is taken into account). The only surviving *T. confusum* were pupae which were buried 35 cm into the dried fruit. It is probable that the low temperature and consequently slower vaporisation of the ethyl formate reduced the effective dosage at this position within the fruit mass. Ethyl formate has been shown to sorb onto dried vine fruit in a similar way to, but at lower amounts than wheat (Hilton and Banks, 1997; Reuss and Annis, 2000). This sorption may have reduced the active dosage at the centre of the fruit bins. Mortality of the test insects due to poor thermal adjustment was ruled out by the use of field control bioassays which survived and continued to multiply after exposure in an adjacent shed on top of identical fruit with near identical temperature conditions.

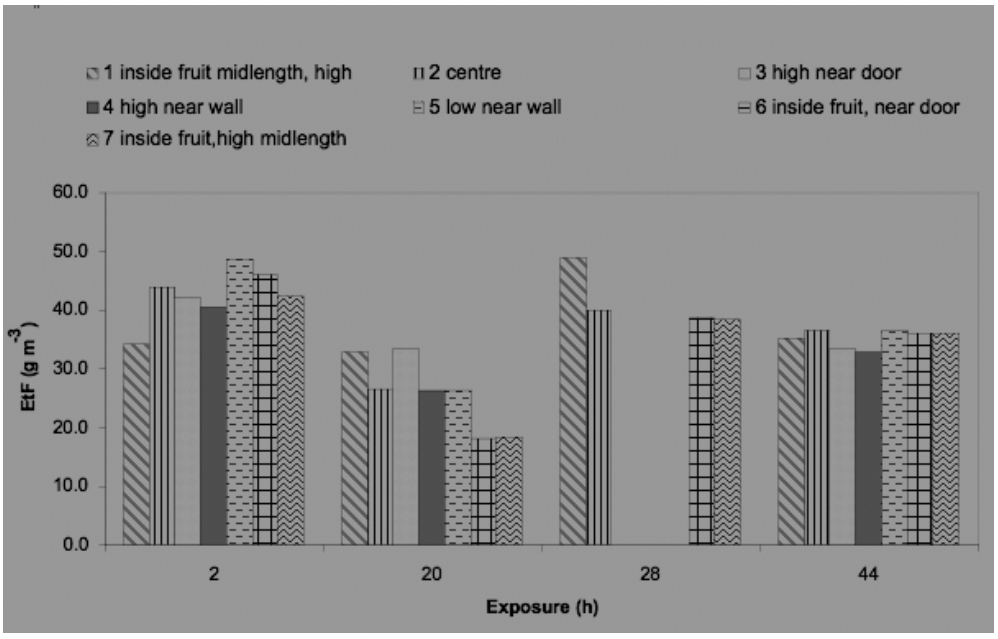

Figure 6. Ethyl formate (EtF) concentrations in headspace and within sultana fruit bins during a 48 hour fumigation with a mixture of ethyl formate and CO_2 in April 2001.

In the first experiment, CO_2 addition was equivalent to 10 % of the shipping containers' area and was presumed to act only as a fire retardant. In the second experimental fumigation the use of CO_2 as an adjunct to ethyl formate as well as acting as a fire retardant was proposed. The use of CO_2 as an adjunct to ethyl formate has much to recommend it. The reduced occupational risk due to CO_2's fire retardant properties and the potential (unquantified) increase in insect toxicity make

this technique an attractive option for the disinfestation of dried fruit in gas-tight containers. An average effective ethyl formate dosage of 35 g m^{-3} was monitored throughout the fumigation in addition to a CO_2 concentration which averaged 41% over the first 24 h of fumigation and increased to 65% prior to the final CO_2 reading (which occurred at 27 h into fumigation). Based on previous research (Hilton and Banks, 1997; Allen and Desmarchelier, 2002; Damcevski and Annis, 2002) an ethyl formate dose rate of 35 g m^{-3} would not be expected to completely control insect infestations with the chosen species. However, with the added CO_2, 100% control was observed. Prior research by Tarr and Reuss (unpublished data) also found that a dosage of greater than 40 g m^{-3} was needed to obtain 100% mortality of *T. confusum* adults and late stage larvae, while a dosage of 35 g m^{-3} caused 100% mortality of *O. surinamensis* and *P. interpunctella* adults and larvae. The possibly synergistic action of CO_2 and ethyl formate during fumigation deserves further research.

Subsequent to this research BOC gases have produced an ethyl formate/CO_2 mixture in a gas cylinder called Vapormate (Ryan and Bishop 2003). This has the potential to make safe fumigation of sultanas in sealed enclosures a reality, providing the mixture produces a lethal concentration sufficient to control dried fruit pests.

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