PFR SPTS No 10678

Comprehensive literature review of fumigants and disinfestation strategies, methods and techniques pertinent to potential use as quarantine treatments for New Zealand export logs

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October 2014

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Scion

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PUBLICATION DATA

Armstrong JW, Brash DW, Waddell BC. October 2014. Comprehensive literature review of fumigants and disinfestation strategies, methods and techniques pertinent to potential use as quarantine treatments for New Zealand export logs. A report prepared for: Scion. Plant Food Research Contract No. 29714. Milestone No. 1.3.1. Job code: P/332016/01. SPTS No. 10678.

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Contents

Executive summary

Comprehensive literature review of fumigants and disinfestation strategies, methods and techniques pertinent to potential use as quarantine treatments for New Zealand export logs

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October 2014

A comprehensive literature review was undertaken to determine whether any fumigants, or disinfestation strategies, methods or techniques presented viable alternatives to methyl bromide fumigation for New Zealand log exports. The viability of alternatives focused on considerations of currency in the literature, economic and regulatory feasibility, environmental and human health concerns, efficacy against target pests, utility for log exports, and commercial application aspects based on current and historical literature.

The primary goal of the literature review was to find two fumigants that could be recommended as viable alternatives for further research under the Ministry for Business, Innovation, and Employment (MBIE) research programme, “Protecting Market Access for Wood Exports”.

Over 30 fumigants, including 15 major fumigants and 18 minor fumigants, were reviewed. The literature review found that the peak for toxic fumigant research was in the 1980s with a marked reduction in research effort through the 1990s. The international ban on ethylene dibromide in 1984, restrictions on methyl bromide beginning in 1991, and concurrent increases in environmental and worker safety regulations that increased the costs to register new fumigants, combined with public pressures for a variety of reasons to decrease insecticide applications regardless of their use, diminished commercial interest in maintaining older fumigants or developing new ones. As commercial interest waned, so did scientific efforts in pursuing fumigant research.

Recommendations:

1. Ethanedinitrile, which is currently under study as a methyl bromide alternative for export logs by Plant & Food, is recommended for further study. Recent (2014) studies determined the efficacy of ethanedinitrile on the life stages of Burnt pine longhorn beetle, *Arhopalus ferus* (Mulsant), adults and the effects of dose, moisture content, end-grain sealing, and load factor on ethanedinitrile sorption rates. These studies were specific to sawn timber, not logs. Additional research is needed to determine penetration and sorption factors for logs, the most tolerant species and life stage to ethanedinitrile for selected forest insects, and, finally, laboratory and commercial efficacy tests. However, these additional studies should be predicated on a technological and economic study to determine the suitability of using ethanedinitrile for logs.
2. Sulphuryl fluoride, a common timber and structural fumigant for termites, was a distant second possibility. Environmental issues and the lack of efficacy against insect eggs cannot be overlooked. However, if ethanedinitrile is rejected pursuant to a technological and economic study, sulphuryl fluoride has positive characteristics that make it the only

additional fumigant alternative to methyl bromide that can be recommended for further study.

3. Current (2014) research at Plant & Food is studying the potential for using reduced rates and/or fumigation times when methyl bromide is used to control forest insects. Although this research obviously is not a “methyl bromide alternative”, positive results from this research could translate into significant reductions in methyl bromide use and cost savings to the log export industry. Hence, continued research on reduced methyl bromide rates is recommended.

In addition to fumigants, the secondary goal of the literature review was to look in-depth at non-chemical treatments and methods, including controlled and modified atmospheres, energy treatments (irradiation, microwave, electrical, infrared), physical treatments (cold, heat, pressure, and vacuum), and other alternatives, such as debarking of logs, pest management systems, and systems approaches. To complete the literature review focus, discussions are provided covering the economic and physical aspects of the New Zealand log export industry specific to the use of methyl bromide and phosphine, the two current phytosanitary fumigants, and a discussion of quarantine security statistics.

Recommendations:

1. Based on the 1997 work of Dentener et al. that showed significant efficacy against *Prionoplus reticularis* in laboratory studies using carbon dioxide or nitrogen and 40°C in under 7 h, the use of combined heat and modified atmosphere is recommended for further study as a potential non-toxic treatment for New Zealand export logs. Laboratory studies on selected forest insects could rapidly establish whether a combined heat and modified atmosphere treatment had any potential for use under commercial conditions. However, research with ethanedinitrile (9.a. above) must take precedent.
2. Further study is needed to determine if in-forest debarking at point of harvest can achieve phytosanitary requirements. This work is needed to establish a technological and economic baseline with which to compare the costs of alternative treatments.

Other than ethanedinitrile and sulphuryl fluoride, no other fumigant had any possibility of being considered for further research as a methyl bromide alternative for New Zealand export logs. Also, no energy (other than the joule heating process currently being studied) or physical treatment (other than a combined heat and modified atmosphere treatmentdescribed above) showed any potential for use on export logs.

This review has been prepared with the understanding that it is a “living” document subject to being amended over time as new information becomes available.

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1 Introduction

1.1 Terms of reference

The literature review provided herein is specific to the fulfilment of Plant & Food Research obligations under Critical Step 1.3.1 New Targeted Fumigants under subcontract with New Zealand Forest Research Institute Limited ("Scion") pursuant to Scion's contract with New Zealand Ministry for Business, Innovation and Employment entitled Protecting Market Access for Wood Exports (CO4X1204).

Specifically, a range of fumigants suited to log fumigation will be evaluated for physical and chemical properties (especially an assessment of penetration in green pine, *Pinus radiata* D. Don, logs), mode of insecticidal action, availability, environmental credentials, and health and safety requirements. Potential synergistic combinations based on mode of action will be identified. Enhancing treatments that can be incorporated at operational scale will be evaluated for potential benefits, e.g., heat, modified oxygen and carbon dioxide. By 2013, at least two new alternative fumigation treatments or treatment strategies will be defined for further testing specific to export *P. radiata* logs.

The resulting report includes the evaluation of a range of fumigants and treatment methods identified from the literature specific to the treatment of fresh log exports subject to ameliorative measures to eliminate target forest insects.

1.2 Authors' notes:

This review identified treatments (fumigant, energy or physical) specific to forest insects that may be found on or in logs, timber and wood products as the key factor to their potential suitability for the treatment of export logs. The use of treatments for other commodities or products (e.g., fruits and vegetables or stored products) or for use against fungi or nematodes in soil or wood are discussed only to provide a general understanding of the treatment using selected references to support the discussion although the treatments are not pertinent to forest insects, logs or timber. The literature was limited in this way to maintain the review focus on log exports. The use of every reference describing a fumigant or treatment method would unnecessarily inflate the content herein and hinder the selection of high-priority fumigants or treatment methods specific to the quarantine treatment of logs for research.

New Zealand does not have any nematode or pathogen issues of quarantine importance with export logs (MPI 2013b). Therefore, our review is specific to references of treatments against insects. Treatments for nematodes (e.g., pine wood nematode, *Bursaphelenchus xylophilus*) or pathogens (e.g., oak wilt, *Ceratocystis fagacearum*) were not considered except where an assessment of penetration in green logs was made and could be related directly to insecticidal action and penetration to the site of the target pests. Literature for treatment of blue sap stain, primarily caused by the ubiquitous *Ophiostoma* spp. fungi in New Zealand, was not considered because the damage caused by this pathogen is a quality issue for logs and timber and not a quarantine issue.

Treatment schedules used to meet phytosanitary regulations consist of specified treatment parameters that must be followed to ensure treatment efficacy and quarantine security (USDA 2013). For example:

- Fumigation schedules specify the fumigant concentration, the temperature (or range of temperatures) at which the fumigation must be carried out, and the fumigation time (the duration the treated material must be exposed to the fumigant.
- Physical treatment schedules, such as cold or heat treatments, specify the temperature or range of temperatures that must be used and the treatment duration for which the material must be subjected to the specified temperature.
- Energy treatments, such as irradiation, specify the number of Grays (the absorption of one joule of radiation energy by one kilogram of matter) that must be absorbed at the centre of the treated material.

Treatments, specifically fumigants, currently being used for the disinfestation treatment of log exports from New Zealand (i.e., methyl bromide and phosphine) are discussed herein for completeness. Other fumigants, such as ethanedinitrile, that are being studied in limited current research trials to determine their efficacy for disinfesting export logs are also discussed. The debarking method, which is approved for some markets, is discussed herein both as an alternative method and as a standard against which to assess the economic cost of alternative treatments.

This review has been prepared with the understanding that it is a “living” document subject to being amended over time as new information becomes available.

2 Background

2.1 New Zealand log exports

New Zealand forest product exports, including logs and poles, sawn timber and sleepers, plywood, paper and paper products, fibreboard, and other wood products, is the third largest export industry following dairy product and meat exports, and valued at $4.48 billion in 2013 (NZTE 2013, MPI 2013c). According to Stakeholders in Methyl Bromide Reduction, Inc. (STIMBR) and (MPI 2013c), New Zealand's log export volumes in the 2012 calendar year were 13.8 million m^3, breaking records in both the June and December quarters. STIMBR found that log export volumes, primarily to China, India, Korea, and Japan (70%, 16%, 9%, and 4% of the total log exports, respectively) in the year ending 30 June 2013 increased by 7.0% for 2012. Coupled with a 4.4 percent price increase, log export values were forecast to increase by nearly 12% for the year ending 30 June 2013 to $1.65 billion (MPI 2013c). Actual figures for log and pole exports to all countries resulted in an FOB value of $1.85 billion for the year ending 30 June 2013 (MPI 2013a). New Zealand forest growers' reliance on the export log trade has grown significantly over the past decade. Current domestic processing capacity has a limited ability to take on a large proportion of the logs currently being exported. In the year ending September 2013, 55% of New Zealand's forest harvest was exported as logs. It is reasonable to assume that New Zealand forest growers will become increasingly reliant on the log export trade (STIMBR, I. Gear, personal communication).

This review of potential alternative treatments for export logs is specific to Monterey pine (or 'radiata pine'), *Pinus radiata* D. Don, which represents about 97% of all log species exported (Statistics New Zealand 2013). Although *P. radiata* is the predominant log species exported from New Zealand, it is not the only export log species. Logs exported from New Zealand from 1 November 2012 through 31 October 2013 for which phytosanitary certificates were issued by MPI encompassed over 30 species, including kauri, *Agathis australis* (D. Don) Loudon; Lawson cypress, *Chamaecyparis lawsoniana* (A. Murray) Parlatore; sugi, *Cryptomeria japonica* (L. f.) D. Don; Mexican white cedar, *Cupressus lusitanica* Miller; brown barrel eucalyptus, *Eucalyptus fastigata* H. Deane & Maiden; flooded (or rose) gum eucalyptus, *Eucalyptus grandis* W. Hill ex Maiden; spotted gum eucalyptus, *Eucalyptus maculata* (Hooker) K. D. Hill & L. A. S. Johnson; shining gum eucalyptus, *Eucalyptus nitens* H. Deane & Maiden; *Eucalyptus* spp.; European larch, *Larix decidua* Miller; Japanese larch (or karamatsu) *Larix kaempferi* (Lambert) Carrière; spruce, *Picea* spp.; lodgepole (or shore) pine, *Pinus contorta* Douglas; shortleaf pine, *Pinus echinata* Miller; slash pine, *Pinus elliottii* Engelmann; bishop pine, *Pinus muricata* D. Don; Australian pine, *Pinus nigra* J. F. Arnold; Corsican pine, *Pinus nigra v. maritima* (Aiton) Melville; Patula (or Mexican weeping) pine, *Pinus patula* Schiede ex Schlechtendal & Chamisso; maritime (or cluster) pine, *Pinus pinaster* Aiton; ponderosa (or bull, blackjack or western yellow) pine, *Pinus ponderosa* Douglas ex C. Lawson; *Pinus* spp.; Weymouth (or eastern, northern, white, or soft) pine, *Pinus strobes* L.; Scots pine, *Pinus sylvestris* L.; Euphrates poplar, *Populus euphratica* Oliver; black poplar, *Populus nigra* L.; *Populus spp*.; Douglas fir (or Oregon pine), *Pseudotsuga menziesii* (Mirbel) Franco; *Pseudotsuga* spp.; California (or coastal or giant) redwood, *Sequoia sempervirens* (D. Don) Endlicher; and *Sequoia* spp. (D. Clarke, personal communication). To obtain phytosanitary certificates, these species were treated by methyl bromide or phosphine fumigation, or by debarking (D. Clarke, personal communication).

2.2 Forest insects

There are a number of forest insects found in New Zealand that have the potential for one or more of their life stages to be found on or in New Zealand logs. Some of these insects may be quarantine pests while others are simply transient forest species that are found only in storm- or fire-damaged trees, fallen trees, tree stumps, or simply as 'hitchhikers'. Examples of commonly found wood boring and bark beetles include burnt pine longhorn beetle, *Arhopalus ferus* (syn. *tristis*) (Mulsant) (Coleoptera: Cerambycidae); black pine bark beetle, *Hylastes ater* (Paykull), and the closely related golden-haired bark beetle, *Hylurgus ligniperda* (F.) (Coleoptera: Curculionidae[1]). The Sirex woodwasp, *Sirex noctilio* F. (Hymenoptera: Siricidae) is rare in plantations following the successful introduction and establishment of biological control tools and improved silviculture practices; while the native huhu beetle, *Prionoplus reticularis* White (Coleoptera: Cerambycidae) requires dead logs to develop and complete its life cycle. The regulatory status of these forest insects is determined through bilateral negotiation between MPI and New Zealand's trading partners. This review of methyl bromide alternatives is not specific to any insect or group of insects, but reviews the potential treatment alternatives that may be available for use when needed for phytosanitary purposes if and when they arise.

2.3 Application of quarantine treatments for export logs

2.3.1 Current phytosanitary treatments

Three phytosanitary treatments are currently used to disinfest logs exported from New Zealand: fumigation either with methyl bromide or phosphine, or debarking. The phosphine fumigation is approved as a phytosanitary treatment only for logs exported to China (MPI 2011a). Debarking is approved as a method for ensuring against potential contamination with bark beetles (e.g., *H. ligniperda*). Phytosanitary regulations specify that the tolerance limits for debarked logs include a 5.0% surface cover of bark on any individual log and a 2.0% total surface cover of bark on any batch of logs (MPI 2011a). Debarking instead of a fumigation treatment is approved as a phytosanitary alternative only for China (MPI 2011a). Table 1 shows the total volumes of export logs fumigated with methyl bromide or phosphine, or debarked and requiring no fumigation.

[1] The reader will note discrepancies between the use of Scolytidae in reference citations and Curculionidae in the text for Coleoptera nomenclature. Coleopteran species in the Scolytidae, e.g., *H. ater* and *H. ligniperda*, were reclassified to the family Curculionidae (subfamily Scolytinae) (Brockerhoff et al. 2003, Wood and Bright 1992). Although reference citations tend to use the older family designation of Scolytidae, the author uses the current family name, Curculionidae, in the text.

Table 1. Total volumes of logs exported from New Zealand during the period 1 November 2012 through 31 October 2013 fumigated with methyl bromide or phosphine, or subject to total debarking as phytosanitary treatments[a b]

Importing country	Vol. exported logs (m^3)	Vol. fumigated with methyl bromide (m^3)	Vol. fumigated with phosphine (m^3)	Vol. debarked (m^3)
China	11,458,014	1,955,217	8,626,091	882,895[c]
India	1,488,457	1,488,457	0	72,446
Taiwan	73,815	0	0	906
Thailand	25,418	0	0	0
Viet Nam	10,348	0	0	3,416
Indonesia	1,679	0	0	1,679
Malaysia	454	454	0	141
Japan	23	0	0	23[d]
France	1	1[e]	0	0
Total[f]	13,058,209	3,444,129	8,626,091	961,506

[a]Data and table provided by New Zealand Ministry for Primary Industries. Data compiled from all phytosanitary certificates issued from 1 November 2012 through 31 October 2013. Not all trading partners require phytosanitary certification for pine logs exported from New Zealand (see footnote f).

[b]Total volume of exports Include over 30 species (see 2.a.). However, *Pinus radiata* is the prevalent export species.

[c]Some debarked logs also were fumigated with phosphine (6,172m^3) or with methyl bromide (16 m^3).

[d]A single shipment of untreated *Eucalyptus nitens*. Japan does not require phytosanitary certification of New Zealand pine logs.

[e]A single shipment of kauri fumigated with methyl bromide.

[f]The total volumes of logs given are for countries that require phytosanitary certification of New Zealand pine logs before export. The countries that do not require phytosanitary certification of pine logs are published on the New Zealand Ministry for Primary Industries website: *http://www.maf.govt.nz/news-resources/statistics-forecasting/forestry/annual-forestry-export-statistics.aspx*

China is New Zealand's largest trading partner for export pine logs with approximately 70% of the total trade for all countries that import New Zealand logs (MPI 2013c). The data (Table 1) show that, for the total volume of logs exported to China, 75.2% of the logs were fumigated in transit with phosphine, 17.1% of the logs were fumigated before transit with methyl bromide, and the remaining 7.7% of the logs were debarked before transit in lieu of a phytosanitary fumigation treatment. Moreover, over 66% of all export logs that require phytosanitary certification are fumigated with phosphine and approximately 15% are fumigated with methyl bromide (Table 1). In economic terms, this translated to $1.3 billion in logs exported to China (MPI 2013c) in 2011-12 of which almost $858 million in export value depends on the continued use of phosphine and over $195 million in export value depends on the continued use of methyl bromide. The economic figures provided here may be conservative because a recent Agrifax report (Agrifax 2013) found that the price for New Zealand export logs actually increased by 23% over previous prices during October 2013.

Current methyl bromide phytosanitary fumigations are carried out under tarpaulin at the port (e.g., Napier, Whangarei, and Tauranga) by approved operators (MPI 2011b). After the tarp is removed, the fumigated logs must be loaded onto a vessel within 36 hours during the *A. ferus* adult flight season during the summer months or 72 hours during periods when *A. ferus* adults are not flying (MPI 2013d). The beginning and end of the flight season varies depending on weather conditions and is determined through a monitoring programme (MPI 2013e). No methyl bromide phytosanitary fumigations are carried out at the point of harvest.

Current phosphine phytosanitary fumigations (China only) are carried out in ship holds starting immediately after the ship leaves port and consists of an initial fumigation of 2.0 g/m^3 followed by a further "top up" after four to five days with up to 1.5 g/m^3 to maintain an in-hold gas concentration of at least 200 ppm for 10 days (MPI 2011a). A number of countries require neither a preclearance treatment nor a phytosanitary certification and fumigation with methyl bromide is usually carried out on arrival, e.g., Japan, Korea (MPI 2013e,f).

Debarking is an alternative method to reduce or eliminate the potential for forest insects to be found on export logs that is an approved option for a number of countries, including China (MPI 2011a). The tolerances for bark remaining on debarked logs are 5% remaining on any individual log and 2% on any batch of logs (MPI 2011a). Debarking is discussed as a separate method for use on export logs in Subsection 8.1.

The following brief overviews of both methyl bromide and phosphine fumigations as phytosanitary treatments for export logs, and the export value of the logs dependent on phytosanitary fumigation treatments, support the immediate need to protect the New Zealand log export industry through the addition of alternative quarantine treatment methods and technologies.

2.3.2 Fumigation of New Zealand export logs with methyl bromide

By the end of 2009, the export log and sawn timber markets were the key area in which methyl bromide was used and the main tool available for ensuring the continuation of trade to the log, sawn timber, and horticulture export industries (NZERMA 2009[2]). Currently, the methyl bromide fumigation rates for New Zealand export logs are not standardised (Table 2, Armstrong et al. 2011). The most significant variation is the pre-shipment methyl bromide schedule required by the largest log trading partner, China. Table 2 shows the China schedules for New Zealand pine logs compared with those for New Zealand's other large Asian trading partners, Japan and Korea. The rates of 80 g/m^3 MB for 16 hours at $\geq$ 15°C or 120 g/m^3 MB for 16 hours at $\leq$ 15°C and their corresponding CT (concentration x time) products (1,280 and 1,920, respectively) are significantly greater than those applied on arrival by Japan or Korea.

[2] Currently the New Zealand Environmental Protection Authority

Table 2. Methyl bromide (MB) fumigation schedules specified by China (MPI 2013b) at export; and by Japan and Korea at import for fumigation temperatures ≥ 15°C.

Country	MB Rate	Time	Temperature	CT product[a]
China[b]	80.0 g/m^3	16 hours	≥ 15°C	1,280
Japan[c]	48.5 g/m^3	16 hours	≥ 15°C	776
Korea[d]	33.0 g/m^3 or 49.5 g/m^3	24 hours or 16 hours[e]	≥ 15°C	792

[a]Concentration x time (CT). Theoretical value derived by multiplying the MB rate by the fumigation time.
[b]Fumigation done in New Zealand before export (MPI 2013b).
[c]Fumigation done at port of entry (Japan MAFF PPS 2011).
[d] Fumigation done at port of entry (MPI 2013G, Yu et al. 1984).
[e]MB rate adjusted to a 16-hour fumigation time that maintains the same theoretical CT product (Bond 1984, Monro 1969).

Continued pressure to reduce methyl bromide emissions under the Montreal Protocol (UNEP 2010), the rising cost of methyl bromide fumigation (Chemtura 2012), and the 2008 International Plant Protection Convention's (IPPC 2008) recommendation for a reassessment of doses to reduce the volume of methyl bromide being used are significant reasons to identify excessive methyl bromide dose rates and seek to have them reduced to reasonable thresholds (UNEP 2010). To address these issues, Armstrong et al. (2011) analysed the data of Cross (1992) for CT products at a 20-mm-depth of penetration required for the pests of concern in New Zealand export logs and the CT products of the China, Japan and Korea methyl bromide rates. Mathematical analysis of the Cross (1992) data and the CT products indicated that the methyl bromide rates required by China, Japan and Korea could be significantly reduced to 49 g/m^3 for fumigations at ≥ 15°C with no loss of efficacy against the target pest species (Armstrong et al. 2011). The additional benefit of reducing the methyl bromide rate is a potential reduction of over 224 tons of methyl bromide compared with the amount used in 2012 (K. Glassey, personal communication).

Very little data exist on the relative efficacy of, or tolerance to, methyl bromide by New Zealand forest insects (Armstrong et al. 2011, 2012b). Efficacy and tolerance data are needed both to determine the potential for reduction in methyl bromide rates for New Zealand export logs (Armstrong et al. 2012b) and to provide a basis for comparison with the efficacy and economic viability of potential alternative treatments, including fumigants. Moreover, a reduction and standardisation of methyl bromide fumigation rates may reduce overall fumigation costs as the cost for methyl bromide increases over time. Great Lakes Solutions, a predominant manufacturer of methyl bromide, announced that effective March 1, 2012 (1) prices in all regions outside of North America for methyl bromide for emissive use were to increase by up to 20%, (2) prices within North America for methyl bromide for regulated critical uses were to increase by up to 40%, and (3) prices for methyl bromide for quarantine and pre-shipment use were to increase by up to 60% because of escalating costs for ongoing input and investment associated with regulatory compliance, advocacy and manufacturing (Chemtura 2012).

2.3.3 Fumigation of New Zealand export logs with phosphine

China permitted New Zealand to use phosphine as a phytosanitary fumigant on an experimental basis against the listed pest species in 2001 (STIMBR, I. Gear, personal communication). The agreed phosphine fumigation schedule is 200 ppm at ≥ 15°C for 10 days (NZMAF 2007b), a schedule known to be efficacious for the control of stored product insects in Africa, Australia, China, United States, and elsewhere (ARC 2011, Bond 1984, Bullen 2007, Lv et al. 2006, Pedersen et al. 1996, Warrick 2011). Although phosphine is used to fumigate wood chips (USDA 2012), New Zealand is the only country using phosphine as a phytosanitary treatment for exported logs, possibly due to the lengthy exposure periods required for phosphine fumigations which are available when shipping from New Zealand to markets in Asia (Brash et al. 2010).

The current phosphine fumigation treatment of logs is carried out during transit after the vessel has left a New Zealand port for its destination port. MPI (2011a) regulations for in-hold fumigation with phosphine specify that the initial fumigation must be at a rate of at least 2 g/m^3, then after 5 days a further “top up” of 1.5 g/m^3 is required. The treatment must maintain an in-hold gas concentration of $\geq$ 200 ppm for 10 days, during which time the hold must remain sealed.

2.4 Methyl bromide alternatives

In 1998, the Methyl Bromide Technical Options Committee (Ozone Secretariat, United Nations Environment Programme) estimated that 12% all methyl bromide produced globally was used to fumigate durable commodities, including timber and wooden products (MBTOC 1998). The 1998 figure of 12% increased to 33% by 2005 (MBTOC 2006), a nearly three-fold increase. The recommendation by the International Plant Protection Convention to reduce the dependence on methyl bromide worldwide (IPPC 2008) and the requirement that all methyl bromide used in fumigations in New Zealand be 100% recaptured or destroyed by 2020 (NZME 2011) have added significant pressure to find alternative treatments for logs and timber exports. Unfortunately, as this literature review will demonstrate, the search for methyl bromide alternatives for logs has been relatively comprehensive, especially in New Zealand, but has not yet produced any methyl bromide alternative (other than phosphine, which has been in use since 2002). Underscoring the lack of alternatives, New Zealand Environmental Risk Management Authority stated in its reassessment decision for the continued use of methyl bromide that “Our decision recognizes that for the time being there is no practical alternative to the continued use of methyl bromide” (NZERMA 2009, 2011a).

Banks (2002) gave an overview of potential methyl bromide alternatives for durables, including logs and timber, which are shown in Tables 3 and 4 for comparison with a more recent overview developed by STIMBR (Table 5) of potential methyl bromide alternatives.

Table 3. Fumigant and non-fumigant alternatives to methyl bromide for durables[a] - principal strengths and weaknesses[b] (Banks 2002)

Fumigant alternatives to methyl bromide		
Fumigant	Weaknesses	Strengths
Methyl bromide	Ozone depletor, residues, taint	Range of registration and acceptance; reputation
Carbon bisulphide	Flammability, registration, residues	None
Carbonyl sulphide	May be difficult to register	Naturally occurring
Controlled atmospheres (atmospheric pressure)	Slow acting	May not need registration, less regulation
Controlled atmospheres (vacuum)	Slow acting	Low technology, may not need registration
Dichlorvos	Poor penetration, residues, resistance	Useable in unsealed enclosures
Ethyl formate	Highly sorbed, registration	Rapid
Ethylene oxide	Carcinogenic, flammable, infrastructure needs, residues	Sterilant
Hydrogen cyanide	Reputation, unstable in storage, highly sorbed	Rapid
Phosphine (cylinder gas)	Flammability, corrosiveness, poor action at low temperatures, slow, resistance	Excellent penetration
Phosphine (metal phosphide formulations)	Flammability, corrosiveness, poor action at low temperatures, slow, resistance, tablet residues	Excellent penetration, low technology, cheap, broad range of registration
Propylene oxide	Infrastructure needs, flammable, registration, highly sorbed	Sterilant
Sulphuryl fluoride	Registration, low effectiveness against egg stage	Good penetration, little sorption

See next page

Non-fumigant alternatives to methyl bromide		
Fumigant	Weaknesses	Strengths
Integrated Pest Management/Integrated Commodity Management	Can be complex to operate	Avoids unnecessary treatments
Biologicals	Registration, often too specific, live material remains present	[no comment provided by Banks (2002)]
Cold treatment (down to 4°C)	Does not kill insects quickly	Long-term protection, no registration required, no toxic chemicals
Cold treatments (below - 15°C)	Not feasible on large scale	Rapidly insecticidal
Heat treatment	Infrastructure requirements for large scale use	Rapid, residue free
Inert dusts	Not active at high humidity, acceptance and product quality, slow acting	Long-term protection, low technology process
Irradiation	Public acceptance, infrastructure required, product quality, live, but sterile pests can remain	Active against all pests
Pest exclusion/physical removal/sanitation	[no comment provided by Banks (2002)]	Simple process
Pesticides of low volatility (e.g. organophosphates, pyrethroids)	Market and regulatory acceptance, slow, resistance, residues	Low technology process, long-term protection

[a] Durables includes dried stored products, grains, dried pulses, tree nuts and fruits, etc., but could include logs, timber and timber products (e.g., heat treatment, irradiation).
[b] Condensed from two tables into one table from Banks (2002) pp. 3-4.

Table 4. Alternatives to methyl bromide for timber and timber products - principal strengths and weaknesses (Banks 2002)

Fumigant or process	Weaknesses	Strengths
Methyl bromide	Ozone depletor, residues, taint	Range of registration and acceptance; reputation
Carbon bisulphide	Flammability, registration, residues	None
Carbonyl sulphide	Registration	Naturally occurring
Controlled atmospheres (atmospheric pressure)	Slow acting	May not need registration, less regulation
Controlled atmospheres (vacuum)	Slow acting	Low technology, may not need registration
Dichlorvos	Poor penetration, residues, resistance	Useable in unsealed enclosures
Ethyl formate	Highly sorbed, registration	Rapid

STIMBR evaluated the potential quarantine treatments listed by the combined Methyl Bromide Technical Options Committee and the New Zealand Environmental Risk Management Authority (NZERMA 2011a) in the Methyl Bromide Reassessment Decision 2010 (Batchelor & Miller 2010) and produced Table 5 (I. Gear, personal communication).

Table 5. Overview of potential quarantine treatment methods for New Zealand export logs prepared by STIMBR pursuant to the assessment of potential quarantine treatments for logs that were listed by the Methyl Bromide Technical Options Committee and New Zealand Environmental Protection Authority in the Methyl Bromide Reassessment Decision of 2010 (I. Gear, personal communication)[a]

Chemical options		
Fumigant	Compared with methyl bromide	Status and/or comments
Carbonyl sulphide	Less toxic	Considered, but less effective
Ethyl formate	Less toxic	Being tested for horticultural crops but unsuitable for logs
Methyl iodide	Equally toxic and carcinogenic	Considered and discounted
Methyl isothiocyanate	More toxic	Considered and discounted
Phosphine	Currently used	Being thoroughly investigated, some questions about on-going use
Sulphuryl fluoride	May have effect of adding to global warming	A possibility; may test if no other fumigants available for logs
Ethanedinitrile	Equivalent toxicity	Promising for sawn timber; under investigation for sawn timber

See over

Non-chemical options		
Debarking	More expensive, but effective; logistically challenging	Benchmarking study completed; all potential alternative chemical or non-chemical methods will be compared with the cost of debarking
Heat - hot water or steam	Very expensive and logistically challenging	No research in progress; may have niche potential
Heat - Joule heating	Untested; potentially expensive	Research in progress under MBIE programme; may have niche potential
Microwave	Expensive, but possible	Approved for use on wood packaging internationally but unlikely for logs
Irradiation	Subject to current MBIE research programme	Research in progress under MBIE programme; may have niche potential
Water soaking	Untested	Logistically difficult; considered and discounted
Integrated pest management	Subject to current MBIE research programme	Already used in horticulture; may only support a decreased need for fumigation during periods of insect inactivity; will require pest-monitoring programmes

[a]Revisions to the original Table 5 were made by the authors to update the information presented therein; all revisions were approved by STIMBR (I. Gear, personal communication).

Table 6 shows the quantities of logs that were loaded at the 13 commercial ports in New Zealand for the year ending in September 2013. Any changes to the current methyl bromide or phosphine phytosanitary treatments will present challenges for all ports. Moreover, alternative treatments, whether using toxic or non-toxic compounds or methods to treat logs before export, must consider the implications of commercial application, including:

- Will the alternative treatment be cost effective at the port based on the value of logs exported from that port (e.g., Auckland Seaport v. Tauranga Seaport, Table 6)?
- Can the alternative treatment be adapted to the current port conditions or will significant infrastructure modification be required?
- Is the alternative treatment viable in the environmental conditions of the port and surrounding area, especially where populations are in close proximity to port operations (e.g., Picton, Tauranga)?
- Sustainable
- Health and safety - EPA requirements.

Table 6. Quantities and estimated value of New Zealand log exports loaded at each port for the period of January through September 2013[a]

Port	Quantity (m^3)	FOB (NZ$000)	Percent of total loaded at port
Whangarei	2,693,531	352,473	16.68
Auckland Seaport	79,370	14,312	0.49
Tauranga Seaport	6,146,784	852,225	38.07
Gisborne	2,168,482	302,502	13.43
New Plymouth	320,488	40,819	1.99
Napier	1,089,360	140,290	6.75
Wellington Seaport	760,159	96,060	4.71
Nelson	625,594	78,966	3.88
Picton	568,196	70,495	3.52
Christchurch Seaport (Lyttelton)	385,404	46,731	2.39
Timaru	255,161	31,633	1.58
Dunedin Seaport	778,661	99,494	4.82
Invercargill Seaport (Bluff)	274,772	31,570	1.70
Total	16,145,961	2,157,569	

[a]Data provided by STIMBR.

3 Fumigants

The fumigation process involves creating a lethal concentration of toxic gas for a time sufficient to kill the target pest (Stark 1994) and a "true fumigant" is a toxic chemical that controls the target pest while the chemical is in the gaseous state (Price 1985). Although the toxicity of some insecticides can be attributed to vapour action (e.g., dichlorvos, Table 7), they are not considered true fumigants (Bond 1984). The lethal effects of an insecticidal fumigant are governed to a great extent by the total uptake of fumigant during the time of exposure (Outram 1967a). Very simply described: General gas exchange in insect life stages, excluding eggs, takes place through smaller and larger spiracles (tracheae and tracheoles, respectively) that carry gases directly to the insect tissues (Will 2009). Insect eggs do not have spiracles and gas exchange takes place through microscopic openings called the micropylar complex and possibly through the protective chorion (outer shell of the insect egg) and embryonic membranes depending on their permeability to gases (Outram 1967a). Whereas gas exchange via the tracheal systems of insect larvae, pupae and adults is a dynamic process (Will 2009), gas exchange in insect eggs is a more passive process (Outram 1967a). Therefore, the uptake of gases, including fumigants, could be expected to be more rapid for larvae, pupae or adults than for eggs, which has been shown to occur for many insect species and different fumigants (Outram 1967a).

Fumigation with toxic gases has been an important and widely used technology for the control of insects and other organisms. Because of their unique characteristics, such as ease of application and rapid removal from commodities without leaving residues, fumigants can often provide effective, economical control where other forms of pest control are not feasible (e.g., eliminating insects from grains where pesticides cannot be applied directly). Additionally, fumigation techniques are widely adaptable to many different commodities from grains to perishables to durables, and in many different situations, such as ship holds, warehouses, food processing plants, under tarpaulins, or in specifically designed fumigation chambers (Bond 1984).

Although many chemical compounds exhibit sufficient vapour pressure (Table 7) and toxicity to act as fumigants, few can be used for this purpose because they are corrosive to metals, dissolve plastics, are destructive to plant tissues, or leave unacceptable residues in the treated commodity (Bond 1984).

Bond (1984) listed a wide range of fumigants for stored products (Table 7). However, 10 years later Banks (1994) found only two fumigants left in widespread use – phosphine and methyl bromide. Modern technology and research have also brought to light certain problems with fumigants that were previously unknown. Numerous investigations made on both the acute and chronic effects of fumigants have shown that some of these materials are capable of producing serious effects on human health. In some cases fumigants with excessive hazard potential have been restricted or prohibited so that they are no longer widely used for pest control in some countries (Bond 1984). The ban on ethylene dibromide in the US in 1984, evidence that acrylonitrile was highly carcinogenic (Stark 1994), the Montreal Protocol limiting the use of methyl bromide because it was a significant cause for atmospheric ozone depletion (UNEP 2010), and the withdrawal of registration application for methyl iodide in the U.S. (Corey 2013) serve as a warning for the continued use of true fumigants in the future. Expectations that new fumigants will be developed may not be realistic because the production of toxicology and residue data for registration of a new compound is so expensive and time consuming that the probability of such development is very low (Reichmuth 1998). In the US, some "older" compounds may be re-evaluated and brought back into the market if a sufficient set of registration data is available and is within the 10-year window for recency to meet the official government requirements (Reichmuth 1998). As of 1998, the global stored-product industry need for insect pest and pathogen control was not great enough to support the approximate US$150 million required to support the development and registration of a new chemical product (Reichmuth 1998).

Two decades ago, Banks (1994) stated that “fumigation is becoming an endangered technology.” At the time of this writing (2014), phosphine and methyl bromide remain the two most universally used fumigants followed by the use of sulphuryl fluoride for structural fumigation (a distant third because the compound has no food registration). Even the testing of new fumigants can be problematic. Annis (1987) calculated that developing a new fumigant would require approximately 10^6 individual treatment tests involving 10^9 test insects representing the life stages of a single target species, to identify the time, temperature and concentration parameters for an efficacious treatment. The important message is that (1) the increased scrutiny of the environmental and health issues associated with fumigants, (2) the significant time required to formulate new fumigants, and (3) investment and costs involved with registering new fumigants (Bond 1994, Reichmuth 1998) will limit the development and registration of new fumigants significantly. Accordingly, we may have to rely less on the true fumigants and more on alternative methods of control, such as treatment with irradiation, controlled atmospheres, heat, and cold.

Generally, there are technically feasible alternatives for almost all non-quarantine phytosanitary uses of MB on durables, but they generally will be situation-specific and the development of a single, direct replacement for MB is most unlikely. Selection of the best alternative will have to be made on a case-by-case basis (Banks 2002). Table 7 lists compounds that have been used as fumigants, some of their important properties, their present status, and some issues of concern regarding their use. With the exception of ethanedinitrile (Brash et al. 2013), and limited uses for ethyl formate (Jamieson et al. 2009b) and sulphuryl fluoride (Zhang 2006) there have been no major recent advances in the field of fumigant development.

Table 7. Fumigants used for insect control and some of their important properties[a]

Name and formula	Molecular Weight (g/mol)	Boiling point (°C at 760 mm Hg)	Solubility in water (g/100 ml)	Flammability (percent by volume in air)	Notes (also see Tables 3 and 5 for comparative strengths and weaknesses)
Acrylonitrile CH_2CHCN	53.06	77.0	7.50 at 25°C	3.0 - 17.0	Extremely hazardous to human health with significant restrictions on exposure limits (e.g., permissible exposure limit (PEL) in the US is 2 ppm per 8 hours and a time-weighted average (TWA) of 10 ppm (Agency for Toxic Substances and Disease Registry 1990).
Carbon disulphide CS_2	76.13	46.3	0.22 at 22°C	1.3 - 44.0	All uses are becoming increasingly restricted because of extreme neurotoxicity and cardiotoxicity exacerbated by rapid skin penetration has led to the recommendation and adoption of 8-h TWA of 5 ppm (Scientific Committee on Occupational Exposure Limits 2008) to an 8-hour PEL of 20 ppm (Agency for Toxic Substances and Disease Registry 2012).
Carbon tetrachloride CCl_4	153.84	77.0	0.08 at 20°C	Nonflammable	Due to its ozone-depleting properties in the stratospheric atmosphere, the use of carbon tetrachloride is restricted by European and international regulations as a raw material in chemicals synthesis or as special solvent in industry or in laboratories only (Rotterdam Convention 2013) and deregistered as a fumigant (Agency for Toxic Substances and Disease Registry 2005, Svoronos & Bruno 2002).
Carbonyl sulphide COS	60.08	– 50.2	122 at 25°C	12.0 - 29.0	Although carbonyl sulphide is a flammable compound with an NFPA Hazard Rating of 4, and its fires can restart after being extinguished, its low mammalian toxicity and apparent insecticidal efficacy indicate it may be a safe fumigant (Svoronos & Bruno 2002).
Chloropicrin CCl_3NO_2	164.39	112.0	Insoluble at 20°C	Nonflammable	A gas developed and used by the Germans in WWI and known today as 'tear gas', chloropicrin is used alone and in combination with methyl bromide or sulphuryl fluoride as a 'warning agent' when used as a pre-plant soil fumigant (USEPA 2008c) and has a significantly low TWA of 0.7 ppm (USEPA 2008b).
Dichlorvos $CCl_2{=}CHO.Po(OCH_3)_2$	221.00	74.1	10.0 at 20°C	Nonflammable	An organophosphate insecticide with significant toxicity to aquatic species that is undergoing continued scrutiny and restrictions (APVMA 2013c, NZEPA 2013).
Ethanedinitrile C_2N_2	52.04	– 21.2	45.00 at 20°C	6.0 - 32.0	Only recently registered for use as a soil and timber fumigant, research is underway in New Zealand to determine its potential for use as a log and timber disinfestation treatment.

Name and formula	Molecular Weight (g/mol)	Boiling point (°C at 760 mm Hg)	Solubility in water (g/100 ml)	Flammability (percent by volume in air)	Notes (also see Tables 3 and 5 for comparative strengths and weaknesses)
Ethylene dibromide CH_2BrCH_2Br	187.88	131.0	0.43 at 30°C	Nonflammable	Deregistered internationally during the 1980s through early 1990s pursuant to the Rotterdam Convention (2013).
Ethylene dichloride CH_2ClCH_2Cl	98.97	83.0	0.87 at 20°C	6.0 - 16.0	Severely restricted pursuant to Rotterdam Convention (2013) Annex III.
Ethylene oxide CH_2OCH_2	44.05	10.7	10,000.00 at 20°C	3.0 - 80.0	Both flammable and explosive, ethylene oxide is considered a very hazardous carcinogen and, therefore, has been restricted to a PEL of 1 ppm in the US (NIOSH 2011).
Ethyl formate $HCOOC_2H_5$	74.05	54.0	11.80 at 25°C	2.7 - 13.5	Although registered as a "generally regarded as safe" (GRAS) compound, ethyl formate is flammable and explosive when mixed at concentrations required to kill insects and must be mixed with CO_2 for safe use (Jamieson et al. 2009a); commercial formulations, such as VAPORMATE® may be expensive in comparison with methyl bromide or phosphine for durables.
Hydrogen cyanide HCN	27.03	26.0	100,000.00 at 20°C	6.0 - 41.0	Extremely soluble in water and very flammable and explosive (Bond 1984).
Methyl bromide CH_3Br	94.95	3.6	1.30 at 25°C	Nonflammable	Restricted to quarantine and pre-shipment use by the Montreal Protocol (UNEP 2010). In-country restriction requiring complete recapture or destruction by 2020 (NZMAF 2007a, NZME 2011) creates additional pressure to identify alternative treatments to methyl bromide. The use of methyl bromide in populated areas may come under further scrutiny and restrictions based on research that indicates residential proximity to methyl bromide use during the second trimester was associated with markers of restricted fetal growth in pregnant women (Gemmill et al. 2013).
Methyl iodide CH_3I	141.94	42.4	14.00 at 20°C	8.5 - 66.0	After first denying registration in 2006, the US Environmental Protection Agency (USEPA 2008a) approved methyl iodide for use as a soil fumigant in the US. However, public concerns over carcinogenicity and other health issues led the manufacturer to withdraw the fumigant registration in the US (Corey 2013, USEPA 2012b) citing lack of market viability (San Jose Mercury News 2012).
Methyl formate $HCOOCH_3$	60.03	31.0	30.40 at 20°C	5.9 - 20.0	Previously used as a fumigant for tobacco, dried fruit and cereals, it was replaced by methyl bromide and phosphine because it was extremely

Name and formula	Molecular Weight (g/mol)	Boiling point (°C at 760 mm Hg)	Solubility in water (g/100 ml)	Flammability (percent by volume in air)	Notes (also see Tables 3 and 5 for comparative strengths and weaknesses)
					flammable and readily forms explosive mixtures with air (Green 2005).
Ozone O_3	48.00	-112.0	0.57 at 20°C	Nonflammable	Highly unstable and highly (dangerously) reactive. Although not flammable, ozone is a strong oxidant that can initiate and accelerate combustion or cause explosions. Severe respiratory toxicity. Used primarily for purposes of odour abatement, oxidation of organic compounds, or antimicrobial intervention, in a variety of applications, from food processing to ground water remediation (Ozone Solutions 2012, 2014). Any use for insect control may require highly specialized equipment (Armstrong et al. 2012c).
Paradichlorobenzene $C_2H_4Cl_2$	147.01	173.0	0.01 at 25°C	2.5 - 73.0	Available in the form of cakes, crystals, balls, sachets, impregnated strips, blocks, varpel rope (rodent repellent), and flakes that slowly evolve (sublimate) an insecticidal and fungicidal gas (Interchem Agencies Limited 2007).
Phosphine PH_3	34.04	– 87.4	26.00 cc at 17°C	1.8	Issues with genotoxic effects to humans, increasing environmental and work space restrictions, and resistance by pests (especially in stored grains) show that phosphine cannot be regarded as immune to further restrictions and limitations on use (Bond 1984).
Sulphuryl fluoride SO_2F_2	102.6	– 55.2	0.06 at 25°C	Nonflammable	Widely used as a structural fumigant (especially against termites) and for stored products and museum pests (Bond 1984, Banks 1994). However, the weakness of sulphuryl fluoride is that it is very ineffective against insect eggs and significantly greater fumigant concentrations are required to control eggs in comparison with the larval, pupal or adult stages (TEAP 2010).
Trichloroethylene $CHClCCl_2$	131.4	86.7	Insoluble	Nonflammable	Used primarily for degreasing, dry cleaning and grain fumigation in the past, most uses were eliminated in the US due to ground water contamination and significant health risks to humans (Agency for Toxic Substances and Disease Registry 2007).

[a]After Bond (1984) with additional compounds and information added for ethanedinitrile (Matheson Tri-Gas 2008), methyl iodide (Klementz & Brash 2010), sulphuryl fluoride (Banks 1994) and their respective material data safety sheets. Ozone is not known as an insecticide although it has been tested against several insect species (Hollingsworth & Armstrong 2004, Jamieson et al. 2010, Leesch et al. 2003).

3.1 Fumigant solubility in water

An important property of any fumigant is its solubility in water (Table 7). The retention of sorbed gases and the reaction of fumigants with components of treated goods are influenced by the moisture content of the goods and by the relative humidity of the air around them and, therefore, sorption usually is higher in materials with higher moisture content (Banks 1986, Bond 1984). Under a given set of conditions, sorption determines the dosage to be applied. This is because the amount of fumigant used must be sufficient both to satisfy the total sorption during treatment and also to leave enough free gas to kill the pest organisms (Bond 1984). Sorption is especially critical when selecting candidate fumigants for logs because recently harvested logs can have moisture contents in excess of 60% based on wet weight with the sapwood being effectively saturated (Cown 1999). Similarly, sorption would be critical for selecting candidate fumigants for sawn timber because “wet” (green) sawn timber that has not been kiln-dried can have a moisture content between 40% and 100% from rain (depending on season and weather conditions) and storage conditions of the sawn timber (T. Charleson, personal communication). For candidate fumigants, the effect of moisture content of fresh logs during fumigation is problematic simply because it is unknown. For example, Zhang (2003a, b) suggested that high moisture levels during in-hold log fumigations may directly impact phosphine fumigation. As a direct result there is a significant decrease in phosphine concentration that requires a “top up” with an additional 1.5 g/m^3 phosphine after five days to maintain the prescribed 200 ppm phosphine concentration (Brash et al. 2010, MPI 2013b). However, phosphine gas is considered only slightly soluble in water (Table 7). If the moisture content of logs directly impacts the sorption rate of phosphine then candidate fumigants with greater rates of solubility in water, such as hydrogen cyanide (Table 7) may present significantly greater sorption issues.

3.2 Effects of temperature on fumigant efficacy

The most important environmental factor influencing the action of fumigants on insects is temperature (Bond 1984). In the range of normal fumigating temperatures from 10°C to 35°C, the concentration of a fumigant required to kill a given stage of an insect species decreases with the rise in temperature (Bond 1984) primarily because the target insects respond to the increase in temperature with an increased rate of respiration (Sun, 1946). Also the physical sorption of the fumigant by the material containing the insects is reduced and proportionately more fumigant is available to attack the insects (Bond 1984). Therefore, within the range of 10°C to 35°C, conditions for successful fumigation improve with increasing temperature (Bond 1984). However, at temperatures below 10°C, the situation is more complicated because below this point increased sorption of the gas by the body of the insect may counterbalance the effects of decrease in respiration, and also the susceptibility of insects may be weakened by the effects of exposure to low temperatures (Bond 1984). With some fumigants, less gas is required to kill certain species as the temperature is raised or lowered on either side of some point at which the insects are most tolerant (Moore 1936, Peters & Ganter 1935, Bond & Buckland, 1976). However, with others, insect toxicity declines as the temperature decreases. For example, there is a moderate decrease in methyl bromide toxicity down to its boiling point (4.4ºC) and below this temperature effectiveness drops off sharply so that the amount of gas required to provide complete kill of the target insects increases dramatically (Bond 1984).

The following examples illustrate the impact of temperature on fumigant efficacy: Armstrong & Whitehand (2005) showed that the amount of methyl bromide required in dose-response tests against Mediterranean fruit fly and oriental fruit fly eggs and larvae decreased with increasing temperature. Additionally, the exposure time required to kill the fruit fly eggs and larvae decreased with increasing temperature (Armstrong & Whitehand 2005). Couey et al. (1985) found that the amount of ethylene dibromide required to provide an efficacious quarantine treatment against Tephritid fruit fly infestations in papaya could be reduced significantly if the papaya were fumigated after a hot-water immersion when the papaya temperatures remained elevated above ambient. Armstrong & Couey (1984) developed methyl bromide quarantine treatments against potential Tephritid fruit fly infestations in apricots, nectarines, peaches, and plums at 30°C that significantly reduced both the methyl bromide concentration and fumigation time required for quarantine security compared with methyl bromide quarantine treatments developed for the same fruits at ambient (21 ± 2.0°C) temperatures (Armstrong et al. 1988). Bell et al. (1998) reported that the tolerance to sulphuryl fluoride fumigation of the eggs of Mediterranean flour moth, *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae), was reduced by less than one-third and the tolerance of confused flour beetle, *Tribolium confusum* Jacquelin du Val (Coleoptera: Tenebrionidae) and the eggs of warehouse beetle, *Trogoderma variabile* (Ballion) (Coleoptera: Dermestidae) was reduced by about one-half when the fumigation temperature was increased from 15°C to 30°C.

3.3 Effects of atmospheres on fumigant efficacy

Whenever logs are held in a closed system (e.g., a fumigation chamber or a ship hold) any residual respiration by the logs will reduce the oxygen concentration and increase the carbon dioxide concentration (D. Brash, unpublished data, Frontline Biosecurity 2005). The impact of reduced oxygen concentration and/or increased carbon dioxide concentration on the efficacy of candidate fumigants must be identified and ameliorated if the change in atmospheric gases negatively affects efficacy.

3.4 Fumigants combined with carbon dioxide and synergism

Synergists have been used commercially for about 70 years and have contributed significantly to improve the efficacy of insecticides, particularly when problems of resistance have arisen (Bernard & Philogene 1993; Kashi & Bond 1975). Synergism is said to occur when the combination of two compounds (either one toxic compound and a non-toxic synergist or two toxic compounds) result in a combined toxicity that produces a significantly greater mortality to the target pest than can be obtained using each of the compounds or toxicants individually or the simple arithmetic sum of their toxicities when combined. For example, piperonyl butoxide is commonly added to pyrethrum and pyrethroids (synthetic pyrethrum compounds) to significantly enhance both the “knock-down” and mortality effects against target pests compared with using pyrethrum or a pyrethroid alone (Cakir et al. 2008, Casida & Quistad 1995). For fumigants, a gas that is commonly used to obtain synergistic effects is carbon dioxide (Bond 1984).

Carbon dioxide enhances both the penetration and distribution of some fumigants, e.g., phosphine, through the substrate being fumigated (Leesch 1995). Carbon dioxide by itself is toxic to insects given adequate concentration and exposure time, and it is a basic component of controlled atmosphere fumigation (Bond 1984). From a mechanical point of view, it can be beneficial to fumigations by increasing penetration into the commodity, thereby increasing efficacy (Leesch 1995). More important, carbon dioxide, in certain concentrations, may stimulate the respiratory movements and opening of spiracles in insects (Bond 1984). As early as 1930, Cotton (1930, 1932) reported that the addition of carbon dioxide increased the efficacy of fumigants in highly adsorptive materials and later determined that carbon dioxide influenced respiration to cause increased fumigant uptake.

In many cases, the addition of carbon dioxide can increase the efficiency of a fumigant more than expected from the fumigant or carbon dioxide individually or added together (referred to as a “synergistic reaction”). Although the use of carbon dioxide can result in synergism, too great a concentration of carbon dioxide can result in a significant decrease in efficacy (referred to as an "antagonistic" reaction). For example, once the carbon dioxide concentration is above 35%, the toxicity of phosphine is gradually decreased because the amount of carbon dioxide has a narcotic effect on the insect, the spiracles close, and the insect respiration rate decreases (Ren et al. 1994).

Because carbon dioxide is the most common gas added to fumigants to increase efficacy and/or reduce flammability (Ryan & Shore 2010), attention is given when applicable to the fumigants combined with carbon dioxide in the respective sections of this review.

3.5 Major versus minor fumigants

Section 3 considers the available fumigants that are used worldwide (e.g., methyl bromide, phosphine), and those fumigants that have received attention as potential methyl bromide alternatives (e.g., methyl iodide, sulphuryl fluoride) and a new fumigant that was recently registered in Australia for use on logs and sawn timber (ethanedinitrile). These are major fumigants that are manufactured in quantity and used for a wide range of quarantine phytosanitary treatments and/or control of insects in stored products or structures. Also considered in Section 3 are minor fumigants that have been used in the past but are no longer widely used or available for a variety of reasons (e.g., safety and health, environmental concerns, residue issues) but have been tested for potential use against pests of logs or timber. Also considered are major or minor fumigants used as individual treatments with no other fumigant or chemical additives or physical enhancements and research on these fumigants in combination with other fumigants, gases or synergists. With respect to their limited reference in the literature for potential use with logs or sawn timber, minor fumigants include carbonyl sulphide, chloropicrin, dichlorovinyl dimethyl phosphate (dichlorvos), dimethyl disulphide, ethyl formate, hydrogen cyanide, methyl isothiocyanate, nitric oxide, and ozone. Both major and minor fumigants are discussed in alphabetical order in section 4 – Major fumigants. Not all fumigants itemised in Table 7 are discussed in section 5 – Minor fumigants because they are either no longer available (e.g., ethylene dibromide) or they have never been associated with logs, sawn timber or forest pests (e.g., carbon monoxide, which is used commercially only as burrow and den fumigant to control rabbits and foxes, respectively, in Australia (Sharp 2012, Sharp & Saunders 2004)).

3.6 Cost comparisons and economics of fumigant use

With rare exceptions, there is a paucity of literature on comparing costs between fumigants or the economic for using a specific fumigant. Too often fumigants are referred to in the literature and, especially, manufacturers' websites and pest control advertisements as "economical", "inexpensive", or "less costly than [another fumigant]". Such claims are rarely, if ever, supported by economic studies or cost benefit analyses. Adam et al. (2010) completed an exhaustive economic study comparing methyl bromide with sulphuryl fluoride fumigations of food processing facilities, warehouses, and cocoa beans (see section 4.15. Sulphuryl fluoride). Although the costs for the two fumigants were comparable (about $15/kg), Adam et al. (2010) found the most important factor affecting relative profitability of the two fumigants was the amount of sulphuryl fluoride required for an effective fumigation because, under typical assumptions and parameter values, a sulphuryl fluoride fumigation required two-thirds more fumigant than methyl bromide.

Every fumigant that shows potential as a methyl bromide alternative must be subjected to cost benefit analysis. An "inexpensive" fumigant can become very costly to use if an insect life stage (e.g., eggs) is particularly tolerant to the fumigant, or there are factors that contribute to more fumigant being required to achieve an efficacious fumigation (e.g., significantly high sorption rates). Other costs are directly related to commercial adoption of a new fumigant on its application in commercial settings. Unfortunately, little or no baseline economic data are available and cost benefit analyses will require substantial efforts to support the commercial application of any methyl bromide alternative.

3.7 Fumigant off-gassing (desorption), safety and the environment

Although fumigation with toxic gases has been an important and widely used technology for the control of insects and other pest organisms, the off-gassing that occurs after fumigations have been completed and during the aeration process as the fumigant is desorbed from the fumigated substrate has come under increasing scrutiny because of health, safety and environmental concerns. Most obvious are the ban on the use of ethylene dibromide in 1984 because the fumigant was found to be a carcinogen and the reductions proscribed for the major uses of methyl bromide (Table 7). The off-gassing during aeration and the fate of any fumigant selected as a methyl bromide alternative must be well documented for both worker safety and environmental impact to ensure that there are no issues, or that any worker safety or environment issues can be ameliorated. Svedberg and Johanson (2013) found that personal exposure to various volatile organic compounds in the worker breathing and work zones of naturally ventilated 40-foot sea containers were 1-7% on arrival but could peak at up to 70% during the container opening and removal of container contents. The total volatile organic compounds off-gassing from the containers often produced average exposure concentrations that violated occupational exposure limits (Svedberg & Johanson 2013). Whether fumigations are carried out in a fumigation chamber, a sea container, under tarpaulin or in a cargo ship hold, the concentrations of fumigant off-gassing from the fumigated substrate will be of concern environmentally and for worker safety. Additionally, as found in the cases of methyl iodide in California (see section 4.10. Methyl iodide) or sulphuryl fluoride in Florida (see section 4.15. Sulphuryl fluoride), public scrutiny of new fumigants and their uses can become negative political issues very quickly. Therefore, any toxic compound selected as a methyl bromide alternative can expect to be vetted through both regulatory (e.g., NZ Environmental Protection Authority) and public channels of which public perception has been demonstrated to be an increasingly strong factor in the approval process (Corey 2013, USEPA 2012b, San Jose Mercury News 2012).

4 Major fumigants

4.1 Carbonyl sulphide

The existence of carbonyl sulphide, overlooked until 1867 because previous investigators had mistaken it for a mixture of carbon dioxide and hydrogen sulphide, is the most abundant sulphur compound naturally present in the atmosphere because it is emitted from oceans, volcanoes and deep sea vents and, as such, it is a significant compound in the global sulphur cycle (Ferm 1957, Wright 2002) and a precursor for carbon disulfide in vegetation and soil (Ren 1999). Therefore, humans are constantly exposed to concentrations of carbonyl sulphide. In addition, other low-level human exposures to carbonyl sulphide arise from its presence in foodstuffs, such as cheese and prepared cruciferous vegetables (Brassicales: Brassicaceae), and its natural presence in grains and seeds (Wright 2002).

Carbonyl sulphide is a colourless, flammable gas that has an unpleasant rotten-egg odour, it is relatively soluble in water (Table 7) and it slowly decomposes by hydrolysis into hydrogen sulphide in water (Svoronos & Bruno 2002). Carbonyl sulphide is compatible with many metals, such as 300-series stainless steels, aluminium, brass, copper, carbon steel, galvanised sheet metal, hard and soft timbers, iron, paper, polyethylene, and polyvinylchloride (PVC). However, according to Svoronos and Bruno (2002) the compatibility is considerably reduced in the presence of moisture, as is commonly observed with many acid gases. Additionally, carbonyl sulphide significantly contaminated with hydrogen sulphide will not be compatible with metal and other materials and, therefore, carbonyl sulphide used for commercial fumigations must be free of hydrogen sulphide (Wright 2002).

According to Viljoen and Ren (2001, 2002) carbonyl sulphide is a good fumigant for insect and nematode control, and a substantial amount of work has been done on stored product pests using this fumigant. Carbonyl sulphide penetrates and diffuses through both hard and soft timber more quickly than does methyl bromide (Ren et al. 1997). The sorption is much less than methyl bromide so that effective internal concentrations may be attained. Desorption is very rapid; one day of airing after fumigation results in a headspace concentration less than the Australian experimental TLV of 10 ppm (Viljoen and Ren 2001, 2002). Similar to phosphine, fumigation time tends to be more important in ensuring insect kill than carbonyl sulphide concentration (Obenland et al. 1998). This important characteristic of carbonyl sulphide must be considered when assessing the potential for this fumigant as a methyl bromide alternative.

In 8-hr fumigation bioassays using carbonyl sulphide or methyl bromide, Gan et al. (2005) found that 10 g/m^3 carbonyl sulphide was required to obtain complete control of hairy powderpost beetle, *Minthea rugicollis* (Walker) (Coleoptera: Bostrichidae) compared with only 5 g/m^3 methyl bromide. However, the work of Gan et al. (2005) and Ren et al. (1997) was the only research using timber as a substrate that was found in our thorough literature search. Hence, the early claims that carbonyl sulphide was a potential fumigant for logs or timber (Ryan et al. 2006a, b; Viljoen & Ren 2001, 2002) were relatively unsupported by research data.

Most studies in the development of carbonyl sulphide as a fumigant were with stored-product pests, especially grains, (Bartholomaeus & Haritos 2005; Desmarchelier 1998; Desmarchelier et al. 1998, 1999; Ren et al. 2008, Tan et al. 1998, Weller & Morton 2001, Zettler et al. 1997, 1998) for which it was considered to be a potential replacement for phosphine where stored-product insects had become phosphine-resistant (Collins 2009). The potential of carbonyl sulphide fumigation also was studied for use on baled hay (Weller 2002) and for fruits and flowers (Obenland et al. 1998). Carbonyl sulphide was found generally too phytotoxic for use on fruits against insect pests (Aung et al. 2001, Obenland et al. 1998).

The Commonwealth Scientific and Industrial Research Organisation (CSIRO) obtained world (except US) and US patents on carbonyl sulphide as a fumigant in 1993 and 2001, respectively (Banks et al. 2001, CSIRO et al. 1993). The patents (Banks et al. 2001, CSIRO et al. 1993) claimed that carbonyl sulphide was an alternative "non-toxic" fumigant to methyl bromide and phosphine for durable commodities (Douglas 1995). Considering the toxicity of carbonyl sulphide to humans and other animals (USEPA 1994) the term, "non-toxic" used by Douglas (1995) is misleading. According to Wright (2002), CSIRO was "in discussion with a number of selected companies and consortia that have the capacity to manufacture, distribute and market carbonyl sulphide worldwide" at that time (viz. 2002). No indication was found in literature and internet searches that carbonyl sulphide was consequently registered anywhere in the world as a fumigant. Around 2005, BOC Gases Limited (BOC) obtained the licence from CSIRO to produce and sell both Sterigas™ (ethanedinitrile) and Cosmic™ (carbonyl sulphide) fumigants (Brash et al. 2013, Ryan et al. 2006a). Although BOC Gases Limited applied for registration for both carbonyl sulphide and Cosmic™ as fumigants in 2007 (APVMA 2007a, b, c), no approvals have been granted, and the last progress on the registration of carbonyl sulphide and Cosmic™ were changes made to the application in 2008 (APVMA 2008a). Currently, BOC does not intend to pursue registrations for carbonyl sulphide and Cosmic™ for logs or timber because of the successful registration of ethanedinitrile (APVMA 2013b). More specifically, the pursuit of carbonyl sulphide and Cosmic™ registrations for logs and timber at this time would be duplicative and not cost effective (C. Dolman, BOC Australia, personal communication).

Other claims for the potential use of carbonyl sulphide for timber led to the consideration of this fumigant as a methyl bromide alternative for solid wood packing materials as early as 2002 (IPPC 2006). However, as noted by the Methyl Bromide Technical Options Committee in its 2010 Assessment Report: "Sorption studies with higher moisture content commodities, such as wheat at 15-18% moisture content, show a rapid loss of carbonyl sulphide, by hydrolysis to hydrogen sulphide and carbon dioxide at rates that would make carbonyl sulphide fumigation impracticable (Wright 2000) and can result in a strong sulphur smell. This characteristic may make it unsuitable for fumigation of products *such as export logs that have high moisture content* within the fumigation enclosure and may result in ephemeral smells after treatment" (MBTOC 2010). (*Author's italics*).

Hence, the Methyl Bromide Technical Options Committee discounted the use of carbonyl sulphide for use as a phytosanitary fumigant for logs. Moreover, no mention is made of carbonyl sulphide in the latest draft of the regulation for wood packaging materials in international trade (IPPC 2013a), which indicates that carbonyl sulphide is not under consideration as a methyl bromide alternative by the Methyl Bromide Technical Options Committee or by the authors of this literature review.

4.2 Chloropicrin

Chloropicrin is a colourless liquid that is highly soluble in water (Table 7) that is used primary as a fumigant because of its toxic properties, or as a warning agent in fumigants (e.g., methyl bromide, sulphuryl fluoride) because it has a low odour threshold (1.1 ppm) and causes sensory irritation at very low concentrations (Beauvais 2010, USDHHS 1978). Because chloropicrin is highly soluble in water and has a low adsorption rate in soil, chloropicrin may have the potential to be detected in groundwater like other compounds with similar solubility characteristics (USEPA 2008c).

Chloropicrin is a powerful lacrimator (tear gas) with effects beginning at a concentration as low as 1.0 ppm observed on all body surfaces with symptoms that can include watering of the eyes, shortness of breath (pulmonary oedema), dizziness, nausea, vomiting, and dermatitis (skin wounds exposed to chloropicrin become septic), and a concentration of 2.4 g/m^3 can cause death from acute pulmonary oedema in one minute (Bond 1984, Chemtura 2005).

The basis for developing buffer zones around sites fumigated with chloropicrin mandated by the US Environmental Protection Agency, the California Department of Pesticide Registration’s Risk Management Directive determined that the primary effect observed with acute exposure to chloropicrin is sensory irritation and that the appropriate regulatory target level to restrict acute exposure to chloropicrin is 73 ppb or 0.073 ppm averaged over an eight-hour period to mitigate exposure to residents and bystanders near the fields being fumigated (Barry 2013).

In addition to the potential harmful effects to humans, chloropicrin is corrosive to metals, is extremely phytotoxic to plant materials, and residues have a tendency to persist as unchanged chloropicrin that require the treated materials to be completely aerated before handling (Bond 1984). For example, Getzendaner et al. (1965) found that dry beans and field peas fumigated with 32 g/m^3 to 64 g/m^3 chloropicrin for 24 h at 25-26°C required four days of aeration to decrease chloropicrin residues below 2.0 ppm.

Chloropicrin was first patented as an insecticide in 1908 (Dungan & Yates 2003). Chloropicrin is a broad-spectrum fumigant that can be used as an antimicrobial, fungicide, herbicide, insecticide, and nematicide, with the highest proportion of usage (e.g., in the U.S.) as a pre-plant soil fumigant at agricultural sites, tree replant sites, and greenhouses and as a warning agent with other soil fumigants. Products containing chloropicrin or chloropicrin in combination with other compounds are ubiquitous. For example, as of 2010 there were 54 registered products containing chloropicrin in the state of California, including seven products intended solely for manufacturing or reformulation use, eight products where chloropicrin was used as a warning agent for odourless compounds, and the remaining uses of chloropicrin were for fumigation (several were mixtures with either methyl bromide or 1,3-dichloropropene) (Beauvais 2010). Additionally, in California at that time, a new product combining chloropicrin with methyl iodide was under consideration for registration but was never approved because the request for registration of methyl iodide as a fumigant was withdrawn (Beauvais 2010, Richardson 2010, USEPA 2012b). Chloropicrin has been such a significant replacement for methyl bromide for pre-plant soil fumigation in the southern U.S. that the years 2000 to 2010 have been called “chloropicrin decade” (Starkey 2012).

In 2009 the US, the US Environmental Protection Agency reregistered chloropicrin as a restricted-use pesticide that was safe for use by licensed farmers and fumigation specialists for soil and space fumigation (USEPA 2009b). In New Zealand, chloropicrin is registered for use both alone and in combination with 1,3-dichlororopene as a soil and space fumigant (NZEPA 2014). However, no registration of chloropicrin for logs, timber or wood products was found in the literature, and studies testing chloropicrin against wood pests are very limited and specific to the control of fungi in sawn timber (Highley 1991; Highley & Eslyn 1989a, b; Hutchinson et al. 2000; Schmidt & Christopherson 1997; Schmidt et al. 1997) with no publications more recent than 2000. Basically, the application of chloropicrin is difficult as it must be injected into the soil and sealed by plastic tarpaulin or the soil must be rolled and watered after application to prevent rapid loss to the air; the difficulties in application represent the primary reason that chloropicrin is not commonly used other than for soil fumigations using special applicators (PMANZ 2011).

Chloropicrin is registered in New Zealand for soil fumigation under the trade name Pic-Fume Chloropicrin, and in combination with 1,3-dichloropropene under the trade name Telone Soil Fumigant. However, the authors do not recommend chloropicrin for consideration as a log fumigant because of the difficulty of application, corrosiveness, and need for buffer zones around the fumigation areas that would not be viable with current fumigation practices at the ports.

4.2.1 Chloropicrin combined with other fumigants or compounds

Chloropicrin combined with methyl bromide, methyl iodide, propagyl bromide, 1,3-dichloropropene, or metam-sodium - Hutchinson et al. (2000) tested known herbicidal soil fumigants (methyl bromide, methyl iodide, propargyl bromide, 1,3-dichloropropene, and metam-sodium) in combination with chloropicrin to control the pathogenic fungi *Botrytis cinerea* Whetzel (Helotiales: Sclerotiniaceae); *Colletotrichum gloeosporioides* Schrenk and Spaulding (Glomerellales: Glomerellaceae); *Fusarium oxysporum* Snyder and Hansen (Hypocreales: Nectriaceae); *Gliocladium virens* Miller, Giddens and Foster (Hypocreales: Hypocreaceae); *Phytophthora citricola* Sawada (Peronosporales: Pythiaceae); *Phytophthora citrophthora* Leonian (Pythiales: Pythiaceae); *Pythium ultimum* Trow (Pythiales: Pythiaceae); *Rhizoctonia solani* Kühn (Cantharellales: Ceratobasidiaceae); and *Verticillium dahliae* Kleban (Hypocreales: Incertae sedis[3]) in laboratory studies to identify the most tolerant fungi. Hutchinson et al. (2003) also studied the ability of chloropicrin to control yellow nutsedge, *Cyperus esculentus* L. (Poales: Cyperaceae) tubers but found no significant difference between any of the fumigant combinations. Glaser and Prugger (2012) provided a theoretical study on the stabilisation of iodomethane in MIDAS pesticide by iodine bonding. Although their results (Glaser & Prugger 2012) elucidated the intermolecular interactions between the two fumigants, it did not further an understanding of the fumigant combination efficacy.

4.3 Dichlorvos (2,2-dichlorovinyl dimethyl phosphate, DDVP, Vapona)

Dichlorvos is a non-flammable colourless liquid that is soluble in aromatic hydrocarbons and readily soluble in water (Hosada 2013, Table 7). Bond (1984) identified four methods by which dichlorvos could be evolved and delivered as a fumigant: (a) by direct evaporation of liquid concentrate by means of heat, (b) by volatilisation from pressurised cylinders with inert Freon®-type gases as carriers, (c) by slow volatilisation from resin strips (adult flies and mosquitoes only), and (d) by evaporation from resin cylinders (glasshouse fumigations). Therefore, despite its high boiling point and low vapour pressure, dichlorvos can be discharged as a true gas to control insects in the open spaces of structures (Bond 1984). However, because of its low vapour pressure, dichlorvos is unable to penetrate into materials and, hence, it is of no value as a commodity fumigant (Bond 1984). Banks (2002) also cites the poor penetration properties of dichlorvos and points out that there are additional issues with residues. Among its positive attributes, Harein et al. (1970) found in studies with the larvae of black carpet beetle, *Attagenus unicolor* (F.) (Coleoptera: Dermestidae), that one characteristic of dichlorvos was that it could result in delayed mortality of up to two weeks after exposure.

Dichlorvos is an organophosphate insecticide that is marketed internationally in a variety of formulations, including granules for bait, as a liquid, in ready-to-use sprays and foggers, and in slow-release formulations of resin strips and pet collars, and it kills target insect and other arthropods by cholinesterase inhibition (Edwards 2006). Dichlorvos was first registered in the US by Shell Chemical Company in 1960 and the chemical was first marketed as the Shell “No-Pest Strip” in 1963 (Hosada 2013). Dichlorvos was used thereafter in agriculture, structural pest control and food processing with primary use in the US as a space or ground spray against such target pests as flies, gnats, mosquitoes, chiggers, ticks, cockroaches, stored-product insects, armyworms, chinch bugs, clover mites, crickets, cutworms, grasshoppers, and sod webworms (Edwards 2006, Hosada 2013). The commercial uses for dichlorvos also include

[3] Uncertain placement.

niche areas such as the fumigation of food storage facilities for peanuts and pistachios, and mushroom farms (Miller 2014).

According to Park et al. (2009) dichlorvos has superior efficacy across a wide range of pests, proven cost effectiveness, excellent penetration (semi-fumigant action) and rapid knockdown, and its short residual effect means it can be used close to harvest, while its broad-spectrum activity provides a useful option when growers are faced with new pests or unexpected or late-season pest build-ups. Moreover, these properties also make it ideal for pre-harvest and postharvest disinfestation where needed to meet quarantine regulations, and the unique properties associated with dichlorvos means most of its uses are for specific purposes for which there are few if any alternatives (Park et al. 2009). The “excellent penetration (semi-fumigant action)” described by Park et al. (2009) are contrary to the earlier statements by Bond (1984) and Banks (2002) that dichlorvos has poor penetration properties and cannot be considered a good fumigant. However, there may be other considerations involved when determining whether the volatility of a compound is the significant characteristic that must be met for that compound to be used as a fumigant. Scharf et al. (2006) developed volatility bioassays for use in evaluating 30 candidate compounds along with known volatile fumigants and found that regression analyses revealed that volatility is not entirely predictive of acute toxicity and that other structural features should be considered when designing and synthesising volatile insecticidal compounds for future study. Moreover, Scharf et al. (2006) used dichlorvos as an example of a volatile fumigant against which other compounds were tested. Or perhaps, the method of delivery (Banks 1984, Hosada 2013), the compactness of the commodity or substrate (i.e., relative size of interstices) being fumigated, or some other factors either increased or decreased the ability of dichlorvos to penetrate and be used as a fumigant. Air movement is also an important factor when relying on the fuming action of dichlorvos. Desmarchelier et al. (1977) demonstrated the potent vapour toxicity of dichlorvos to rice weevil, *Sitophilus oryzae* Schoenherr (Coleoptera: Curculionidae), and lesser grain borer, *Rhyzopertha dominica* (F.) (Coleoptera: Bostrichidae), on freshly treated wheat at 20°C where the lethal effect of dichlorvos was predominantly due to a mobile form of dichlorvos vapour that was toxic to the target insects when moved through grain for up to 4 m using air flows comparable to those used in aeration of bulk stored wheat.

Dichlorvos has had a long and contentious regulatory history after the US Environmental Protection Agency first raised concerns about it in 1982. Dichlorvos has been undergoing a special safety review since 1988 (Miller 2014). Exposure to dichlorvos can cause flu-like symptoms and the insecticide is listed by California as a known carcinogen and has been linked to developmental damage in children (Miller 2014).

The US Environmental Protection Agency moved to cancel the registration for dichlorvos in 1995 (Hosada 2013), but the US Food Quality Protection Act of 1996 resulted in a comprehensive overhaul of the US pesticide and food safety laws that required new studies that would implement stricter safety standards, especially for infants and children, and a complete reassessment of all existing pesticide tolerances (USEPA 2014b). Following extensive review by the US National Academy of Sciences in 2004 and human studies by the US Environmental Protection Agency in 2006, dichlorvos was allowed re-registration with the loss of some uses, greatly increased safety requirements and reduced permissible residue and exposure tolerances (Edwards 2006).

Since the 2006 decision by the US Environmental Protection Agency to reregister dichlorvos, the Agency has been under continuous legal challenges to restrict further the uses of dichlorvos, especially over the issue of safety tolerances (InsideEPA.com 2013). Moreover, dichlorvos and dichlorvos-containing substances have been reviewed in a number of countries, including New Zealand, the US, Australia, Canada and Europe and all of these reviews have resulted in restrictions, prohibitions or voluntary removal from the market (NZEPA 2013).

In Australia, dichlorvos has been used since the early 1960s, similar to the use pattern in the US, and is currently a pesticide used to a large extent in non-agricultural situations and/or in enclosed areas or slow-release formulations with very minor and restricted use on crops in the field specific to leafroller pests on avocados (APVMA 2008b). Much greater use occurs to disinfest harvested and stored products (grain, potatoes, tobacco) and to treat produce storage and handling areas (silos, warehouses, etc.), wineries, grain mills, animal housing, manure heaps and abattoirs or meat works (non-food production areas). Major uses also include space spray, surface or spot treatment and slow-release methods for the control of a wide range of pests (flies, mosquitoes, moths, spiders) in domestic, recreational and industrial areas. These may range from confined spaces such as clothes cupboards and rubbish bins, to specific areas such as the vicinity of European wasp nests, to treatment of open areas such as rubbish dumps (APVMA 2008b). It is noteworthy that the use of dichlorvos in Australia is strictly regulated with only limited field use for avocados (APVMA 2008b). Because dichlorvos is extremely toxic to birds, fish, aquatic crustaceans, bees, and other non-target organisms, harmful effects from direct overspray or from spray drift may occur (APVMA 2008b). Had the use of dichlorvos not been restricted only to New South Wales, it would have required impracticably long spray buffer areas to protect non-target organisms. In any event, dichlorvos is now rarely used for avocados (APVMA 2008b). The registered uses for dichlorvos in Australia are shown in Table 8 for comparison with the registered uses for dichlorvos in New Zealand (Tables 9 and 10).

Table 8. Approved use patterns of dichlorvos in Australia for products containing dichlorvos as the sole active ingredient (APVMA 2008b).

Situations (crop/animal/use)	Formulation and maximum rate of active ingredient per application and frequency of application	Application method and comments
	Glasshouse and field crops (≈1.7% of use)	
Avocados	EC[a]: 500 g/acre/ha (tank mixed with 1 kg chlorpyrifos/ha) repeated as necessary	spray - apply at first sign of pest activity before larvae move to fruit
Greenhouses, glasshouses	EC: 6.7-7.5 g acre/100 m^3; PG: 200 g acre/300 m^3; whenever necessary or unspecified	EC: spray, fog, wooden block method, PG: spray into air space
Mushroom houses	EC: 6.7-7.5 g/acre/100 m^3; PG: 200 g/300 m^3; whenever necessary or unspecified	EC: spray, fog, wooden block Method; PG: spray into air space
	Direct animal treatment and animal housing (≈2.4% of use)	
Animal house and pens	EC: 10 g/10 L water at 15 L/100 m^2 (15 g/100 m^2); frequency unspecified	spray on walls and other surfaces or into air as a mist
Stables and piggeries	EC: 35 g/1000m^3	space spray or mist
Dairies, cattle sheds	EC: 25 g/ 10L at 600 mL/50 m^2 (6 g/100 m^2)	coarse spray on floor and around doorways and windows
Poultry manure	EC: 30 g/10 L water applied to 12 m of manure under cages, repeated every 3 weeks	spray for control of fly maggots
	Crop storage areas and stored-product treatment (≈55% of use)	
Stored grains	EC: 25-50 g/100 m^2 grain surfaces; frequency unspecified	spray grain surface
Infested grain held by flour millers	EC: 60-120 g/10 L water (1 L spray/t - 6-12 ppm on grain); frequency unspecified	spray during movement on elevator - higher rate for lesser grain borer
Bagged and stored potatoes	EC: 25 g/5 L water to treat 16 bags; frequency unspecified	spray bag surfaces
Warehouse	EC: 100 g/1000 m^3 repeated as necessary	spray or fogging
Empty silos	EC: 50 g/10 L water; frequency unspecified	spray inside wall and chutes to run-off
Stored-product facilities (warehouses, silos, farm machinery, storage bins, etc.)	PG: 200 g/300 m^3 (stored-product moths and flour beetles); 400 g/300 m^3 (tobacco beetle and tobacco moth); frequency unspecified	spray into air space
	Domestic uses, recreational areas, industrial areas etc (≈41% of use)	
Domestic, recreational and industrial areas	EC: 6 g/L water; PG: 200 g/300m^3; frequency unspecified	EC: spray to treat bee and wasp nests PG: spray into air space
Flies, etc., in domestic areas, moths and silverfish in linen cupboards, etc.	SR: 20 g SR plastic strip (186 g/kg), to treat 3 m^3; continuous release with 4 months claimed effective life	hang or place in cupboard or other confined space to be protected

Situations (crop/animal/use)	Formulation and maximum rate of active ingredient per application and frequency of application	Application method and comments
Rubbish bins	SO (with naphthalene): One 55 g unit per wheelie bin; continuous release with 3 months claimed effective life	hang unit inside wheelie bin
Household	EC: 6 g/L water; frequency unspecified	spray or sprinkle where pests occur
Factories stores, mills, food warehouses	EC: 17.5-75 g/1000 m^3; repeated as necessary for flies, etc.; twice per week for moths etc	space or surface spray or fogging 2.5 g + 50 g sugar/L at 0.6-0.7 L/50 m^2 spray in strips or patches as a liquid bait
Wineries (vinegar fly)	EC: 70 g/1000 m^3 or 10-10.5 g/10 L water at 10 L/50 m^2 - 20-21 g/100 m^2; frequency unspecified	coarse wet spray on floor and around doorways and windows, or as a space spray or fog
Meatworks (nonproduct areas)/abattoirs	EC: 10 g/10 L water at 15 L/100 m^2; frequency unspecified	coarse spray to walls and other surfaces or into air as a mist
Garbage dumps, picnic and recreational areas	EC: 150 g/ha; frequency unspecified	space spray, mist or fog
European wasps	EC: 6-10 g/L; PG: 200 g/300 m^3; frequency unspecified	EC: spray in and around entrance holes at 1 L per nest (less for very small nests) PG: direct nozzle into cavity or nest

[a]Formulation – EC emulsifiable concentrate, PG pressurized gas, SO solid fogging, SR sustained release.

In New Zealand, dichlorvos is considered an inexpensive but effective broad-spectrum organophosphate insecticide that is registered for use on a wide range of horticultural crops including cut flowers (particularly orchid production), glasshouse vegetables, field vegetables, persimmon, tamarillo, passionfruit, berryfruit, the postharvest fumigation of asparagus, and it is used in fruit fly surveillance traps (Park et al. 2009). However, there is also occasional use on other crops, such as vegetable seed production and ornamentals, and the potential for use in grain and food storage silos and warehouses (Park et al. 2009).

Dichlorvos was included in the New Zealand Environmental Protection Authority review of organophosphate insecticides with the conclusion that, given the very high benefits to the New Zealand primary production industry and for biosecurity purposes, the adverse effects of organophosphate insecticides (including dichlorvos) can be managed to a level where the positive effects outweigh the risks with the implementation of revised management regimes requiring additional controls and, therefore, retain approvals with additional controls (decision on the Application for reassessment of organophosphate insecticides – APP201045 (NZEPA 2013)). However, in an opening review statement, the New Zealand Environmental Protection Authority stated that “it is clear that some uses overseas of…dichlorvos…had been retained for socio-economic reasons rather than because the risks to human health or the environment could be adequately controlled” (NZEPA 2013).

Table 9 shows the uses of dichlorvos in the New Zealand horticultural industry as of 2004, and also shows the products containing dichlorvos that were registered with the New Zealand Food Safety Authority as of 2009 (Park et al. 2009). A review of the New Zealand Food Safety

Authority database (Table 11) found that only Nuvos™, Divap® and DDVP (dichlorvos) Insecticide strips were still registered for use in early 2014 (NZFSA 2014).

In New Zealand, dichlorvos is primarily used as a contact insecticide for field crops to control aphids, caterpillar, mites, moths, and whiteflies (MPI 2014a, Park et al. 2009). In addition to the use of dichlorvos for the field crops shown in Table 9 and 10, dichlorvos is also used in the New Zealand mushroom-growing and glasshouse industries where it is applied as a fog to control Phorid and Sciarid flies, mites, aphids, caterpillars, thrips, and whiteflies (Park et al. 2009). The use of DDVP insecticide strips is primarily for the Ministry for Primary Industries' use in fruit fly surveillance programme traps (Park et al. 2009).

There are both similarities and marked differences between the uses of dichlorvos in Australia compared with New Zealand (Tables 8, 9 and 10), basically due to differences in agricultural production. However broad the range of use under approved labels, there are no registered uses for dichlorvos in New Zealand or Australia (or in the US) for logs, timber or wood products.

Table 9. 2004 sector-based dichlorvos use estimates in New Zealand (Manktelow et al. 2005[a]).

Sector	Total area (ha)	High use total kg active ingredient/year	Low use total kg active ingredient/year
Asparagus spp.	2015	20	0.02
Blueberries, *Vaccinium spp*.	430	170	0.17
Nerines[b]/Paeonies[c]/*Sandersonial*[d]	50	10	0.01
Passionfruit, *Passiflora spp*.	70	70	0.42
Persimmons, *Diospyros spp*.	282	320	1.29
Tamarillos, *Solanum betaceum* Cavanilles	270	540	2.16

[a]Tables 1, page 3, Park et al. (2009).
[b](Asparagales: Amaryliidacaea).
[c](Saxifragales: Paeoniaceae), peony.
[d](Liliales: Colchicaceae), lily of the valley, Christmas bells, Chinese lantern lily, Chinese lantern bulb.

Table 10. Current (2014) dichlorvos registration for horticultural crops in New Zealand (MPI 2014a).

Crop	Pest	Rates	Comments
Clover seed crops	Clover case-bearer moths	150-220 ml/ha	Apply in 110-170 liters water when moths are prevalent. Repeat 7-10 days later if moth flights continue.
Brassicas, cereals	Aphids, caterpillars	350-750 ml/ha	Apply in 220-450 liters water/ha.
Tamarillos	Aphids, caterpillars, whitefly	100 ml/100 liters	Commence applications approximately 3 weeks from harvest and repeat at 7-10 day intervals.
Passionfruit	Aphids, caterpillars, whitefly	100 ml/100 liters	Commence applications approximately 3 weeks from harvest and repeat at 7-10 day intervals.
Persimmons	Caterpillars and latania scale	100 ml/100 liters	Commence applications approximately 3 weeks from harvest and repeat at 7-10 day intervals.
Vegetables	Aphids, caterpillars, mites	500-800 ml/ha or 60 ml/100 liters	Boom spray: 220-450 liters water/ha. Mist blower: 60 liters water/ha. Handgun: Apply to run-off.
Berry fruit	Aphids, caterpillars, mites	500-800 ml/ha or 60 ml/100 liters	Boom spray: 220-450 liters water/ha. Mist blower: 60 liters water/ha. Handgun: Apply to run-off.
Ornamentals	Aphids, caterpillars, mites	500-800 ml/ha or 60 ml/100 liters	Boom spray: 220-450 liters water/ha. Mist blower: 60 liters water/ha. Handgun: Apply to run-off.

Phytotoxicity: Do not apply to the chrysanthemum varieties 'Dawn Star' and 'Hurricane', nor any 'taffetas' or 'shastas'.

Table 11. Registered products in New Zealand containing dichlorvos, registration number and date, registrant, the active ingredient and content, and formulation type (NZFSA 2014)[a].

Product name	Registration number (and date)	Product Registrant	Active ingredient (and content)	Formulation type
Nuvos™	P001132 (14/03/68)	Orion Crop Protection Ltd., New Zealand	Dichlorvos (1000 g/litre)	Emulsifiable concentrate
Divap®	P006080 (07/06/02)	United Phosphorous Ltd., distributed by Adria New Zealand Ltd	Dichlorvos (1140 g/litre)	Emulsifiable concentrate
ArmourCrop[b] Insecticide	P005877 (31/01/02)	BOC Gases Ltd., New Zealand	Dichlorvos (50 g/kg)	aerosol
DDVP Insecticide Strip	P007362 (12/10/05)	Biosecurity New Zealand, manufactured by Agrisense-BCS Ltd., United Kingdom	Dichlorvos (188 g/kg)	Vapour releasing strip

[a]Tables 2 and 3, page 4, Park et al. (2009).

[b]Also called Insectigas-D® (5% dichlorvos in carbon dioxide balance).

4.3.1 Dichlorvos combined with other fumigants or compounds

Dichlorvos combined with carbon dioxide Hosada (2013) reported new application methods for dichlorvos for space treatments using cylinderised dichlorvos with a carbon dioxide propellant, called Card-O-Vap™8. Card-O-Vap is similar to ArmourCrop (Table 9) except that it uses an on-site mixing system. The Card-O-Vap™8 system is purported to be a high vapour pressure application that evolves dichlorvos quickly and provides for shorter application times at lower doses (Hosada 2013). Field trials of the Card-O-Vap™8 space fumigation technology began in 2013 and will continue through 2014 following the label amendment in 2013 for the technology to proceed (Hosada 2013). The Card-O-Vap™8 system was shown to treat a 69,120 m^3 warehouse at a rate of 0.25 g/m^3 within 3.0 h with monitored concentrations of 25-50 ppm dichlorvos (Hosada 2013). Because the Card-O-Vap system allows on-site mixing, it may be less expensive than other technologies for use on logs if both the residue issues and subsequent potential run-off at the point of use can be ameliorated in the approval process.

Although the Card-O-Vap™8 technology may or may not be appropriate for logs, it may be applicable to timber in enclosed areas. However, although dichlorvos and products containing dichlorvos are approved for use in New Zealand, they are strictly controlled (NZEPA 2013). Additionally, because dichlorvos is highly toxic to birds, fish, aquatic crustaceans, bees, and other non-target organisms (APVMA 2008b), the environmental impact of use rates that would be required for logs or timber, which would be far greater in volume than presently used in New Zealand (Table 9), could be a significant issue.

Dichlorvos combined with ethyl formate A fumigant mixture combining dichlorvos with ethyl formate called “Ethos” was developed by Specialty Gases, Sydney, Australia (R. Ryan, personal communication). The combination of dichlorvos with ethyl formate was found to provide improved efficacy against target insect life stages because of a “complementary effect.” According to Specialty Gases, dichlorvos at very low concentrations (about 4.0 ppm) is a potent fumigant while ethyl formate has a very low toxicity that requires a high concentration (about 20,000 ppm) to provide efficacy. The highly volatile ethyl formate is a solvent for trace levels of dichlorvos, which assists in vaporising the dichlorvos liquid into the atmosphere. The mixture is further improved by combining the ethyl formate and dichlorvos mixture with carbon dioxide which provides the dual benefits of eliminating the flammability hazard of ethyl formate and reducing the overall concentration of the ethyl formate and dichlorvos mixture required to obtain efficacy (R. Ryan, personal communication). Ethos was not registered for use at the time this review was written.

4.4 Dimethyl disulphide

Dimethyl disulphide is a pale-yellow liquid that is highly volatile and has a pungent odour that resembles pungent garlic, propane, decaying fish, or decomposing materials (USEPA 2010). Dimethyl disulphide is a natural chemical given off by some plants, such as dead-horse arum, *Helicodiceros muscivorus* (Araceae: Aroideae) syn. *Dracunculus crinitus*), to mimic the smell of a dead animal to attract flies that pollinate the flowers (Stensmyr et al. 2002). Dimethyl disulphide, which is one of the volatile compounds identified from human faecal odour, is listed by the US Food and Drug Administration as a flavouring substance that is permitted for direct addition to food as an additive in onion, garlic, cheese, meats, soups, savoury flavours, and fruit flavours for human consumption because it occurs naturally in certain foods (e.g., cabbage, Brussels sprouts, garlic, onions) (USOSHA 2007).

Valmas and Ebert (2006) referred to dimethyl disulphide as a “botanical” fumigant because of its dead-horse arum origin and tested it as a potential soil fumigant against the nematode, *C.*

elegans (Valmas & Ebert 2006) (see Phosphine combined with diethyl maleate or mitochondrial uncouplers). In a comparison with phosphine that had an LC_{50} of 732 ppm after 24 h at 20°C against *C. elegans*, Valmas and Ebert (2006) found that dimethyl disulphide had an LC_{50} of 1.24 ppm after 24 h at 20°C, or 600 times more potent than phosphine.

Dimethyl disulphide is a soil fumigant registered in the US and used as a new pesticide since 2010 that is formulated as the technical product Paladin® Technical and the two end-use products Paladin® and Paladin® EC [emulsifiable concentrate] (USEPA 2010). Paladin® contains 98.8% dimethyl disulphide and Paladin® EC contains 93.8% dimethyl disulphide; Paladin® is used in liquid form applied by shank injection (a tube behind a blade that slices through the soil) to raised beds and as a broadcast application. Paladin® EC is applied by drip irrigation to raised beds. Dimethyl disulphide applications are made pre-plant to fields that will be used to grow berry (blueberry and strawberry), cucurbit vegetable (cucumber, squash, and melon), fruiting vegetable (tomato, pepper, and eggplant), field-grown ornamental, and forest tree nursery crops (USEPA 2010).

USOSHA (2007) points out that dimethyl disulphide vapour mixtures in air above 24°C may be explosive, which is an important factor if dimethyl disulphide was considered as a potential methyl bromide alternative for fumigation of logs under tarpaulin or as a phosphine alternative for log fumigation in ship holds. Moreover, above 24°C, dimethyl disulphide should only be used in a closed system with adequate ventilation and explosion-proof electrical equipment (NIOSH 2005).

A search of the Ministry for Primary Industries online database (NZFSA 2014) of registered veterinary medicines, agricultural chemicals and vertebrate toxic agents found no registrations for either dimethyl disulphide or the US soil fumigant, Paladin®. Because dimethyl disulphide is a soil fumigant and is explosive USOSHA (2007), the authors recommend no further consideration be given this compound as a potential fumigant for export logs.

4.5 Ethanedinitrile

Ethanedinitrile is the most recent compound to be registered (in Australia) as a potential fumigant for logs and sawn timber. Ethanedinitrile was first prepared by Gay-Lussac in 1815 but was not manufactured on a large scale until the late 19th century because its preparation was relatively expensive (Bircumshaw et al. 1954, Fierce & Sandner 1960). Large-scale preparation of ethanedinitrile began about mid 1916 when it was used in the development of cyanogen chloride, one of the numerous poison gases used against combatants during World War I (Kikilo & Ternay 2005), and in the production of nitrocellulose, a combustible explosive component in military armaments (Fierce & Sandner 1960). Fierce and Sandner (1960) patented an inexpensive method for preparing ethanedinitrile, which by then had become useful in the nitrate fertiliser industry (CSIRO et al. 1996).

In 1996, CSIRO (along with Inventors/Applicants O'Brien I., Desmarchelier, F. J. M., and Ren, Y.) patented ethanedinitrile internationally as "a fumigant …[that] provides a viable alternative to conventional fumigants, such as methyl bromide, phosphine, and carbonyl sulphide." Although there were a number of preceding patents on ethanedinitrile uses and production, the CSIRO et al. (1996) patent was the first to identify ethanedinitrile specifically as a fumigant.

CSIRO publicised in 2005 that the ethanedinitrile patent would be licensed to BOC as an ozone-safe alternative to MB and that the intellectual property licensing would enable BOC to obtain registration (i.e., a "label") for the various uses of ethanedinitrile as a fumigant (CSIRO 2005). The agreement between CSIRO and BOC was signed in September, 2004 (Ryan et al. 2006a).

The following year, Waterford (2005) gave an update on ethanedinitrile registration, and a year later Ryan et al. (2006a, b) announced that BOC would market ethanedinitrile under the name of Sterigas™. Both Waterford (2005) and Ryan et al. (2006a, b) stated that the registration application would be for the devitalisation of grains and weed seeds (including sterilisation of seed pathogens), disinfestation of timber and logs for export, and as a soil fumigant for strawberry runners and fruit growing.

The registration process for Sterigas™ showed little or no progress between 2006 and 2012 based on review of the Application Summaries and Gazettes through 2012 that include Sterigas™ 1000 Fumigant, Application No. 37416, Australian Pesticides and Veterinary Medicines Authority (APVMA 2013a). However, progress towards labelling finally occurred in mid-2013 with the publication by APVMA of Public release summary on the evaluation of the new active constituent ethanedinitrile in the product Sterigas™ 1000 fumigant (APVMA 2013b).

The only trial conducted using ethanedinitrile on insects infesting logs was by Cho et al. (2011) who reported the results of two separate tests against the Japanese termite, *Reticulitermes speratus* (Kolbe), nymphs and adults and [yellow] minute pine bark beetle, *Cryphalus fulvus* Nishima (Coleoptera: Scolytidae), larvae and adults. Tests were done in chambers made of PVC tarpaulin covering a metal frame. The fumigation parameters were 50 or 70 g/m^3 for 6 h at 22.0 $\pm$ 5.0°C or 24 h at 4.1 or 6.1°C. Insect mortality was 100% in all tests, and mortality in parallel tests with MB against yellow minute bark beetle larvae and adults also was 100%. The authors stated that the 6-h fumigations were done"…at relatively high temperature conditions…" and that they "…did not get a comparison…" between the 6- and 24-h fumigations. The results were said to show the potential of ethanedinitrile for eliminating insects that infest logs. Most wood-related research with ethanedinitrile was carried out on insect pests of sawn timber (CSIRO et al. 1996, Viljoen & Ren 2001, Ren et al. 2006, and others). However, Brash et al. (2013) found little or no supporting data for many of the claims made regarding the efficacy of ethanedinitrile. Brash et al. (2013) stated that there is a paucity of information specific to fumigation of sawn timber or logs and, with the exception of Brash et al. (2007), there is no information on the efficacy of ethanedinitrile against the life stages of New Zealand forest insects. Moreover, there is no applicable information on which to base potential treatment parameters for the New Zealand forest insect species regardless of the proposed label for timber and logs of 50 g/m^3 and a 6-h exposure identified by Ryan et al. (2006a) for logs (Brash et al. 2013). However, after mid-2014 this scenario began to change in for sawn timber, if not yet for logs, in New Zealand. Pranamornkith et al. (2014a) evaluated the effects of dose (20 g/m3 or 50 g/m3), timber moisture content (green or kiln dried sawn timber), end-grain sealing (sealed or unsealed timber end-grain) and load factor (11% or 44%) on the sorption of ethanedinitrile by sawn timber at 15°C. Pranamornkith et al. (2014a) found that the chamber loading significantly influenced sorption, with higher loading resulting in greater sorption. Hence, as discussed above (Brash et al. 2013), sorption of ethanedinitrile remains a major question regarding the amount of ethanedinitrile that would be required for efficacy against forest insects on logs. However, Pranamornkith et al. (2014a) also found that:

- Changes in the dose of ethanedinitrile did not affect the sorption pattern.
- Increased moisture content reduced sorption.
- End-grain sealing reduced sorption
- Reductions in sorption from both increased moisture content and end-grain sealing were relatively small and the differences in sorption patterns caused by moisture content or end-grain sealing decreased over time.

The results of Pranamornkith et al. (2014a) that showed that sorption was reduced at higher moisture content in sawn timber is contrary to much of the literature that indicated (but did not necessarily prove) that ethanedinitrile would combine quickly with water or that sorption would increase as moisture content increased (Brash et al. 2013). These results indicate that the moisture content of logs may not be an impediment to using ethanedinitrile as a phytosanitary treatment. However, their results corroborate the fact that ethanedinitrile is a highly sorptive material that has ramifications regarding the amount of fumigant that may be needed to obtain effective control of forest insects on logs (Brash et al. 2013, Pranamornkith et al. 2014, Table 7).

Pranamornkith et al. (2014b) studied the efficacy of ethanedinitrile against *A. ferus* adults. Using a range of ethanedinitrile concentrations they determined that the LD_{99} for adult *A*. *ferus* after a 3-h exposure was 12.6 g/m^3, which is significantly less than the approved Australian pesticide use label for ethanedinitrile that recommends 50 g/m^3 for 10 h (APVMA 2013b, Pranamornkith et al. 2014b). Their initial results indicate that ethanedinitrile may also have potential as a methyl bromide alternative disinfestation treatment for logs exported from New Zealand. To determine the potential use for logs, ethanedinitrile efficacy at the LD99 level is needed for life stages of other forest insects, such as *H. ligniperda*, *H*. *ater* and the other life stages of *A*. *ferus*, and ethanedinitrile sorption by logs and penetration into logs must be elucidated (Pranamornkith et al. 2014b).

The registration of Sterigas™ 1000 (APVMA 2013b) in Australia as a fumigant for logs and sawn timber does not mean that it is immediately applicable for New Zealand export logs. With the exception of limited preliminary data provided by Brash et al. (2007), there are no complete datasets for determining the ethanedinitrile dosage rates or exposure times needed to obtain efficacy against New Zealand forest insects. Brash et al. (2013) outlined an ethanedinitrile work plan that is designed to provide a scientific basis for developing log fumigations under commercial conditions that will ensure quarantine security. The work of Pranamornkith et al. (2014a, b) includes the initial studies outlined in the ethanedinitrile work plan (Brash et al. 2013).

Sterigas™ is registered for experimental use ‘in containment’ in New Zealand in fumigation trials on timber/logs and soil (NZERMA 2011c). Some of the Australian registration restrictions (APVMA 2013b) are significant and may be problematic for the use of ethanedinitrile as a disinfestation treatment for logs in New Zealand. Specifically, (1) the commodity load factor must be ≤ 20%. BOC advised the authors that it is negotiating for this to be changed (C. Dolman, personal communication), (2) the fumigated commodity temperature must be ≥ 15°C, and (3) a 4-h scrubbing period using a specialised liquid scrubbing system (such as the Nordiko scrubber, see http://www.industrysearch.com.au/) followed by a 24-h aeration period are prescribed (APVMA 2013b). In contrast with the registration requirements, (1) the log loading factor in either the stacks presently fumigated at New Zealand ports or in ship holds during transit exceed 50% (M. Goss, personal communication), (2) log temperatures during the autumn and winter months at some ports in New Zealand may be below 15°C (Armstrong et al. 2012b), and (3) the number of log stacks fumigated with methyl bromide under tarpaulin before export and the number of ship holds containing logs fumigated with phosphine during transit (see 2.c.1) could be physically, technically and/or economically infeasible to incorporate a 4-h scrubbing period with a commercial liquid scrubber. Although not necessarily an impediment to its use for logs, the Australian registration for ethanedinitrile (APVMA 2013b) made a significant increase in the fumigation time from 6 h, as described Ryan et al. (2006a) and others, to 10 h.

These potential impediments to the commercial use of ethanedinitrile for export logs are not necessarily permanent. Registration restrictions, such as those for ethanedinitrile (APVMA 2013b) are subject to modification based on new research data. Research carried out under the ethanedinitrile work plan (Brash et al. 2013) may provide data that can be used to increase the load factor, allow for ethanedinitrile fumigation of logs ≤ 15°C, eliminate or reduce the need for post-fumigation scrubbing, and decrease the fumigation time.

4.5.1 Ethanedinitrile research to control fungi and nematodes

A major potential use for ethanedinitrile fumigation that has received attention in the past decade is soil fumigation for seeds, plant pathogens, and nematodes (Camkin 2012; Chung 2007a, b; CSIRO et al. 1996; Lendler et al. 2010; Lopez-Aranda et al. 2009; Mattner et al. 2003, 2004a, b, 2006; Ren 2003; Rosskopf et al. 2007; Waterford et al. 2004) and seed for seed-borne fungi (Smith et al. 2003; Waterford et al. 2008).

4.5.2 Ethanedinitrile combined with other fumigants

No references to combinations of ethanedinitrile with other fumigants or compounds were found in the literature, which can be expected because ethanedinitrile has not been registered for use until recently (APVMA 2013b).

4.5.3 Recommendation for further research with ethanedinitrile

Based on the recent findings of Pranamornkith et al. (2014a, b), especially because Pranamornkith et al. (2014a) found that moisture content was not a major factor in ethanedinitrile sorption, the authors recommend further research to determine the viability of ethanedinitrile as a potential methyl bromide alternative for New Zealand export logs. However, the literature (Brash et al. 2013) and the results of Pranamornkith et al. (2014a) clearly show that the sorptive properties of ethanedinitrile require a technological and economic study before further research on efficacy or penetration into logs is initiated. If the sorption results with sawn timber (Pranamornkith et al. 2014a) are not adequate to provide sorption data for a technological and economic study, a study of ethanedinitrile sorption by logs in the laboratory may be required. While the economic aspects are more specific to sorption and the cost related to the potential use of ethanedinitrile for logs, the technological aspects include commercial application, safety, recapture and destruction, and other potential commercial or regulatory components that add cost to the use of ethanedinitrile for logs.

4.6 Ethyl formate

Ethyl formate is a natural plant volatile that is colourless as a liquid, has a pleasant aromatic fruity odour and is highly flammable as a gas (Chemical Book 2010). Ethyl formate occurs naturally in a variety of products, including essential oils of grasses, beer, rice, beef, and cheese (Desmarchelier & Ren 1999).

Among the earliest fumigants used, ethyl formate effectiveness against dried fruit pests was first reported in 1925 (Ryan & De Lima 2012). The insecticidal properties of ethyl formate were again demonstrated by Vincent and Lindgren (1971, 1972) and tested as a fumigant by Aharoni et al. (1980) and Rohitha et al. (1993). An historical overview of the use of ethyl formate from 1925 to 2012 was published by Ryan and De Lima (2012).

An important advantage of using volatiles, such as ethyl formate, for fumigation is that residues found on treated commodities are found only in trace amounts (Desmarchelier & Ren 1999, Muthu et al. 1984). Ducom (2006) stated that “ethyl formate, not alone, but as a mixture with some other compounds or in a vacuum, may be the most promising fumigant for grains and all other stored and fresh products” when compared with current and potential alternatives to methyl bromide. Similar to many fumigants, the insect egg stage, followed by the pupal stage, is the most difficult to control using ethyl formate (Ducom 2006, Vincent & Lindgren 1972). Soderstrom et al. (1991) found that a 2% vol:vol concentration of ethyl formate in air caused no mortality to the eggs of Fuller's rose weevil, *Naupactus godmanni* (Crotch) syn. *Asynonychus godmanni* Crotch (Coleoptera: Curculionidae), after 2 h at 21°C. Although ethyl formate provides rapid kill of larvae and adults (usually within 6 h), the insect egg stage may require much longer fumigation periods of 48 to 72 h (Ducom 2006). Moreover, Harein (1962) demonstrated that the effects of ethyl formate on insect mortality of three stored-product beetles and their life stages were significantly variable between both species and life stages.

Dojchinov and Haritos (2003) determined the acute toxicity of a range of alkyl esters, ethanol and formic acid against two species of stored-product insects and found that all alkyl formates and formic acid were similarly toxic and twice as potent as ethyl propionate, methyl acetate or ethanol. They found that alkyl formates were rapidly metabolised *in vitro* to formic acid when incubated with insect homogenates, presumably through the action of esterases, to produce 8-fold to 17-fold higher concentrations of formic acid in the bodies of the target insect (Dojchinov & Haritos 2003). Hence, it is the metabolism by the insect of ethyl formate into formic acid and the resulting high levels of formic acid in the insect that causes death (Dojchinov & Haritos 2003).

Ethyl formate is highly flammable at 2.7-16.5% vol:vol in air (TCI America 2006) and explosive at concentrations required to kill insects (Ryan & Bishop 2003). To make ethyl formate safe to use as a fumigant, it must be mixed with carbon dioxide (Ducom 2006, Jamieson et al. 2009a). Ethyl formate is mixed with liquid carbon dioxide and sold under the trade name, VAPORMATE® by BOC in both Australia and New Zealand, where it is approved for use on fresh produce and stored products (Jamieson et al. 2009).

Although ethyl formate can provide rapid mortality in insects, high concentrations are required to obtain control (Haritos et al. 2003). Also, ethyl formate is highly sorptive in substrates. Haritos et al. (2003) stated that a major challenge for ethyl formate for use on grain was the large capacity of grain to absorb ethyl formate. To ameliorate the sorption issue, ethyl formate had to be moved through the grain by "forced-flow" to reduce the residence time of ethyl formate near the grain and so reduce sorption (Haritos et al. 2003). Darby et al. (2009) found that grain rapidly adsorbs ethyl formate, a characteristic which could lead to inadequate fumigant concentrations to control target pests. Learmonth and Ren (2012) found that the load factor (90-95%) of apples in storage affected the efficacy of ethyl formate fumigations against adult eucalyptus snout weevil (= gum tree weevil), *Gonipterus scutellatus* Gyllenhal (Coleoptera: Curculionidae), whereby sorption was considered the reason that 40 mg/litre ethyl formate for 24 h at 22-24°C was required for complete control when only 25-30 mg/litre under the same conditions were required in the absence of apples. Hence, sorption may be an issue whenever ethyl formate is used as a fumigant in a static-air system (e.g., fumigation under tarp or in a ship hold).

Although direct correlations were difficult to assess from the literature, temperature appears to be a limiting factor in ethyl formate fumigations. Much of the ethyl formate fumigation literature (e.g., Aharoni & Stewart 1980, Aharoni et al. 1980, Griffin et al. 2013, Harein 1962, Hilton & Banks 1996, Rohitha et al. 1993, Stewart & Mon 1984, Vincent & Lindgren 1972) applied ethyl formate at temperatures of 18-27°C. Approved VAPORMATE® applications in Australia and New Zealand are recommended at temperature >15°C (BOC 2014, Jamieson et al. 2009). Although Pupin et al. (2013) fumigated thrips-infested navel oranges with VAPORMATE® immediately after they were removed from 5.0°C cold storage "…to keep the thrips inside the fruit…", they stated that their study showed no negative [phytotoxic] effect of ethyl formate on oranges fumigated at 38 g/m^3 for 1 h at 20°C.

According to the Methyl Bromide Technical Options Committee 2002 Assessment, ethyl formate is highly sorbed by commodities, especially at raised humidity, and it is difficult to attain adequate distribution (MBTOC 2002). Thus, in practice long exposure times may be needed to ensure adequate penetration of bulk commodities (MBTOC 2002). Little change in this issue was noted by the Methyl Bromide Technical Options Committee (MBTOC 2010) in its 2010 Assessment report that stated that ethyl formate had potential as a methyl bromide replacement for some uses against stored-product insects, in grain storage and handling facilities and equipment, and for dried fruits, such as sultanas and dates, on which ethyl formate has been used historically (Ryan & De Lima 2012). However, the Methyl Bromide Technical Options Committee (MBTOC 2012) noted that ethyl formate was not effective against insect pests found in dates with high moisture content, a reiteration of the issue of using ethyl formate in the presence of moist substrates or high humidity.

In addition to mixing carbon dioxide with ethyl formate to reduce flammability and increase efficacy, Aharoni and Stewart (1980), Aharoni et al. (1980), Griffin et al. (2013), Liu (1983), Misumi et al. (2013), Stewart and Mon (1984) and others used vacuum (- 7.99 to - 70.0 kPa) to reduce the fumigation time required for ethyl formate and to provide better product quality (e.g., lettuce, strawberry) or increase efficacy against insect pests and their life stages that were more difficult to kill without using vacuum.

Registration of ethyl formate in Australia includes (1) VAPORMATE® (BOC Gases Limited, Sydney) containing 16.7% ethyl formate in 83.3% carbon dioxide (w/w); (2) ERANOL® (Orica Australia Pty. Limited, Melbourne) containing 98% ethyl formate in 2% carbon dioxide (w/w); and (3) *eMate®* (VAPORFAZE, Sydney) containing 98% ethyl formate (w/w) (Ryan & De Lima 2012). Only VAPORMATE® (BOC Gases Limited, Auckland, New Zealand) is registered In New Zealand (MPI 2013g, NZFSA 2013). Both *ERANOL® and eMate®* can be mixed on-site with carbon dioxide to dispense ethyl formate as a non-flammable gaseous mixture (Ryan & De Lima 2012).

Ethyl formate under its various trade names is registered in Australia and New Zealand for use on cereal grains, oilseeds, flour, dried fruits, nuts, dates, grain storage premises and equipment, lettuce, onion sweet pepper or capsicum, cut flowers, tubers (kumara and rhubarb), pineapples, table grapes, strawberry, kiwifruit, blueberries, and persimmons (MPI 2013g, Linde Group 2013). VAPORMATE® is not registered for use on logs or timber (Linde Group 2013). All target insects for which ethyl formate-based fumigants are used are surface pests (e.g., mealybugs, thrips, mites) because ethyl formate does not penetrate readily through fruit surfaces (e.g., grapes, kiwifruit) (L. Jamieson, personal communication). For example, papaya were infested with fruit fly larvae and exposed to 12.5, 25.0 or 50 g/m^3 ethyl formate at 21$\pm$ 2°C and normal atmospheric pressure failed to kill any of the larvae (Y. Aharoni & J. Armstrong, unpublished data). Moreover, the high rates of sorption and poor penetration characteristics through barriers, e.g., bark and cambium where forest pest insect larvae are present, suggest that ethyl formate would not be a good candidate as a methyl bromide alternative for logs (F. De Lima, personal communication).

4.6.1 Ethyl formate combined with other fumigants or compounds

<u>Ethyl formate combined with carbon dioxide</u> - As previously stated, ethyl formate, when used as a fumigant, is combined with carbon dioxide to eliminate flammability issues (Ryan & Bishop 2003). However, combining ethyl formate with carbon dioxide also was found to provide increased efficacy against a number of pests, especially when ethyl formate alone was ineffective. For example, Haritos et al. (2006) that ethyl formate alone (12.5 g/m^3) resulted in 3.0, 82.0 and 91.0% mortality of adult *T. castaneum*, *S. oryzae* and *R. dominica*, respectively.

However, when Haritos et al. (2006) added 5% carbon dioxide to the ethyl formate the mortality for each species increased to 99.5, 100 and 100%, respectively. Adding 10 and 20% carbon dioxide to ethyl formate resulted in 100% mortality in all species, indicating that there was no antagonism at higher carbon dioxide concentrations (no insect mortality was caused by 5, 10 and 20% carbon dioxide alone) (Haritos et al. 2003).

The increased efficacy provided by the addition of carbon dioxide to ethyl formate tends to vary with the target species. De Lima (2006) reported increased mortality in aphids, thrips, *T. castaneum*, and light brown apple moth, *Epiphyas postvittana* (Walker) (Lepidoptera: Tortricidae), by the addition of 10-20% carbon dioxide to ethyl formate, but only a 22% increase in mortality for red back spiders, *Latrodectus hasseltii* Thorell (Arachnida: Theridiidae), Fuller's rose weevil, and an unidentified species of *Helicoverpa* (Lepidoptera: Noctuidae). Simpson et al. (2007) demonstrated a significantly wide range of dose-mortality responses to varied concentrations of ethyl formate combined with carbon dioxide to all life stages of western flower thrips, *Frankiniella occidentalis* (Pergande) (Thysanoptera: Thripidae), and the adult and crawler stages of grape mealybug, *Pseudococcus maritimus* (Ehrhorn) (Homoptera: Pseucococcidae), and the eggs, protonymphs, deutonymph, and adults of Pacific red spider mite, *Tetranychus pacificus* McGregor (Acari: Tetranychidae), both between species and among the life stages tested.

<u>Ethyl formate combined with methyl isothiocyanate</u> Following on the work of Ren et al. (2005), CSIRO et al. (2006) patented the fumigant combination of ethyl formate and methyl isothiocyanate. Thereafter, Lee et al. (2007) and Ren et al. (2008) reported the use of a "new" ethyl formate formulation consisting of 95% ethyl formate and 5 % methyl isothiocyanate at a dose rate of 80 g/m^3 in each of two 50-tonne sealed metal vertical silos containing wheat. The fumigation consisted of pouring the calculated amount of liquid ethyl formate and methyl isothiocyanate mixture onto the top of the wheat (Ren et al. 2008). That same year, Banks (2008) reiterated the potential for using the ethyl formate and methyl isothiocyanate mixture for fumigating wheat and as a methyl bromide replacement. Ren et al. (2012) published laboratory efficacy data on the use of the 95% ethyl formate and 5 % methyl isothiocyanate mixture against six stored-product beetles and reported the residues following laboratory fumigations of wheat, barley, peas, oats, and canola to provide further support for the use of the ethyl formate and methyl isothiocyanate mixture as a potential stored grain fumigant. However, there is no evidence in the literature that the use of ethyl formate combined with methyl isothiocyanate became a commercial fumigation method.

<u>Ethyl formate combined with dichlorvos</u> Refer to page 35, dichlorvos combined with ethyl formate.

The authors do not recommend ethyl formate for further consideration as a potential alternative fumigant to methyl bromide because of its highly sorptive characteristics, especially in the presence of moisture, and because of its flammability issues which require that it be mixed with carbon dioxide to reduce the potential for ignition and explosion.

4.7 Ethylene oxide

Ethylene oxide used as a fumigant is one of the most commonly used sterilisation methods in the healthcare industry because of its non-damaging effects for delicate instruments and devices that are needed sterile, and for its wide range of material compatibility for those instruments composed of, or containing, components that cannot tolerate heat, moisture or abrasive chemicals, such as electronics, optical equipment, paper, rubber and plastics (USEPA 2004, 2011; USDHHS 2011).

Ethylene oxide itself is a very hazardous substance. At room temperature it is a flammable, carcinogenic, mutagenic, irritating, and anaesthetic gas with a misleadingly pleasant aroma (USOSHA 2002). Because an increased risk of cancer has been demonstrated in epidemiological studies of workers using ethylene oxide as a sterilant for medical devices and spices and in chemical synthesis and production, ethylene oxide is classified as a Class 2 carcinogen (breast cancer in women is a major factor) and, in the US, the time-weighted exposure limit is 1 ppm in an 8-h period (USDHHS 2011, USEPA 2011). Ethylene oxide degradation in air is relatively slow with a potential lifetime of 333 days (Rebsdat & Mayer 2012), hence it is considered a significant air pollutant that can remain a health issue for long periods of time (USDHHS 2011). For example, a study was conducted by the New Zealand Customs Service (2012) at the port of Tauranga in which air samples were taken from containers of equipment for hospitals, medical equipment and laboratory hygienic ware entering New Zealand from overseas to detect if any hazardous gases were present. The air samples found that one gas, ethylene oxide, was detected in 4.6% of the total samples taken, that 22 out of 23 air samples detected ethylene oxide above the safe reporting level, and that the highest concentration of ethylene oxide was 19 times greater than the safe reporting level (New Zealand Customs Service 2012). Presumably, the ethylene oxide detected in the containers was the result of ethylene oxide desorbing from materials that had been fumigated previously with ethylene oxide.

Ethylene oxide was first proposed and tested as a fumigant for food and other commodities by Cotton and Roark (1928) and Back et al. (1930). The flammable nature of ethylene oxide required that it be used in combination with a fire suppressant when used as a fumigant, the most common suppressant used was carbon dioxide (Fulton et al. 1963). Richardson and Roth (1963) and Roth (1971) tested ethylene oxide combined with carbon dioxide as a quarantine treatment against potential infestations of *Cochlicella barbara* (L.), *C. ventrosa* (Ferussac), *C. conoidea* (Draparnaud), and *Theba pisana* (Miller) (Mollusca: Helicidae) snails on cargo entering the US. In the most recent, and last publication of research on ethylene oxide for use against insects, Childs and Overby (1976) studied combinations of ethylene oxide and dichlorodifluoromethane (12% to 88% vol:vol, respectively) for control of cigarette beetle, *Lasioderma serricorne* F. (Coleoptera: Anobiidae), and tobacco moth [= warehouse moth or cacao moth], *Ephestia elutella* (Hübner) (Lepidoptera: Pyralidae).

Research on ethylene oxide nearly disappeared after the 1970s, possibly because methyl bromide and phosphine were more practical fumigants than ethylene oxide, the restrictions on ethylene oxide use and cost for application chambers, or the discovery that ethylene oxide was a significant carcinogen and mutagen (USEPA 2004, 2011). One exception, Ryan et al. (2004, 2010), reported on Ethoxofume 1000, an ethylene oxide fumigation system that is carried out in vacuum chambers against quarantine pests by the Australian Quarantine Inspection Service for non-food import and export commodities under the AQIS Guideline: Ethylene Oxide treatment code T9020 that used 1,200 g/m^3 ethylene oxide for 5 h at 50°C (Australia Department of Agriculture 2009). Ryan et al. (2010) reported to a conference on stored-product protection that a “disadvantage of vacuum is the capital investment in vacuum chambers and associated equipment and the small size of the chambers”. Hence, ethylene oxide chamber throughput based on both chamber size and treatment time (e.g., 5 h, Australia Department of Agriculture 2009) would not be suitable for large volumes of commodity (e.g., grain, logs).

Ethylene oxide is not a practical choice as a methyl bromide alternative for logs because (1) it is highly explosive and reactive, (2) the equipment used for its processing consists of tightly closed and highly automated systems constructed from stainless steel, (3) ethylene oxide is a persistent air pollutant, and (4) ethylene oxide dissolves rapidly in water and is miscible in all proportions (Rebsdat & Mayer 2012, Table 7, USEPA 2004, 2011). Moreover, the issue with ethylene oxide as a persistent compound that desorbs over time from fumigated substrates (New Zealand Customs Service 2012) combined with the ease with which ethylene oxide dissolves in water (Rebsdat & Mayer 2012) indicates that logs fumigated with ethylene oxide may absorb significant quantities of ethylene oxide that may be released into the atmosphere as the logs dried or were processed.

4.8 Hydrogen cyanide

Hydrogen cyanide is a colourless to slightly bluish gas with a mild almond odour that is flammable (Table 7) (CRC 2013). Hydrogen cyanide is a quick-acting poison that was one of the first fumigants to be used extensively under modern conditions and was originally used for treating trees under tents against scale insects in California in 1886 (Bond 1984). Gunderson and Strand (1939) found hydrogen cyanide was an excellent fumigant to control bedbugs, *Cimex lectularius* L. (Hemiptera: Cimicidae) and that the egg was the most susceptible life stage. However, Soderstrom et al. (1991) found that 8.4, 10.8 or 126 g/m^3 hydrogen cyanide for 30 min at 21°C caused little or no mortality to Fuller's rose weevil eggs and concluded that hydrogen cyanide was ineffective for this species.

The use of hydrogen cyanide has been declining since the 1950s, because it is one of the most toxic of the insect fumigants, it is highly flammable and it is infinitely soluble in water at all temperatures (Bond 1984, Table 7). Registration for hydrogen cyanide application as a fumigant has declined. For example, France rescinded the hydrogen cyanide fumigations for bulbs, rhizomes, and tubers (in 1984) and woody plants (in 2007) to control insect and mite pests (EMPPO 2014). Banks (1994) noted that the Codex Alimentarius[4] registration for hydrogen cyanide had lapsed and that (at that time) there did not appear to be sufficient data on the health and environmental effect sufficient to permit re-registration. Moreover, the lapse of the Codex Alimentarius registration was caused by the loss of historical maximum residue limits and, because hydrogen cyanide is a commonly available chemical without patent protection, chemical companies were unlikely to develop the costly full toxicological data sets and extensive field trials required for its reinstatement (Banks 1994). Hydrogen cyanide is currently registered only in India, New Zealand and with severe restrictions in Germany (Navarro 2006). Hydrogen cyanide is not approved for use by the US Department of Agriculture and the US Department of Agriculture's Treatment Manual no longer has a section on hydrogen cyanide fumigation (Stibick 2007, USDA 2014b).

Although hydrogen cyanide has been employed for stored products and for structural wood fumigation in historical buildings for almost 100 years, only a few studies concerning rates of hydrogen cyanide wood penetration have been published (Stejskal et al. 2014). Early work with hydrogen cyanide for wood products was done by Parkin and Busvie (1937) and Bletchly (1953) in fumigation studies on the efficacy of hydrogen cyanide on wood boring insects and the eggs of the common furniture beetle, respectively. Research on timber then disappears from the literature until recent work in the Czech Republic. Capoun and Krykorkova (2008) reported on the penetration of hydrogen cyanide in wood; Stejskal et al. (2012) reported on a phytosanitary quarantine treatment for wood packaging; and on the penetration of hydrogen cyanide in wood and its efficacy to control the larvae of two beetle species, Asian long-horned beetle, *Anoplophora glabripennis* (Motschulsky) [syn. *Anoplophora nobilis* (Ganglbauer)] and old-house borer, *Hylotrupes bajulus* (L.) (Coleoptera: Cerambycidae) (Stejskal et al. 2014).

[4] The Codex Alimentarius Commission, established by FAO and WHO develops harmonised international food standards, guidelines and codes of practice to protect the health of the consumers.

The penetration characteristics of hydrogen cyanide are debated in the literature. Schwarz and Deckert (1930) claimed that wood can be penetrated easily by hydrogen cyanide and that "the gas has very great penetrative power, and it is unimportant whether the material be coarse like rice or fine like potato flour. Penetration deep into the mass of a highly absorbent material is slower than in a less absorbent one, and the gas is subsequently given up more slowly by the former material." Kenz et al. (1964) described a slow rate of passive diffusion for hydrogen cyanide through a mass of grain sorghum and slow penetration (and high absorption) was reported for mill-flour residues (Rambeau et al. 2000). Stibick (2007) stated that hydrogen cyanide has poor penetration characteristics because it has a high rate of sorption and, hence, its efficacy does not conform to concentration x time (CT) products. Capoun and Krykorkova (2008) measured hydrogen cyanide residues in spruce and pine wood and discovered considerably higher hydrogen cyanide content in spruce wood than in pinewood. Stejskal et al. (2012, 2014) reported on the temporal rate of hydrogen cyanide penetration inside spruce blocks under typical atmospheric and temperature conditions, and demonstrated that the hydrogen cyanide penetration into the blocks was adequate to obtain 100% mortality of the larvae of *A. glabripennis* and *H. bajulus*. The moisture content of the blocks was 18.5 $\pm$ 0.44% (Stejskal et al. 2012, 2014) and, although the moisture content of the wood used by Schwarz and Deckert (1930) was not given, the moisture contents of the grains tested for penetration by Kunz et al. (1964) and Rambeau et al. 2000) were $\leq$ 15.0%. The most likely scenario based on the literature is that hydrogen cyanide has quite different penetration characteristics depending on the substrate through which it is moving, and little inference can be made between the penetration studies through spruce blocks at $\leq$ 19% moisture content and freshly harvested logs at $\geq$ 50% moisture content. Moreover, the propensity for hydrogen cyanide to dissolve in water (Table 7) would make the use of this fumigant for logs under tarpaulin or in a ship hold questionable.

Stejskal et al. (2012, 2014) used a hermetically sealed steel chamber to study hydrogen cyanide penetration and absorption rates in wooden blocks and its efficacy against *B. xylophilus* in sawdust and *A. glabripennis* and *H. bajulus* larvae in spruce blocks (100 mm by 100 mm by 120 mm). A 20-g/m^3 hydrogen cyanide concentration equilibrium between the fumigation chamber headspace and the centre of the treated blocks was obtained after 48 h in the 100% hydrogen cyanide atmosphere. A dose of 10-g/m^3 hydrogen cyanide in the centre of the blocks was obtained for both 100% and <100% hydrogen cyanide atmospheres after 24 h of fumigation. The wood absorbed approximately 40-45% of the hydrogen cyanide until equilibrium was reached. The highest tested dose of 20 g/m^3 hydrogen cyanide resulted in 100% mortality of *A. glabripennis* and *H. bajulus* larvae after less than 1 h of exposure. Both hydrogen cyanide doses of 10 g/m^3 and 20 g/m^3 resulted in 100% mortality of *B. xylophilus* in 40 h and 18 h, respectively (Stejskal et al. 2014).

Hydrogen cyanide fumigant is registered in New Zealand under the trade name, CYANOSIL® Discoids, by PharmoChem Company, Auckland (NZFSA 2014) and under its approved label the discs that emit hydrogen cyanide can be used to fumigate mills, warehouses, food factories, ships' holds, nursery stock in dormant stage, to treat imported bananas, and to control wood-boring insects (e.g., termites) (NZFSA 2012, Table 12). However, there is no maximum residue level established for hydrogen cyanide in New Zealand (NZFSA 2014), therefore, with the exception of bananas, imported or exported edible commodities cannot be fumigated legally (the approved label fumigation for bananas would have to be done when live insects are found as an emergency quarantine procedure).

Table 12. Approved uses for CYANOSIL® Discoids (hydrogen cyanide) in New Zealand[a]

Application	Dosage (g/m^3)	Exposure time (h)	Temperature (°C)
Control of storage pests in mills, warehouses and food factories	5-12	6-48	≥ 15
Control of rodents in empty warehouses, ships' holds	2-4	2-4	≥ 4
Fumigation of nursery stock in dormant stage	5-10	0.5-1.0	≥ 4
Control of wood-boring insects	10-15	40-72	≥ 15
Control of storage pests in empty ships' holds	10	10-12	5 - 9
Treatment of bananas	3	2	13.5 - 15.0

[a]NZ Food Safety Authority approved use label (NZFSA 2012).

Japan fumigates fresh produce imported from New Zealand with methyl bromide, phosphine or hydrogen cyanide if insect pests are found on the produce (Beever & Yearsley 1987). However, Japan is reviewing the maximum residue tolerances for methyl bromide, phosphine and hydrogen cyanide, which could result in significant restrictions on the use of these fumigants (MPI 2013h). However, a request for a show of industry concern regarding the fumigants found only methyl bromide was of concern (MPI 2013h) and the New Zealand Plant Market Access Council received no interest in supporting hydrogen cyanide from its members (H. Gear, Plant Market Access Council, personal communication).

A literature search indicated that research on or recommendations for the use hydrogen cyanide as a fumigant declined rapidly after the 1950s until relatively few references could be found. Beever and Yearsley (1987) reported on the phytotoxicity of fumigants, including hydrogen cyanide, on kiwifruit when fumigated by Japan after arrival due to insect interceptions. Hansen et al. (1991a, b) reported on the efficacy of a 30-minute hydrogen cyanide fumigation treatment to eliminate quarantine pests from Hawaiian cut flowers and foliage after harvest, but the treatment was never commercialised because of phytotoxicity issues and the eventual success of a hot-water quarantine treatment (Armstrong & Mangan 2007, Hansen et al. 1991b). Cassells et al. (1994) reported on the use of hydrogen cyanide fumigation to control two snail pest species found as a grain contaminant. Although some authors suggest "renewed interested in old fumigants" or new uses for hydrogen cyanide or that hydrogen cyanide presents a methyl bromide alternative (Navarro 2006, Rambeau 2000, Reichmuth 2002, Stibick 2007), a review of the literature found that there has been little research to develop new uses or treatment schedules for hydrogen cyanide with the exception of the work in the Czech Republic that is relevant to timber and logs (Capoun & Krykorkova 2008; Stejskal et al. 2012, 2014).

A request for further information on proposed wood packaging materials treatment using hydrogen cyanide was given high priority by the Methyl Bromide Technical and Economic Assessment Panel of the United Nations Environmental Programme in the 2010 report, but no information was provided by any interested parties by 2013 (TEAP 2010, 2013a). Obviously, the research reported by Capoun and Krykorkova (2008) and Stejskal et al. (2012) should have some relevance to the use of hydrogen cyanide for wood packaging materials, but none of these references were cited by TEAP (2010, 2013a). Perhaps these references, along with Stejskal et al. (2014), will be found in the next TEAP report.

4.8.1 Hydrogen cyanide combined with other fumigants or compounds

Hydrogen cyanide combined with sulphuryl fluoride Reichmuth and Klementz (2008a) showed that combining sulphuryl fluoride with hydrogen cyanide was a very effective combination in controlling the eggs of *T. castaneum*, *E. kuehniella* and *S. granarius* at 25°C when sulphuryl fluoride alone would not control the eggs of these stored-product insects.

Hydrogen cyanide combined with carbon dioxide AliNiazee and Lindgren (1969) demonstrated that the addition of carbon dioxide increased the efficacy of hydrogen cyanide fumigation against four stored-product insects by 1.4 to 4.0 times depending on the concentration of carbon dioxide mixed with hydrogen cyanide.

Hydrogen cyanide has a number of issues, including worker and public safety concerns, significant sorption issues, and the only research demonstrating its use for logs or timber requires that fumigation take place in costly enclosed systems (Capoun & Krykorkova 2008, Stejskal et al. 2012). Therefore, the authors do not recommend hydrogen cyanide for consideration as a potential methyl bromide alternative.

4.9 Methyl bromide

New Zealand is the eighth highest user of methyl bromide for quarantine and pre-shipment in the world, consuming 560 tons in 2012 with the highest per capita consumption for treating exports in the global context (K. Glassey, personal communication). Much of the methyl bromide used in New Zealand is for disinfestation treatment of export logs and timber. The use of methyl bromide in New Zealand continues to increase directly correlating with, and is solely due to, the increase in log trade to countries that require methyl bromide fumigation (UNEP 2010).

In 2011, the controls on the use of methyl bromide became more restricted because of safety concerns that limited the locations in which methyl bromide fumigation under tarpaulin could be done (New Zealand Environmental Risk Management Authority 2011), and the complete recapture and/or destruction of methyl bromide following treatment will be required to be in place by 2020 (Gear 2011). The 2008 International Plant Protection Convention recommendations for reduction and replacement of MB for phytosanitary measures stressed the need for continued research to find alternative quarantine treatments to MB fumigation (UNEP 2010).

Pursuant to the goals of reducing methyl bromide use, Plant & Food Research initiated studies in 2013 at the request of the Stakeholders in Methyl Bromide Reduction Inc. on the efficacy of methyl bromide on New Zealand forest insects to determine whether the lowered dosage rates of Armstrong et al. (2011) could be implemented. Initial data from the Plant & Food Research studies indicate the potential for significant dosage decreases without compromising quarantine security (Somerfield et al. 2013). Oogita et al. (1998) also found that the nine species of forest insect pests they tested required $\leq$ 15 g/m^3 methyl bromide for 25 h at 15°C compared with the 80.0, 48.5 or 49.5 (Table 2) for 16 h and $\geq$ 15°C currently used for New Zealand logs imported by China, Japan or Korea, respectively.

To research more fully the potential for reducing methyl bromide dosage rates for logs will require a concerted effort because almost no data exist on the relative efficacy of, or tolerance to, methyl bromide by New Zealand forest insects (Armstrong et al. 2011, 2012b). Efficacy and tolerance data is needed both to determine the potential for reduction in methyl bromide rates for New Zealand export logs (Armstrong et al. 2011) and to provide a basis for comparison with the efficacy and economic viability of potential alternative treatments, including fumigants. The work by Somerfield et al. (2013) provides only a small fragment of information that could, with sustained research, lead to the reduction in methyl bromide rates (and reduction in use), standardisation of methyl bromide dosage rates for all countries importing New Zealand logs (Armstrong et al. 2011), and significant reductions in fumigation costs for exporters. Therefore, the authors recommend that any reduction in the use of methyl bromide be considered equally important to finding an alternative fumigant to methyl bromide.

4.9.1 Methyl bromide combined with other fumigants and gases

Methyl bromide combined with carbon dioxide Bond and Buckland (1976, 1978) first described the synergistic effects of adding carbon dioxide to methyl bromide whereby efficacy against stored-product insects was significantly increased at lower than calculated CT values. Williams et al. (1983) reported a two-thirds reduction in required CT product to obtain complete control of four stored-product insect species using a mixture of methyl bromide and 40-60% carbon dioxide.

Scheffrahn et al. (1995) obtained a maximum synergism ratio of 1.8 (i.e., 1.8 times more efficacy than provided by the fumigant alone) when either 10% or 20% (vol:vol) carbon dioxide was added to methyl bromide in dose-response tests against the common drywood termite, *Incisitermes snyderi* (Light) (Isoptera: Kalotermitidae), and recommended the addition of 10% (vol:vol) carbon dioxide to methyl bromide for house fumigations to control termites.

Lewis and Haverty (1996a, b) reported that a 1:22 mixture of methyl bromide and carbon dioxide under the trade name of MAKR® provided ≥ 99% mortality to termites in controlled tests. Although minor reports of significant increases in efficacy against insect pests are found in the literature through the late 1990s (e.g., Zettler & Gill 1997), there is no evidence in the literature that any methyl bromide and carbon dioxide combination (including MAKR®) became a viable commercial fumigant combination.

Cross (1994, unpublished data) found no enhancement of mortality in tests comparing methyl bromide alone with methyl bromide combined with carbon dioxide fumigation of *P*. *reticularis* eggs.

Methyl bromide combined with methyl iodide and/or chloropicrin Refer to page 28, Chloropicrin combined with methyl iodide and/or chloropicrin.

Methyl bromide combined with sulphuryl fluoride Cross (1994, unpublished data) found that combining methyl bromide with sulphuryl fluoride (156:182 mg/litre) obtained better efficacy and killed the eggs stage of *P. reticularis* more rapidly that methyl bromide alone or combined with carbon dioxide or carbon monoxide. Soma et al. (2004) reported on the efficacy of combining 15.0 g/m^3 methyl bromide with either 30.0 g/m^3 or 50.0 g/m^3 sulphuryl fluoride to control all life stages of an ambrosia beetle, *Xyleborus perforans* Wollaston (Coleoptera: Scolytidae), in logs imported from Papua, New Guinea; all life stages of an ambrosia beetle, *X*. *pfeili* Ratzburg, adult *C*. *fulvus* Niijima, infesting Japanese red pine; and all stages of small Japanese cedar longhorn beetle, *Callidiellum rufipenne* (Motschulsky) (Coleoptera: Cerambycidae), infesting Japanese cedar. Fumigations were done under tarpaulin at 18.4-20.3°C for 24 h. The objective of the research was to develop a methyl bromide and sulphuryl fluoride fumigant combination that would control all life stages (including the egg stage) to overcome the lack of efficacy of sulphuryl fluoride against insect eggs when used alone (see 3.n. Sulphuryl fluoride efficacy against insect eggs). Although Soma et al. (2004) reported complete control of all species and life stages treated, the data are difficult to assess because low numbers of control insects were reported (e.g., in the controls there were no *X. perforans* or *X. pfeili* eggs, and only 1 each *C. fulvus* egg and pupa). Moreover, of the total 1098 insects reported killed using 15.0 g/m^3 methyl bromide combined with 30.0 g/m^3 sulphuryl fluoride, there were no *X. perforans* or *X. pfeili* eggs treated and only nine each *C. fulvus* pupae or adults, and of the total 992 insects reported killed using 15.0 g/m^3 methyl bromide combined with 50.0 g/m^3 sulphuryl fluoride, there were no *X. pfeili* eggs and only six and five each C. *fulvus* eggs and pupae, respectively, were treated (Soma et al. 2004). Therefore, although the use of the methyl bromide and sulphuryl fluoride fumigant combination may present an interesting possibility, no degree of confidence can be assigned to the potential for the fumigant combination to provide a solution for controlling insect eggs compared with using sulphuryl fluoride alone. Significantly, no further research using methyl bromide combined with sulphuryl fluoride to control forest insect pests (or insect pests of any commodity) has been reported in the literature since the work of Soma et al. (2004).

4.10 Methyl iodide

Methyl iodide is a volatile organic halogen compound that can be found in nature and also is known as iodomethane. Methyl iodide is naturally produced and occurs in the global ocean but the processes involved in its formation are not fully understood (Stemmler et al. 2013). Significant methyl iodide emissions also occur globally from rice agriculture (Redeker et al., 2000). Methyl iodide is produced on a limited commercial scale for use as a methylating agent, laboratory reagent, pesticide, fumigant, and chemical intermediate (CDC 1984).

Methyl iodide has been evaluated for efficacy against a number of different organisms, including fungi (e.g., Hutchinson et al. 2000, Schmidt & Amburgey 1997, Schmidt & Christopherson 1997, Tubajika & Barak 2011), insects (Kawakami 2007; Naito et al. 2003; Shamilov 2012; Soma et al. 2005, 2006, 2007; Tubajika & Barak 2007, 2008), and nematodes (e.g., Dwinell et al. 2005). According to Klementz & Brash (2010), five articles appeared between 1974 and 2005 on the use of methyl iodide to control stored-product insect pest species that suggests a lack of interest in using methyl iodide for edible crops. Although research against insects, weeds, nematodes, and fungi has been tested for efficacy, most of the research consists of using methyl iodide volatilized *in situ* in small-scale laboratory trials (Klementz & Brash 2010). Currently, methyl iodide is registered as a fumigant only in Japan and Turkey (Klementz & Brash 2010).

Methyl iodide was registered in the US for use as a soil fumigant in 2007 (USEPA 2007, 2008a) specifically as a pre-plant biocide used to control insects, plant parasitic nematodes, soil-borne pathogens, and weed seeds for field-grown strawberries, peppers, tomatoes, stone fruits, tree nuts, grape vines, ornamentals and turf and nursery grown strawberries, stone fruits, tree nuts, and conifer trees (USEPA 2007). Methyl iodide was not registered for use as a fumigant against insects in any food crops (e.g., grains, fruits) or durables, such as logs, timber or wood products in the US (USEPA 2007).

4.10.1 Methyl iodide registration issues in the US

The first use of methyl iodide in the US was proposed for the pre-plant fumigation of soil for chilli pepper plantings, strawberry beds, and new fruit and nut tree orchard plantings in California (California EPA 2009, Urevich 2011). The manufacturer, Tokyo-based Arysta LifeScience Corporation, began product registration under the name Midas with the California Environmental Protection Agency (Urevich 2011). Extensive field and safety studies indicated that methyl iodide could be used safely as a soil fumigant (California EPA 2009) and the registration process progressed accordingly. Although a number of legal actions were brought against the state of California in 2010 seeking to reverse the methyl iodide registration process, none was successful in court and the registration of methyl iodide as a pre-plant soil fumigant appeared imminent (Pesticidereform.org 2010).

In 2012, however, Arysta LifeScience Corporation unexpectedly withdrew its application for registration of methyl iodide in California without comment (Corey 2013) and voluntarily withdrew its registration in the US (USEPA 2012b). Whether based on the lack of use by California farmers caused by adverse publicity created by the lawsuits, lack of economic viability because the fumigant proved to be too expensive, because adherence to the state-mandated 0.8-km buffer zones around treated areas proved too difficult (Urevich 2011), or simply because the costs of re-registration became uneconomic, Arysta LifeScience Corporation has no registration for use of methyl iodide in the US (USEPA 2012b) and appears to be planning no further soil fumigation research trials in the US (Starkey 2012). Table 13 shows the methyl iodide-containing products that Arysta LifeScience Corporation intended to market in the US.

Table 13. Methyl iodide products intended for marketing in the US as a liquid under pressure combined with chloropicrin in six formulations[a]

Product Names[b c]	Percent methyl iodide	Percent chloropicrin
Methyl iodide technical	99.80	N/A
Midas® 98:2	97.80	1.99
Midas® 50:50	49.90	49.75
Midas® EC[d] Bronze	49.90	44.78
Midas® 33:67	32.93	66.67
Midas® EC[d] Gold	32.93	61.69
Midas® 25:75	24.95	74.63

[a]After USEPA (2007).

[b]Midas® is the registered name for Arysta LifeScience Corporation products containing methyl iodide.

[c]The application for registration of Midas® in the US was voluntarily withdrawn by Arysta LifeScience Corporation in 2012 (USEPA 2012b).

[d]Emulsifiable concentrate for mixing with water.

Although, methyl iodide is currently registered as a fumigant in Japan and Turkey (Klementz and Brash 2010), there was no mention of Midas® on the corporate website (http://www.arystalifescience.com/) that lists their major products. No other countries were found to have methyl iodide registered as a fumigant.

Most work on methyl iodide as a fumigant for controlling insects was done in Japan. Naito et al. (2003) reported that a 24 h methyl iodide fumigation at 15°C against most life stages of nine forest insect pest species resulted in complete mortality of all stages for all species except one at a dosage rate of 50 g/m^3. Egg stages were controlled by dosage rates of 5-10 g/m^3 methyl iodide and most larval and pupal stages found under the bark or in the xylem or treated in artificial diet were controlled by 30 g/m3 methyl iodide. The xylem-dwelling larvae of *C. rufipenne* survived.

Soma et al. (2006) carried out fumigation tests to study the methyl iodide efficacy against the pinewood nematode and the larvae and pupae of two Cerambycid beetles. Fumigations were carried out for 24 h at 10, 15, 20 or 25°C using infested logs (100-200 mm diameter and 1.0 m long) under tarpaulin using a 51.2% load factor. Complete mortality of the Cerambycid larvae and pupae was obtained with fumigations using methyl iodide dosage rates and treatment temperatures of 84 g/m^3 at 10°C, 60 g/m^3 at 15°C, 48 g/m^3 at 20°C, and 36 g/m^3 at 25°C (Soma et al. 2006).

Soma et al. (2007) expanded their methyl iodide fumigation studies to include a wider range of forest insect pest species, including some that were found in logs imported from Malaysia. Complete mortality of eggs, larvae, pupae, and adults of four species and the adults or larvae (the only life stages tested) for two species was obtained using methyl iodide fumigations under tarpaulin with a 72 $\pm$ 2% load factor and 60 g/m^3 for 24 h at 7.9-10.6°C.

In a submission to the International Forestry Quarantine Research Group of the International Plant Protection Commission, Kawakami (2007) concluded that methyl iodide was a broad-spectrum fumigant that was nearly as efficacious as methyl bromide and he recommended the establishment of phytosanitary treatment schedules for fumigation with methyl iodide to control all forest pests (Table 14) and that a circulation fan be used for more than 30 minutes at the beginning of methyl iodide fumigations. However, these recommendations by Kawakami (2007, Table 14) were not adopted.

Table 14. Proposed methyl iodide treatment schedule for control of insect and nematode pests in infested wood (Kawakami 2007)a.

Temperature (°C)	Duration (h)	Dose (g/m3)	Load factor (%)	Minimum methyl iodide concentration (g/m3)			Minimum CT Product (g·h/m3)
				1 h	4 h	24 h	
10.0-14.9	24	84	≤ 50	42	20	14	450
15.0-19.9		60		36	18	12	400
20.0-24.9		48		30	16	10	350
≥ 25.0		36		24	14	8	300

[a]Taken from Klementz and Brash (2010), URL to Kawakami (2007) no longer available.

Japanese researchers carried out scaled-up evaluations of methyl iodide fumigation on infested logs using commercially viable delivery systems that they developed and patented (Klementz & Brash 2010). Klementz and Brash (2010) identified two methyl iodide delivery systems from the literature based on research done in Japan and one delivery system developed in the US, including:

1. A pressurised mixture of methyl iodide and carbon dioxide was first described by Soma et al. (2006). The mixture consists of a 50% w/w mixture of methyl iodide and carbon dioxide in a high-pressure gas cylinder. The methyl iodide and carbon dioxide mixture is released from the cylinder as an aerosol into the fumigation space. The method (Soma et al. 2006) was registered in Japan as an agrichemical for log disinfestation in 2005 and then patented for the control of wood parasitic nematodes (Abe et al. 2005).
2. A forced convection method first described by Soma et al. (2007) consists of a methyl iodide and air mixture in a high pressure cylinder. The pressurised methyl iodide is dispersed by release from the cylinder into the fumigation space.

3. Poss et al. (2009) and Singh et al. (2010) patented a low-boiling or azeotrope-like composition of methyl iodide and hydrofluorocarbons that boil at temperatures below 42.4°C. The hydrofluorocarbons use in combination with methyl iodide are 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane and cis-1,3,3-tetrafluoropropene. The addition of the azeotrope allows the mixture to be handled like methyl bromide and the same fumigation equipment to be used (Poss et al. 2008). However, since the patent of Singh et al. (2010) there has been no further research pertinent to chemical additions to methyl iodide to facilitate handling or the use of methyl bromide application equipment.

Klementz and Brash (2010) were unable to find any references to methyl iodide residues, but they determined that methyl iodide, like methyl bromide, is heavily sorbed by some commodities, especially logs and wood packaging, and could pose a hazard from desorption after treatment. Sorption for methyl iodide appears to be greater than for methyl bromide (although they have not been compared directly). Naito et al. (2003) found that only 20-36% of the applied methyl iodide in laboratory fumigations of logs remained at the end of a 24-h treatment at 15°C with a 25% load factor. Studies by Soma et al. (2005) resulted in gas ratios (gas concentration at the end of fumigation/applied dose x 100) of 24-45% after a 24-h fumigation of pine wood packing materials with a 25% load factor. In a fumigation test with 51% load factor of red pine under tarpaulin, Soma et al. (2006) found gas ratios dropped to 15-30% after 24 h treatment (51% loading). Similar studies by Soma et al. (2007 with logs and Zettler et al. (1998) with walnuts found similar decreases in methyl iodide caused by sorption during fumigation (Klementz & Brash 2010). Although variations in sorption rates were found by the Naito et al. 2003 and Soma et al. 2005, the losses to sorption during methyl iodide fumigation are significant. The variations reported in the literature suggest that the losses may be dependent on the dosage applied, the treatment temperature and the load factor (Klementz & Brash 2010). Unfortunately, there is no information in the literature on the fate of methyl iodide that has been sorbed or the rates of desorption after fumigation (Klementz & Brash 2010), which is problematic when considering the potential for using methyl iodide as a disinfestation treatment for logs.

Although Klementz and Brash (2010) suggested that methyl iodide warranted further investigation as a biosecurity treatment because methyl iodide has a broad spectrum of activity against a wide range of pests and their life stages, more recent literature, especially the withdrawal of registration in the US, suggests that methyl iodide has a number of serious issues that must be resolved, including sorption, penetration and residues. With little or no support worldwide for the use of methyl iodide based on relatively little research compared with methyl bromide or phosphine, any attempt to prioritise methyl iodide as a potential methyl bromide alternative for export logs must first consider the issues, including those defined by Klementz and Brash (2010), that will require further study:

- Efficacy data for key New Zealand forest insects must be developed. Specifically, the most methyl iodide-tolerant species and life stage must be identified for use in establishing dosage rates and fumigation times at selected temperature ranges, and the CT Products used in monitoring regulatory fumigation treatments.
- Penetration studies must be done to ensure that methyl iodide penetrates to the site at which the target pest is found.
- Both the sorption and the fate of methyl iodide during fumigation and post-fumigation aeration must be quantified for logs and predictive models must be developed to extrapolate the gas concentrations needed to kill the target pests per volume of logs and to provide the data that will be required to develop safety standards.

- Some literature indicates that methyl iodide is similar to methyl bromide and can be used as a substitute (Kawakami 2007, Klementz and Brash 2010). The lack of basic methyl bromide efficacy data for New Zealand forest insects was noted in section 2.3.2. The methyl bromide efficacy data must first be obtained before comparisons with methyl iodide, or any other candidate fumigant, can be made. When the methyl bromide efficacy data become available, methyl iodide and other fumigants can be compared directly on the basis of efficacy, commercial application, economic viability, etc.
- Can methyl iodide fumigation be adapted easily into the New Zealand log export pathway without adversely affecting the movement of logs through the port? Fumigation times at the temperature ranges found at New Zealand ports, and post-fumigation aeration and handling, must fit within the commercial time parameters.
- A cost-effective methyl iodide delivery system must be developed. Any methyl iodide delivery system used in New Zealand will depend on industry preferences and must provide both safety and efficiency.
- The costs for the introduction and use of methyl iodide in New Zealand must be evaluated. These costs will depend on a number of factors, including costs for methyl iodide registration in New Zealand, fumigation delivery method, safety requirements, required modifications to current port and log handling practices, and product cost.
- Health and safety issues, including stewardship, must be examined and established, e.g., can methyl iodide be handled in the same way as methyl bromide; is desorption after treatment a problem and, if so, how can that be managed; what safety requirements are required for handling methyl iodide will be necessary; will a buffer zone be required and, if so, will the buffer zone adversely affect port operations?
- An important consideration is whether to attempt registering a chemical in New Zealand that has significant “negatives” from the legal actions taken against its use in the US (Pesticidereform.org 2010). There an atmosphere was created that adversely impacted the economic viability of methyl iodide (Urevich 2011), became national news (Wollan 2013), led to state bans on its use (Richardson 2010), and caused the manufacturer to withdraw its legal registration (San Jose Mercury 2012, USEPA 2012b). The following example is provided to emphasise the point specific to New Zealand:

  In addition to their US application, Arysta LifeScience Corporation application ERMA200392 was approved 24 March 2010 by the New Zealand Environmental Risk Management Authority (now New Zealand Environmental Protection Authority) to import or manufacture (into containment) Ripper 500, a combination of 50% methyl iodide and 50% chloropicrin “for field trials and to evaluate lower application rates using virtually impermeable film with the intended use to treat soil before the planting of strawberry runners” (NZERMA 2010a, b). Shortly thereafter, Auckland-based Elliott Technologies Limited (now Etec Crop Solutions Limited) application HSR07095 (tendered in 2008, about two years before the Arysta LifeScience Corporation application) was approved on 21 June 2010 by the Environmental Risk Management Authority to import or manufacture Ripper 330 (33% methyl iodide and 67% chloropicrin), Ripper 500, and Ripper 980 (98% methyl iodide and 2% chloropicrin) (NZERMA 2010c). The approvals for the two Ripper applications came to the attention of the New Zealand Environmental Risk Management Authority 2011 Annual Monitoring Report that provided oversight of the Hazardous Substance and New Organisms Act performance and controls (NZERMA 2011b). The remarks in the Monitoring Report (NZERMA 2011b) are reproduced here *verbatim* because of their importance to methyl iodide as a potential fumigant for New Zealand export logs.

> "Hazardous substances decisions and decision-making (NZERMA 2011b, page 16): Approval for the soil fumigant 'Ripper'
>
> In June 2010, the soil fumigant Ripper was approved by ERMA New Zealand. Ripper contains methyl iodide and chloropicrin, and approval was sought for its use within the strawberry industry as an alternative to methyl bromide, an Ozone Depleting Substance (ODS). Although Ripper is not an ODS, it is highly toxic and was approved with stringent controls to protect workers and the public from exposure.
>
> The need to apply for a highly toxic substance approval was directly associated with the requirement under the Ozone Layer Protection (OLP) Act to phase out methyl bromide. This decision demonstrates how the requirements of one regulatory regime (OLP Act) *can have potentially perverse outcomes in another regime* (HSNO Act). The search for alternatives to ODS requires that consideration be given to substances *significantly more harmful to human health and the environment*, other than the ozone layer." (authors' italics)

These comments from the Monitoring Report (NZERMA 2011b) indicate that the Environmental Protection Authority may take issue with an application for approval for large-scale use of methyl iodide alone (or in combination with chloropicrin) as a phytosanitary treatment for New Zealand logs. A footnote to the Ripper 500 trial approval (NZERMA 2011b): According to the Ministry for Primary Industries Agricultural Chemicals and Veterinary Medicines register (https://eatsafe.nzfsa.govt.nz/web/public/acvm-register, updated 24 January 2013), there is no registration or use label for Ripper 330, 500 or 980, or any fumigant containing methyl iodide in New Zealand.

4.10.2 Methyl iodide research to control fungi and nematodes

In addition to insect control, methyl iodide also has been studied as a fumigant for the control of fungal pests of logs (Hutchinson et al. 2000, Schmidt & Amburgey 1997, Schmidt & Christopherson 1997, Tubajika & Barak 2011) and nematodes in unseasoned pine (Dwinell et al. 2005). However, the body of literature, as shown here, is very small.

4.10.3 Methyl iodide combined with other fumigants and gases

<u>Methyl iodide combined with chloropicrin</u> Refer to page 28, Chloropicrin combined with methyl bromide and/or methyl iodide.

<u>Methyl iodide combined with carbon dioxide</u> Abe et al. (2009) and Soma et al. (2006) reported research on the efficacy of methyl iodide combined with carbon dioxide for controlling wood parasitic nematodes and longhorn beetles. Abe et al. (2009) attempted to patent the methyl iodide and carbon dioxide fumigant combination, but the patent was either rejected or abandoned in 2010. No other research related to combining methyl iodide with carbon dioxide was found in the literature.

<u>Methyl iodide combined with isothiocyanate</u> - Abe et al. (2005) reported on results of combining methyl iodide with isothiocyanate to control *B. xylophilus* in solid wood packing materials. Abe et al. (2009) were granted a US Patent for fumigant for wood parasitic nematodes and wood fumigation method; the method consisting of "using methyl iodide dissolved in liquefied carbon dioxide in combination with one or more compounds selected from the group consisting of sulphuryl fluoride, methyl isothiocyanate, phosphine, ethylene oxide, carbonyl sulfide, and propylene oxide." An internet search found no further discussion of applications specific to the Abe et al. (2009) patent.

Other than the references cited above, no other references to the use of methyl iodide combined with other fumigants or compounds were found in the literature.

Because of the issues illustrated in this section, the record of methyl iodide use in the US, and the comments made in the Monitoring Report (NZERMA 2011) that are available to the public, the authors consider that methyl iodide should not receive further consideration as a potential methyl bromide alternative.

4.11 Methyl isothiocyanate

Methyl isothiocyanate is an organo-sulphur fumigant that is a highly flammable colourless liquid with a sharp odour that can be lethal by inhalation of even small quantities of vapour and has no warning odour at low concentrations (Chemical Book 2010). Similar to carbonyl sulphide, methyl isothiocyanate is a strong lachrymator (tear gas) (Chemical Book 2010). Methyl isothiocyanate is a general biocide used to control weeds, nematodes, and soil and wood fungi that may be mixed with 1,3-dichloropropene when used as a soil fumigant and also is the active principle of the soil fumigant, metam-sodium (*referred to by some authors as metham sodium*), a dithiocarbamate, from which methyl isothiocyanate is evolved as a gaseous degradation product (Rubin 2003).

Metam-potassium was first registered in the United States in 1973 as a fungicide, a bacteriostat, and a microbiocide in a variety of commercial and industrial applications, such as pulp and paper mills, cooling tower waters, metalworking cutting fluids, and adhesives, and in 1994, the use of metam-potassium expanded to include food and feed uses when used as a soil fumigant (USEPA 2009a). Metam-sodium was first registered in the United States in 1975. Metam-sodium is one of the most widely used agricultural pesticides in the United States and is presently registered on a wide variety of food and feed crops along with a variety of antimicrobial and industrial uses (USEPA 2009a). Metam-sodium and metam-potassium are converted to methyl isothiocyanate in the environment, particularly in the presence of moisture and it is methyl isothiocyanate that performs the fumigating activity (USEPA 2009a). Methyl isothiocyanate and methyl isothiocyanate-generating compounds are considered to be very effective in controlling *B. xylophilus* (Liu et al. 2010).

Generally, registered metam-sodium and metam-potassium application/fumigation uses fall into four basic categories: (1) use as an agricultural soil fumigant for all food, feed, and fibre crops; (2) use on golf course turf and for application to small areas of turf and soil; (3) use as a root-control agent in drains and sewers; and (4) use for a number of antimicrobial and industrial uses, including treatments for sugar (raw beets and cane sugar) processing facilities; leather; sewage, sludge, and animal waste; cooling water facilities; industrial water purification facilities; paints and coatings; petroleum operations; and remedial wood treatment (USEPA 2009a). In the US, methyl isothiocyanate (as a stand-alone compound not evolved from metam-sodium or metam-potassium) is registered as an active ingredient for only one use, as an antimicrobial agent for remedial wood treatment (USEPA 2009a).

Products registered in the US, such as MITC-Fumigation®, G-Fume 96 Granular®, Pole Fumigation, and Wood Fume, are used in the form of metam-sodium applications to Douglas fir poles (e.g., utility poles), sleepers (railroad ties), and other large wood construction pieces (e.g., bridge timbers) primarily for the prevention or amelioration of fungal rot and insect attack (e.g., termites) (Morrell 2012). Specifically, the three fumigants are metham sodium (32.7% sodium n-methyldithiocarbamate in water) and methyl isothiocyanate (97% active in aluminium vials), and dazomet (which produces methyl isothiocyanate) are registered as restricted-use pesticides for wood in the US and provide protection to Douglas-fir poles for 7-10 years and to southern pine poles for 3-6 years (Morrell 2012, Zahora 1988). The methyl isothiocyanate residue is long-lasting and both penetration and protection longevity are based on wood species, temperature, and moisture content (Lebow & Morrell 1993, Morrell 1994). Methyl isothiocyanate and compounds that evolve methyl isothiocyanate for protecting utility poles, sleepers, etc., cannot be applied by standard commercial fumigation methods but are placed into holes drilled into the wood (the holes are then sealed) to facilitate the long-term diffusion of the fumigant through the wood (Morrell 2012).

Methyl isothiocyanate-generating products are registered in New Zealand as a fungicide, herbicide, bactericide, and nematicide under the trade name, FUMASOL™, by ETEC Crop Solutions Limited, Manukau, and BASAMID® Granular by Mitsui & Co., Auckland (NZFSA 2014).

Sasaki et al. (1998) patented a “new insect fumigant for timber pest which can treat on a large scale with a small amount in a short time by dissolving methyl isothiocyanate gas (2%:98% wt:wt). Timbers are fumigated by “jetting” the active ingredients into the treatment room using the pressure of the liquefied high-pressure gas” (Sasaki et al. 1998). However, further internet search found neither the company by name nor any more references to the patent.

Because the primary treatment method for using methyl isothiocyanate and methyl isothiocyanate-generating compounds is by insertion into holes drilled in wood (e.g., utility poles), and because methyl isothiocyanate is highly toxic to both fish (lowest LC_{50} = 51.2 ppb) and aquatic invertebrates (lowest LC_{50} = 55 ppb) (USEPA 2009a), the authors do not consider methyl isothiocyanate as a candidate methyl bromide alternative.

4.11.1 Methyl isothiocyanate combined with other fumigants or compounds

<u>Methyl isothiocyanate combined with ethyl formate</u> – Refer to section 4.6.1, ethyl formate combined with methyl isothiocyanate.

<u>Methyl isothiocyanate combined with sulphuryl fluoride</u> - Soma et al. (2004) reported on the efficacy of combining 15.0 g/m^3 or 21.0 g/m^3 sulphuryl fluoride with 15.0 g/m^3 or 21.0 g/m^3 methyl isothiocyanate to control *X. perforans* (all life stages) in logs imported from Papua, New Guinea; *X. pfeili* (all life stages) and *C. fulvus* Niijima (all life stages) infesting Japanese red pine; and *C. rufipenne* adults infesting Japanese cedar. Fumigations were done under tarpaulin at 18.3-21.2°C for 24 h and a 73-76% load factor. The objective of the research was to develop a sulphuryl fluoride and methyl isothiocyanate fumigant combination that would control all life stages (including the egg stage) to overcome the lack of efficacy of sulphuryl fluoride against insect eggs when used alone (see 4.15.2 Sulphuryl fluoride efficacy against insect eggs). Although Soma et al. (2004) reported completed control of all species and life stages treated with the two sulphuryl fluoride and methyl isothiocyanate combinations, the data are difficult to assess because low numbers of control insects were reported (e.g., in the controls there were no *X. perforans* or X. *pfeili* eggs, and only one each *C. fulvus* egg and pupa). Moreover, a total of only 852 or 519 insects were tested for all species and life stages fumigated with 15 g/m^3 sulphuryl fluoride combined with 15 g/m^3 methyl isothiocyanate or 21 g/m^3 sulphuryl fluoride combined with 21 g/m^3 methyl isothiocyanate, respectively. Therefore, although the use of the sulphuryl fluoride and methyl isothiocyanate fumigant combination may present an interesting possibility, no degree of confidence can be assigned to the potential for the fumigant combination to provide a solution for controlling insect eggs compared with using sulphuryl fluoride alone.

Abe et al. (2004) reported on a "new" fumigant called Ecotwin that was a mixture of 30.0% each sulphuryl fluoride and methyl isothiocyanate in a liquefied carbon dioxide formulation in a pressurised cylinder. The data provided as a basis for the efficacy of Ecotwin to control pests in logs was identical to the results of Soma et al. (2004) that were discussed above. The six authors listed on Abe et al. (2004) were among the 15 authors listed on Soma et al. (2004), hence the data were recycled to facilitate the announcement of the new fumigant, Ecotwin.

Following Abe et al. (2004), Kawakami (2005) reported the results of dose-response tests with *B. xylophilus* using sulphuryl fluoride combined with methyl isothiocyanate at equal g/m^3 rates of 15:15, 21:21, 27:27, and 33:33 g/m^3 at 10, 15 or 25°C for 24 h to develop fumigation schedules. Additionally, Kawakami (2005) reported the results of dose-response tests using sulphuryl fluoride combined with methyl isothiocyanate at equal g/m^3 rates of 15:15 g/m^3 at 18.3 - 21.2°C to develop fumigation schedules for *C. rufipenne* (20 insects tested), *C. fulvus* (92 insects tested), *X. pfeili* (366 insects tested), and *X. perforans* (41 insects tested) with only one replication reported for all species. The dose-mortality data of Kawakami (2005) for developing fumigation schedules for pine saw nematode provided large numbers of treated individuals (totals 11,500 to 97,400 nematodes per test replication) with 100% mortality obtained in all but two treatments. However, Kawakami reported only one test replication for each temperature (10, 15 or 25°C) and sulphuryl fluoride-methyl isothiocyanate mixture (15:15, 21:21, 27:27, or 33:33 g/m^3) tested. The lack of test replications for both the nematode and insect dose-response studies and the low numbers of test insects used in the insect dose-response studies would not meet the criteria for statistical analysis of quarantine treatments data described by Robertson et al. (1994) to demonstrate any degree of confidence that fumigation schedules developed from the Kawakami (2005) data would ensure quarantine security.

Another issue with the Kawakami data is the survival of nematodes in the dose-response tests using 15:15 or 21:21 g/m^3 mixtures of sulphuryl fluoride and methyl isothiocyanate at 15°C. With only single replications for each test, Kawakami (2005) reported that the survival was the result of a shortage of applied dose in one case of survival and the result of a lower CT product in the other. With only one replication per dose-response treatment, these explanations for the survival would appear problematic. Regardless, Kawakami (2005) provided the fumigation schedules shown in Table 15.

Table 15. Proposed mixture of methyl isothiocyanate and sulphuryl fluoride fumigation schedule[a]

Temperature (°C)	Time (h)	Dose (g/m^3)	Minimum gas concentration of sulphuryl fluoride (mg/l)			Minimum CT product for sulphuryl fluoride (mg•h/l)
			1 h	4 h	24 h	
10.0-14.9	24	33:33	29	25	12	490
15.0-24.9		27:27	24	21	11	420
≥ 25		21:21	19	17	10	350

[a]From Kawakami (2005)

Abe et al. (2009) were granted a US Patent for fumigant for wood parasitic nematodes and wood fumigation method; the method consisting of "using methyl iodide dissolved in liquefied carbon dioxide in combination with one or more compounds selected from the group consisting of sulphuryl fluoride, methyl isothiocyanate, phosphine, ethylene oxide, carbonyl sulfide, and propylene oxide." An internet search found no patent for a sulphuryl fluoride-methyl isothiocyanate combination called Ecotwin, but the fumigant combination descriptions in the US patent (Abe et al. 2009) include sulphuryl fluoride and methyl isothiocyanate mixtures. Abe et al. (2004) identified Ecotwin as a trademark of Yashima Sangyo Limited, a multinational chemicals and chemical preparation corporation that holds the Abe et al. patent. However, a review of the Yashima Sangyo company profile and products did not find any references to the production or sale of Ecotwin, nor could "Ecotwin fumigant" be found on the internet with the exceptions of the Abe et al. (2004, 2009), Kawakami (2005) and Soma et al. (2004) citations discussed above. The subject of using Ecotwin has been reviewed for a number of years by the Technical Panel on Phytosanitary Treatments (International Plant Protection Convention, Food and Agriculture Organization of the United Nations), but there has been no approval for the use of Ecotwin. Perhaps noteworthy is the brief comment in the most recent Technical Panel on Phytosanitary Treatments report (TEAP 2013b) that states: "The lead for methyl isothiocyanate and sulphuryl fluoride (Ecotwin mixture) fumigation for *Bursaphelenchus xylophilus*, Coleoptera: Cerambycidae, and Coleoptera: Scolytinae of wood packaging material (2007-102) was concerned of the fact [*that the responsible party or parties*] had not yet responded to requests for information." Whether the limited data provided by Abe et al. (2004), Kawakami (2005) and Soma et al. (2004) may or may not have met the criteria and standards for approval by the Technical Panel on Phytosanitary Treatments for use on solid wood packing materials became irrelevant. At the Quadrilateral Methyl Bromide Alternatives Project Working Group Meeting In Association with The Conference on Methyl Bromide Alternatives & Emissions Reductions (Methyl Bromide Alternatives Outreach) Wednesday 7 November 2012, Mr. Kunihiko Yamada, Yokohama Plant Protection Station, Japan, announced the proposed fumigant for the treatment of logs called Ecotwin (sulphuryl fluoride combined with methyl isothiocyanate) had been deregistered on 26 September 2012 (K. Glassey, personal communication).

The Ecotwin story is similar to that of MAKR® (Lewis and Haverty 1996a, b) discussed in section 4.9.1 regarding methyl bromide combined with carbon dioxide, and that of methyl iodide (e.g., Ripper®) (Corey 2013; NZERMA 2010c, 2011b; USEPA 2012b; Starkey 2012) discussed in section 4.10. Methyl iodide. Together they exemplify the difficulty and complexity chemical companies face in obtaining registration for new fumigant use, the loss of registration after commercialisation for economic, environmental or other reasons, and the reason there are lost trails of reference citations in the literature whereby fumigants are reported as if labelled for use only to disappear within a few years.

Liu et al. (2010) reported results of studies in which fumigations with sulphuryl fluoride combined with methyl isothiocyanate in concentrations of 11.8, 38.7, 35.5 or 33.8 g/m^3 sulphuryl fluoride to 2.5%, 5.0%, 10.0%, or 50% methyl isothiocyanate, respectively, provided synergistic effects in obtaining 99% mortality of *B. xylophilus* compared with 75.5 g/m^3 sulphuryl fluoride required to provide 99% mortality of the nematode when used alone. The results of Liu et al. (2010) were reported as an abstract for a presentation and they are not found in a refereed journal article in the literature.

4.12 Nitric oxide

Nitric oxide is a naturally produced small molecule in almost all types of organisms including bacteria, fungi, plants and animals, and functions as a ubiquitous signal molecule to modulate a wide range of biological and physiological processes (Liu 2013). Most literature pertaining to nitric oxide in the postharvest field is specific to the ability of nitric oxide to inhibit or delay ripening in fruits and vegetables (Leshem et al. 1998, Soegiarto & Wills 2004). Nitric oxide is mentioned in this review only because Liu (2013) demonstrated that nitric oxide could be used as a fumigant to control the life stages of some postharvest pests, including aphids, thrips, and a stored-product beetle. From this work, Liu (2013) recommended that nitric oxide could be considered as a potential fumigant alternative for both methyl bromide and phosphine. Because nitric oxide reacts readily with air to form nitrogen dioxide, Liu (2013) carried out fumigation with nitric oxide under ultra low ($\leq$ 50 ppm O_2) oxygen conditions. In comparing nitric oxide fumigation with methyl bromide and phosphine, the strongest argument for further research was that nitric oxide was environmentally friendly. Although ultra-low oxygen conditions may be practical for high-value fresh produce (e.g., lettuce or fruit), it would not be practical for logs.

4.13 Ozone

Ozone is formed naturally in the upper atmosphere from oxygen by ultraviolet light and by atmospheric electrical discharges, such as lightning or the aurora borealis and aurora australis, and it is found in lower levels of the atmosphere, primarily as a result of photochemical oxidation of hydrocarbons from automobile and industrial emissions, and is coincidentally produced by photocopiers, electrical transformers, and other electrical devices with the result that humans are exposed to low levels of ozone on a daily basis (Guzel-Seydim et al. 2004, Xiu 1999).

Ozone is a strong antimicrobial agent that has been recognised internationally as a safe (GRAS) compound with numerous potential applications in the food industry (Kim et al. 1999). Following four decades of inactivity in developing new ozone uses since the USDA first approved the use of gaseous ozone for meat storage (Majchrowicz 1998), the US Food and Drug Administration allowed the use of ozone in gaseous and aqueous phases as an antimicrobial agent on food, including meat and poultry, and as an additive on raw agricultural commodities for commercial purposes (Guzel-Seydim et al. (2004).

Ozone is an unstable three-atom allotrope of oxygen formed by the excitation of molecular oxygen (O_2) into atomic oxygen (O) in an energising environment that allows the recombination of atoms into ozone (O_3). Ozone is a powerful oxidising agent that is used for disinfection processes in aquaculture, marine aquaria, fish disease laboratories, heating and cooling units, water treatment, food processing, bleaching of paper pulp, and treatment of contaminated groundwater (Weavers & Wickramanayake 2001). Ozone generation is more efficient at low temperatures as a result of thermal decomposition of ozone at high temperatures, and gaseous ozone is more stable than aqueous ozone (Weavers & Wickramanayake 2001). In the generation of ozone for commercial applications, a corona discharge is widely used, which consists of passing dry air or oxygen between two electrodes separated by a glass or ceramic dielectric material resulting in 1-3% ozone concentrations (Weavers & Wickramanayake 2001).

The idea of using ozone against insect pests has gained increasing interest over the past decade to control pests of stored products (e.g., Callahan 2003; Frazer 2004; Leesch et al. 2003, 2004; Mendez et al. 2003; Rajendran & Parveen 2004) and phytopathic fungi (Palou et al. 2003). A bibliography of literature reporting on ozone efficacy against various invertebrates and pathogens was provided by Jamieson et al. (2009a). Jamieson et al. (2009a) studied the feasibility of using of ozone as a potential fumigant for treating sea containers. Jamieson et al. (2009a) and found that brown garden snails, *Helix aspersa* (Müller) (syn. *Cornu aspersum*), were the most tolerant pest to ozone with an exposure time of 11.3 h at 10,000 ppm ozone to obtain 99.9% mortality. However, mould mites, *Tyrophagus putrescentiae* (Schrank) (Sarcoptiformes: Acaridae); *E. postvittana* eggs and pupae; American cockroach, *Periplaneta americana* (L.) (Blattoidea: Blatidae), and greedy scale, *Hemiberlesia rapax* (Comstock) (Hemiptera: Diaspididae), immatures and adults; hide beetle, *Dermestes maculatus* De Geer (Coleoptera: Dermestidae), larvae; white-footed house ants, *Technomyrmex jocsus* Forel (Hymenoptera: Formicidae); false katipo, *Steatoda capensis* Hann (Arachnida: Theridiidae); and nurseryweb spiderlings, *Pisaurina mira* Simon (Arachnida: Pisauridae); were more tolerant and required < 11 h at 10,000 ppm ozone to obtain 99.9% mortality (Jamieson et al. 2009a)

Armstrong et al. (2012c) suggested that ozone, using a patented OzoFume® process that provided dry ozone gas under vacuum fumigation in a closed system that could control the surface pests on kiwifruit exported from New Zealand. Work also has been done on the use of ozone to control coffee berry borer and coffee leaf rust urediospores in green coffee (J. Armstrong, unpublished data).

Ozone has a number of important characteristics that make it a poor choice as an alternative fumigant to methyl bromide for New Zealand log exports:

- Ozone is a powerful oxidising agent that reacts with a wide range of materials, including dust in the air, natural products, such as rubber, and synthetic compounds, such as plastics (Guzel-Seydim et al. 2004, Jamieson et al. 2009, Mustafa 1990, Ozone Solutions 2014, USEPA 1999). Therefore, fumigation must be done in stainless steel chambers or metal chambers with non-reactive coatings and all seals must be non-reactive materials (Jamieson et al. 2008). Fumigation under tarpaulin would not be an option unless the tarpaulin was made of non-reactive material.
- Ozone does not penetrate through barriers readily. Armstrong (unpublished data) found that the OzoFume® process described above would not kill fruit fly eggs or larvae inside papaya fruit, and other barriers such as fruit surfaces were nearly impermeable to ozone gas under fumigation conditions (Hollingsworth & Armstrong 2004, Leesch 2003, Palou et al. 2003). Therefore, ozone may not be able to penetrate into sites in the bark or cambium, or into tunnels and chambers sealed by frass where the target forest insects are found.
- Ozone dissolves rapidly in water (Table 7) and then degrades rapidly to oxygen (half-life = 15 minutes at 25°C) and ozone in air also degrades rapidly to oxygen with a half-life of about 30 minutes (Ozone Solutions 2014). Therefore, ozone absorbed by water and degraded in air would need to be replaced continuously to maintain the ozone concentration required for treatment efficacy.
- Additionally, as ozone readily dissolves in water and, therefore, the substrate (e.g., wheat or grains) must have low moisture content (Guzel-Seydim et al. 2004, Leesch et al. 2003). The use of “dry” ozone gas under vacuum appears to be the only technology that can get ozone to disperse readily through small interstitial spaces, such as surrounding particles of garlic powder (G. Carman, personal communication). Therefore, logs with high moisture contents could be expected to absorb and degrade ozone rapidly. Moreover, an OzoFume®-type closed system on a scale needed for log exports would not be economically feasible, nor would the energy costs for drawing a vacuum > 1m^3 required to carry out the OzoFume® process.

Ozone is not considered to be a potential methyl bromide alternative for these reasons.

4.14 Phosphine

Richardson (1974) studied phosphine for freight container fumigation and for wood penetration, which the reviewers found to be the first report on the use of phosphine to control a forest insect in wood (*S. noctilio*). The test insects included three stored-product species, a termite (a structural pest rather than a forest insect pest), and *S. noctilio* (the only forest insect tested). Although Richardson (1974) used Dräger phosphine detector tubes (Heseltine 1973) to determine phosphine concentrations during fumigations in the aluminium freight containers (33.4 m^3), steel fumigation chambers (0.7 m^3), or metal drums (208.2 m^3), no actual phosphine concentrations in ppm were given. Instead, Richardson (1974) reported only the fractional number of 3.0 g aluminium phosphide (Phostoxin®) tablets used as an equivalent of 20, 30, 40 or 60 tablets/28.32 m^3 (= /1,000 ft^3, the standard fumigation schedule volume used in the US). For example, 0.06 tablets/m^3 were used in freight container fumigations, 0.7 or 1.41 tablets/m^3 were used in tests in the fumigation chambers, and 1.06, 1.41 or 2.10 tablets/m^3 were used in the metal drum fumigations. The three studies Richardson (1974) carried out include:

- Wood penetration was tested by confining ≈10 *O*. *surinamensis*, ≈20 *S*. *granarius* and ≈50 *T*. *confusum* in wire cages in a small (8 mm x 8 mm x 20 mm) cavity centered between two blocks (150 mm x 100 mm x 25 mm) of smoothly planed *P*. *radiata* that were held together with masking tape. Two 72-h fumigations were done at 21-24°C. No humidity conditions were given. Because all test insects died, Richardson (1974) concluded that the results demonstrated good penetration by phosphine through the wood.
- Efficacy against the subterranean termite, *Nasutitermes exitiosus* (Hill) (Isoptera: Kalotermitidae), and penetration into the nest was tested by exposing 1-liter glass containers topped with screen containing a nest of 4,000 to 5,000 termites that had been built up inside each container from decayed wood and soil over a 3-4 week period (Richardson 1974). Two fumigation tests with the termites were done in the 33.4 m^3 freight containers for 72 h at 4-16°C and using an 85% load factor achieved by filling the container with sealed fibreboard boxes filled with newspapers or polyethylene bags. No humidity conditions were given. Because complete mortality was obtained, Richardson (1974) concluded that phosphine "had high efficiency" against termites in nests.
- The efficacy of phosphine against *S*. *noctilio*, the only forest insect pest used, in "small pine logs" (size, species or moisture content of logs not given) in the 208.2-liter metal drums (≈33% load factor) covered with tarpaulin. Three fumigations were done in the metal drums at 26-31°C and 50-75% RH. Richardson (1974) was only able to achieve 6.0, 93.7 and 94.1% mortality for 1.06, 1.41 and 2.10 tablets used. Because there were no controls, the percent mortalities were estimated based on the 6.0% mortality in the fumigation using 1.06 tablets. Richardson (1974) reported that the Dräger tube readings indicated the tarpaulins used to seal the drums permitted significant leakage and, because there was less phosphine than expected, concluded that the mortality data indicated that phosphine "showed some promise against" *S*. *noctilio*.

Richardson (1974) was published in a non-peer reviewed trade journal and has numerous flaws in experimental design, including:

- The 'wood penetration' studies consisted of only two fumigations in which blocks of wood were held together with masking tape. The combined termite efficacy and termite nest penetration studies also consisted of only two fumigations.
- The three replications claimed for the efficacy tests against *S*. *noctilio* actually consisted of only one fumigation at each of the phosphine doses tested. Moreover, the infestation was limited to 16-17 insects per fumigation with no mention of life stage, log diameter, or position of insects in the logs and there were no untreated controls in the test. Also, the three fumigations with *S*. *noctilio* were done at 26-31°C, which is a relatively high fumigation temperature compared with the other tests described by Richardson (1974).
- No actual phosphine concentrations were given. Therefore, the actual amount of phosphine in the freight containers, fumigation chambers and metal drums during fumigation is unknown. Moreover, the accuracy of Dräger tube readings depends on the consistent purging of sampling tubes (the tubes that pass through the wall of the fumigation vessel to the point where the gas sample is taken) (Heseltine, 1973). Therefore, Dräger tube readings

give approximate concentrations and test validity depends on checking Dräger tube readings against a gas chromatograph set up to analyze for phosphine (P. Hartsell, personal communication).

- The validity of the phosphine concentrations used is further confused by the use of fractions of aluminium phosphide tablets. If the 3.0 g tablets were 55% aluminium phosphide and 45% inert ingredients by weight (Richardson 1974), cutting them into fractions may or may not have altered the amount of phosphine gas that would evolve during fumigation. The phosphine concentrations during the different fumigations were claimed to be based on "theoretical dosages" no direct comparisons of the fractions of tablets used with phosphine concentrations expected from 20, 30, 40 or 60 tablets under similar conditions.

The work of Richardson (1974) was, at best, very preliminary and the results are questionable because of the experimental design flaws and lack of viable data. No subsequent research was reported by Richardson or by any other author based on the work of Richardson (1974). With the exceptions of Leesch et al. (1984) and Oogita et al. (1997), no research using phosphine to control log or timber pests was done until Primaxa (2002) and Whitham (2002).

An overview for the use of phosphine as a phytosanitary treatment for New Zealand export logs is provided in 2.3.3, Fumigation of New Zealand export logs with phosphine and in referenced reports of research with overview information by Brash et al. (2010). Research specific to the use of in-transit phosphine fumigation of New Zealand export logs in ship holds has been ongoing since 2002 and is represented by the work of Brash et al. (2010), Frontline Biosecurity (2003a, b; 2005), Genera (2007), Glassey et al. (2005), Hosking (2005a, b, c; 2008), NZMAF (2007b), Primaxa (2002), Spiers (2003), Wang and Goss (2010), and Whitham (2002). The only other report of phosphine fumigation in ship holds was for the control of pinewood nematode in wood chips (Leesch et al. 1989).

Oogita et al. (1997), Soma et al. (2005), Tumambing (2005, 2007), and Wang et al. (2003b) reported on the efficacy of phosphine fumigation to control forest insects other than those found in New Zealand, with the exception of efficacy studies against *A. ferus* by Tumambing (2007). Ren et al. (2011) studied the penetration and sorption rates of phosphine and other fumigants into timber blocks. However, the timber blocks used by Ren et al. (2011) were relatively dry in comparison with ≥ 52% moisture content of export logs, which makes any direct correlation difficult.

Because phosphine is currently used as a methyl bromide alternative, it is not considered further here.

4.14.1 Phosphine combined with other fumigants or compounds

<u>Phosphine combined with carbon dioxide</u> - A number of studies indicate that phosphine toxicity can be increased by the addition of 5-40% carbon dioxide (Page 2011). Athié et al. (1998) were able to increase the efficacy of phosphine against phosphine-resistant strains of several stored product insects by adding carbon dioxide to the fumigant. Similarly, El-Lakwah et al. (1989) increased the efficacy of phosphine to control khapra beetle, *Trogoderma granarium* Everts (Coleoptera: Dermestidae). Tumambing (2007) reported that the synergistic effects of carbon dioxide added to phosphine only became significant after the level of carbon dioxide exceeded 20%. Ren et al. (1997) reported that carbon dioxide concentrations between 5-35% were optimum for synergy with phosphine in killing flour mill beetles, *Cryptolestes turcicus* (Grouvelle) (Coleoptera: Laemophloeidae), adults, but concentrations exceeding 35% carbon dioxide were less effective because oxygen uptake decreased significantly and a carbon dioxide narcosis effect diminished phosphine uptake. But they had no explanation for the fact that oxygen

consumption in their test insects peaked at about 30% carbon dioxide and phosphine uptake increased only slightly above 20% carbon dioxide (Ren et al. 1997). Their results demonstrate a relationship between carbon dioxide concentrations and phosphine uptake in insects that can be either beneficial or detrimental to fumigation efficacy. Sen et al. (2009) used magnesium phosphide to generate phosphine in chambers holding figs under normal atmospheric pressure for 5 d or high pressure (2500 kPa) for 2 h in combination with 94 $\pm$ 3% carbon dioxide to control fig moth [= almond moth, tropical warehouse moth, dried current moth], *Ephestia cautella* (Walker) (Lepidoptera: Pyralidae), and fig mite, *Carpoglyphus lactis* (L.) (Acari: Carpoglyphidae). Although both treatments obtained 100% mortality in tests, Sen et al. (2009) recommended the 5-d treatment at normal atmospheric pressure citing the higher cost for equipment used for the shortened fumigation under high pressure.

Others also have shown the limits to the additive or synergistic effects of carbon dioxide when combined with phosphine. Desmarchelier & Wohlgemuth (1983) and Desmarchelier (1984) showed that 1-50% concentrations of carbon dioxide increased phosphine toxicity to some stored-product insects but not to the most tolerant stages. Phosphine was not effective as a fumigant against the cockroach, *Periplaneta americana* (L.), in a 100% carbon dioxide atmosphere that forces the spiracles to remain widely open to enhance respiration, which suggests that phosphine is not absorbed to any appreciable extent in the absence of oxygen (Bond et al. 1967). Damcevski et al. (1988) observed a progressive change in apparent RQ [respiratory quotient] from 1.0 to 0.5 in 5 hours as carbon dioxide rose to exceed 1% and warned that caution is needed when interpreting fumigation dosage/response data obtained in sealed systems where carbon dioxide concentrations may increase due to the substrate. Johnston and Whittle (1994) stated that, while carbon dioxide concentrations between 15-30% were synergistic with phosphine, concentrations in excess of 35% were toxic to insects.

There is no issue with combining carbon dioxide with phosphine. Products, such as ECO_2FUME®, containing 2% phosphine in 98% carbon dioxide are used regularly to control stored-product insects (Cytec 2005) and new equipment that mixes phosphine and carbon dioxide are reported frequently in the literature (e.g., Chadda et al. 2007, Li et al. 1998, Mueller 1994, Winks 1989). Hartsell et al. (2005) demonstrated efficacy using ECO_2FUME® (98% carbon dioxide and 2% phosphine) against all life stages of eight stored-product insects at 26.7°C, which indicates that the high carbon dioxide levels did not impede efficacy. Zhang (2003b) purportedly used ECO_2FUME® (Brash & Page 2009) against the naked *A. ferus* eggs or adults and naked *H. ater* adults and larvae at 0, 200, 700, or 2000 ppm for 10 days at $\geq$ 16°C to obtain 100% mortality. However, the tests, as reported by Zhang (2003b), had too few replications and the reporting of methodology lacked significant information so that little can be ascertained from the results regarding the effects of carbon dioxide in this instance.

The advent of ECO_2FUME®, originally developed by BOC (R. Ryan, personal communication) was a major change in phosphine fumigation technology and circumvented the problems associated with the use of aluminium phosphide and magnesium phosphide, such as flammability and phytotoxicity to fruits and vegetables. ECO_2FUME® is a cylinderised gas formulation of 2% phosphine in carbon dioxide balance (carrier gas) and originally was developed for use in the Siroflo® system for the grain industry (Latif & Ryan 1989; Winks 1989, 1993a, b; Winks & Russell 1994). Siroflo® is a flow-through fumigation system developed to fumigate non-gastight storage that provides one air change of a dilute mixture of phosphine in air per day for exposure times up to 28 days. Siroflo® may be considered the forerunner to $VAPORPH_3OS$® and the Horn Diluphos® system (Armstrong et al. 2012a, Horn et al. 2007), which is cylinderised pure phosphine diluted with high velocity air to below the flammability limit of 18,000 ppm before it is dispensed into a sealed fumigation chamber, tent system, or storage facility. ECO_2FUME® has the advantages that (1) it can be applied rapidly to provide a desired concentration of phosphine, (2) it can readily be used to top up phosphine concentrations, and (3) it can be used for low-temperature fumigations near 1-2°C and up to 15°C to maintain cold storage cycles in fruits and vegetables (Jamieson et al. 2009; Ryan et al. 2007; Williams & Ryan 2001).

Valizadegan et al. (2012), Yokoyama (2010) and others provide more recent research on the mixing of phosphine with carbon dioxide to increase fumigant efficacy, and Chadda et al. (2007) developed a “fumigation machine” that generated phosphine combined with carbon dioxide for the fumigation of stored products in developing countries. Phosphine may be the fumigant most often studied in combination with carbon dioxide for use against pests of stored products and for the surface pests of fruits and vegetables (Armstrong et al. 2012a). However, phosphine combined with carbon dioxide has not been studied seriously as a potential methyl bromide alternative for treating logs against forest pest insects. Testing the efficacy of phosphine combined with carbon dioxide may be a worthwhile, albeit brief, laboratory study.

<u>Phosphine combined with sulphuryl fluoride</u> - Soma et al. (1998) tested gas mixtures of 30 g/m^3 or 50 g/m^3 sulphuryl fluoride combined with 1 g/m^3 or 2 g/m^3 phosphine for 24 h or 48 h at 15°C against the egg stage of *C*. *rufipenne* (eggs on paper), *M*. *alternatus* (eggs under bark), *C*. *fulvus* (eggs under bark), *I*. *cembrae* (eggs under bark), *P*. *perlatus* (eggs under bark), pine weevil, *Pissodes nitidus* Roelofs (Coleoptera: Curculionidae) (eggs under bark), and sugi bark borer, *Semanotus japonicus* Lacordaire (Coleoptera: Cerambycidae), and all stages of *X*. *validus* (all stages in xylem), *X*. *pfeili* (all stages in xylem) and the ambrosia beetle, *Scolytoplatypus tycon* Blandford (Coleoptera: Curculionidae) (all stages in xylem). Fumigation for 24 h with either 30 g/m^3 or 50 g/m^3 sulphuryl fluoride combined with 1 g/m^3 or 2 g/m^3 phosphine provided 100% mortality only for all species and life stages except *S*. *japonicus* and *P*. *nitidus* eggs and all stages of *X*. *pfeili* (Soma et al. 1998). When the fumigations with 30 g/m^3 or 50 g/m^3 sulphuryl fluoride combined with 1 g/m^3 or 2 g/m^3 phosphine were extended to 48 h, 100% mortality for both *S*. *japonicus* and *P*. *nitidus* eggs on paper was obtained using 30 g/m^3 phosphine combined with 1 g/m^3 phosphine and 50 g/m^3 sulphuryl fluoride combined with 2 g/m^3 phosphine, respectively. Only 99.4% mortality was obtained for *X*. *pfeili* life stages in the xylem using 50 g/m^3 sulphuryl fluoride combined with 2 g/m^3 phosphine (Soma et al. 1998).

Misumi et al. (2011) reported on the synergistic effects of fumigation with sequential dosages of sulphuryl fluoride and phosphine using 2.2 g/m^3 sulphuryl fluoride for 24 h followed by a consecutive fumigation with 1.0, 1.5 or 2.0 g/m^3 phosphine for 48 h at 15°C that provided 100% mortality of all life stages of the maize weevil, *Sitophilus zeamais* (Motschulsky) (Coleoptera: Curculionidae).

<u>Phosphine combined with diethyl maleate or mitochondrial uncouplers</u> - An interesting and unusual combination with phosphine was reported by Valmas and Ebert (2006) from studies that identified the synergistic properties of mixing the glutathione depletor diethyl maleate to a sublethal dose of 70 ppm phosphine against laboratory-reared phosphine-resistant strain of the soil nematode, *Caenorhabditis elegans* (Maupas). The combination of the phosphine and glutathione depletor doubled *C. Elegans* mortality (Valmas & Ebert 2006). Later, Valmas et al. (2008) reported the results of tests with phosphine-resistant *C. Elegans* which they treated with a combination of a sublethal dose of phosphine and one of three mitochondrial uncouplers, carbonylcyanide p-trifluoromethoxy-phenylhydrazone (FCCP), 2,4-dinitrophenol (DNP), or pentachlorophenol (PCP). The combination of phosphine and a mitochondrial uncoupler led to strong synergism that increased the efficacy of phosphine against the nematode (Valmas et al. 2008) and their results, they claimed, supported their hypothesis that phosphine-induced mortality results from the *in vivo* disruption of normal mitochondrial activity. Furthermore,

Valmas et al. (2008) claimed to have found a novel pathway that can be targeted to overcome genetic resistance to phosphine.

However, despite the work of Valmas and Ebert (2006) or Valmas et al. (2008), the value of adding diethyl maleate or mitochondrial uncouplers, respectively, remains questionable, as does the actual mode of action(s) for phosphine. In an extensive review carried out by Nath et al. (2011), the authors concluded that phosphine‘s mode of action consisted of three very different, but potentially interrelated mechanisms: (1) signalling through acetylcholine, which is not only an excitatory neurotransmitter, but also the primary regulator of metabolism through the parasympathetic nervous system; (2) acetylcholine toxicity, which is probably mediated through its role as a metabolic regulator, and (3) ultimately, toxicity may be the result of a metabolic crisis, the generation of reactive oxygen species or some other reduction-oxidation activity of phosphine. In other words, the complete mode of action for phosphine toxicity in insects is not yet completely understood.

4.15 Sulphuryl fluoride

Sulphuryl fluoride was reported to be an “ideal” fumigant for structures against termites (Stewart 1956) and commodity insect pests (Kenaga 1957) because it is toxic to insects under all temperature and exposure conditions, non-flammable, non-explosive, easily dispersed, essentially non-reactive with a wide range of metals, fabrics, leather and paper goods, wood, plastics, and rubber products, non-sorptive in commodities, and able to penetrate rapidly through infested materials (Kenaga 1957). Sulphuryl fluoride is stable at temperatures up to 400°C and can be used safely in conjunction with heating equipment (Bell 2006), and sulphuryl fluoride is non-corrosive to equipment and electronics (Bell 2006, Thoms et al. 2010b). Another important attribute is that, unlike methyl bromide and other ozone-depleting compounds, sulphuryl fluoride does not contain either chlorine or bromine and, therefore, does not adversely impact the atmospheric ozone layer (Thoms & Scheffrahn 1994, USEPA 1996b).

4.15.1 Sulphuryl fluoride penetration into substrates

Kanega (1957) and Stewart (1956) noted the importance of fumigant penetration into the substrate being fumigated. Scheffrahn and Thoms (1993) studied the penetration of methyl bromide and sulphuryl fluoride through disks of construction grade pine (southern yellow pine, Douglas fir and western hemlock) and two hardwood heartwoods (red oak and mahogany). The results showed that sulphuryl fluoride penetrated the end grain of pine rapidly, but penetration through the side grain was significantly slower (Scheffrahn & Thoms 1993) and penetration through red oak and mahogany heartwoods was the slowest for all woods tested. Penetration of sulphuryl fluoride was significantly greater than for methyl bromide (Scheffrahn & Thoms 1993) for all woods tested when the wood was dry, but methyl bromide showed greater penetrability than sulphuryl fluoride when the woods were hydrated, which was attributed to the greater water solubility of methyl bromide. Moreover, the hydrated woods significantly reduced fumigant penetration for both methyl bromide and sulphuryl fluoride when compared with dry woods (Scheffrahn & Thoms 1993).

Ren et al. (2011) studied the penetration and sorption of dry Douglas fir wood blocks by equal concentrations of ethanedinitrile, methyl bromide, phosphine, or sulphuryl fluoride for 48 h. The results showed that all fumigants penetrated into all parts of the wood blocks but that the speed and extent of penetration was significantly different (Ren et al. 2011). The penetration ranking based on (concentration) after 48 h for each fumigant concentration measured at the centre of the fumigated block was methyl bromide (70%) > ethanedinitrile (63%) > sulphuryl fluoride (35%) ≥ phosphine (25%); statistical analysis showed that there was no significant difference between the penetrability of sulphuryl fluoride and phosphine (Ren et al. 2011). Based on achieving CT for control of a particular wood pest (larvae of *A. glabripennis*) at 50 and 150mm depths in wood blocks, Ren et al. (2011) ranked the best fumigants for wood as ethanedinitrile > phosphine > sulphuryl fluoride > methyl bromide, which is different from the ranking of penetrability because of the differing amounts of each fumigant required to achieve 100% mortality. Ren et al. (2011) did not test the penetration or sorption rates for the fumigants with wet wood blocks.

Scheffrahn and Thoms (1993) found that sulphuryl fluoride is both less permeable and less sorptive than methyl bromide for tarpaulin materials. Their results showed that sulphuryl fluoride was ≈ 19 to 224 times less permeable through fumigation tarpaulins than methyl bromide and ≈ 2.3 to 4.3 times less sorptive than methyl bromide on fumigation tarpaulin materials, which can limit the loss of sulphuryl fluoride compared with methyl bromide when applied under tarpaulin (Scheffrahn & Thoms 1993). However, the integrity of the tarpaulin can be a significant contributor to fumigant loss. Maier et al. (2010) showed in quantitative side-by-side comparisons of methyl bromide and sulphuryl fluoride that the leakage rates for both fumigants was essentially the same.

Sulphuryl fluoride was developed by Dow Chemical Company in the United States and registered for use as a fumigant in 1959 (Kenaga 1957, USEPA 1993) under the trademark name Vikane. Vikane was developed specifically for the control of drywood termites that are typically found in warm climates, such as the southern US (Derrick et al. 1990), and over the years many studies advanced the use of Vikane as a major structural fumigant, especially for termites (Lewis and Haverty 1996a, b; Osbrink et al. 1987; Su and Scheffrahn 1986; Su et al. 1989; USEPA 1996c). Nitschke and Eisenbrandt reported in 2001 that from the time that sulphuryl fluoride was first marketed in 1961 as Vikane structural fumigant it was used to fumigate over one million buildings in the US, and by 2010 the number had increased to over 2 million, including cathedrals, houses, museums, historical landmarks, rare book libraries, government archives, and scientific and medical research laboratories (Binker et al. 2011, Nitschke & Eisenbrandt 2001, Phillips et al. 2011, Shamilov 2012, Su & Scheffrahn 1990, Thoms et al. 2010b). Vikane fumigation is considered especially beneficial for structural fumigation because of the non-reactivity of the gas (Derrick et al. 1990).

Vikane is a gas at atmospheric conditions and released from cylinders in which it is stored as a liquid under its own pressure (Drinkall & Schneider 2002). Because sulphuryl fluoride gas is colourless and odourless (Kenaga 1957), a warning agent called chloropicrin is generally added because chloropicrin can be detected by odour at concentrations as low as 1.1 ppm and is a severe irritant that cannot be tolerated by humans for more than 1 minute at a concentration of 4.0 ppm (Derrick et al. 1990, USDHHS 1978).

Although sulphuryl fluoride was not developed originally for edible commodities (Bond 1984, Banks 1994), it was developed as a cylinderised fumigant by Dow AgroSciences under the trade name, ProFume® at the request of food industries as a methyl bromide alternative for postharvest insect control (Thoms et al. 2010a). Cylinderised ProFume® is 99.8% sulphuryl fluoride and 0.2% air balance (Dow AgroSciences 2013). ProFume® was intended for use on dried stored products, such as grains, seeds, pasta, dried fruits and tree nuts, cocoa, pet food, dried legumes, and peanuts, and for corn, rice and wheat milling and food processing facilities (Thoms et al. 2010b, Williams et al. 2009). As of 2011, ProFume® is registered for use in 17 countries and approved by the CODEX Alimentarius Commission and the European Union for a wide range of uses (Barnekow 2011). Guogan et al. (1998) reported on the uses in China for sulphuryl fluoride as a methyl bromide replacement for stored products.

Although sulphuryl fluoride can control a wide range of insects, including household, stored product, structural, and soil pests, the activity of this fumigant is dependent on the concentration reaching the target pest and the duration of exposure (Nitschke & Eisenbrandt 2001, Misumi et al. 2010). Insect eggs require much more sulphuryl fluoride exposure when compared with postembryonic life stages (Nitschke & Eisenbrandt 2001). Nitschke and Eisenbrandt (2001) pointed out that where immature stages, e.g., termites and ants, cannot survive without adult care, substantially less sulphuryl fluoride can be used to obtain control of the egg stage. The efficacy in controlling insect eggs using sulphuryl fluoride as a fumigant is considered to be a major weakness in using this fumigant as an alternative treatment for export logs.

4.15.2 Sulphuryl fluoride efficacy against insect eggs

Issues regarding the ability of sulphuryl fluoride to control insect eggs were identified soon after it was developed and released as a fumigant. Kenaga (1957) showed that sulphuryl fluoride killed all life stages of 17 insect species, but that the egg stage was significantly more tolerant to sulphuryl fluoride than the larvae, pupae or adults. For example, the egg stage was 6.33 times more tolerant for the most sulphuryl fluoride-susceptible species tested and 22.0 times more tolerant for the least sulphuryl fluoride-tolerant species tested (Kenaga 1957). However, Kenaga (1957) pointed out that under similar conditions, and at all concentrations, temperatures and exposure periods tested against *T. confusum*, and black carpet beetle sulphuryl fluoride was more toxic than methyl bromide, and that for all stored-product insects tested against methyl bromide, the egg stage was the most tolerant life stage. Kenaga (1957) found that the egg stage was also the most tolerant life stage to other commercial fumigants used during that time, including carbon tetrachloride, carbon disulfide, ethylene dichloride, and benzene. Regardless, the results of Kenaga (1957) demonstrated that increased sulphuryl fluoride concentrations, exposure times and/or fumigation temperatures were required to kill insect eggs when compared to those parameters required to kill larvae, pupae or adults.

Outram (1967a, b) showed that the uptake of sulphuryl fluoride by the eggs of desert locust, *Schistocerca gregaria* (Forskal) (Orthoptera: Acrididae) and yellow mealworm beetle, *Tenebrio molitor* (L.) (Coleoptera: Tenebrionidae), was through the micropyle complex of the chorion and that the degree of susceptibility between eggs may be based on the amount of embryonic differentiation taking place. Moreover, Outram (1967a, b) determined that the chorion of the insect eggs tested was relatively impermeable to sulphuryl fluoride and stated that chorion impermeability was most likely the cause for “the poor ovicidal characteristics” of sulphuryl fluoride.

The early discovery that eggs of many species were hard to kill gave rise to concerns over the practicality of choosing sulphuryl fluoride as a replacement for methyl bromide (Bell 2006). The literature is replete with articles that demonstrate the greater tolerance to sulphuryl fluoride by the egg stage compared with the other life stages of the wide range of insect species tested, including Barak et al. 2009; Barakat et al. 2009; Bell 2006; Bell et al. 1998; Derrick et al. 1990; Reichmuth & Klementz 2008a, b; Reichmuth et al. 1999; Soma et al. 2005; Walse et al. 2009; Williams & Sprenkel 1990; Xu et al. 1998; and Yann & Ducom 2009. The most significant review of insect egg tolerance to sulphuryl fluoride is the 2011 Report of the Technology and Economic Assessment Panel of the United Nations Environmental Programme (TEAP 2010). This special review on achieving control of pest eggs by sulphuryl fluoride found that the crucial factors for limiting egg tolerance were temperature, length of exposure, and the concentration, which operated differently on different species (TEAP 2010). Other important factors affecting the response of insect eggs to sulphuryl fluoride included the developmental period of the embryo, the structure of the egg shell and compounds found within the egg (Barakat et al. 2009, TEAP 2010). The most significant problem with egg tolerance was the potential for eggs to survive sulphuryl fluoride fumigations and that the survivors of repeated unsuccessful fumigations would eventually become resistant to the fumigant (TEAP 2010). Therefore, sulphuryl fluoride fumigation schedules must be developed to provide the concentration, exposure time and fumigation temperature parameters required to obtain complete mortality for the eggs of each target insect pest (TEAP 2010). Another possibility is to develop fumigation procedures that combine sulphuryl fluoride with other fumigants that kill insect eggs rapidly and thereby enhance the overall fumigation process (TEAP 2010).

Little research has been done on the use of sulphuryl fluoride against forest pests pertinent to the potential use of this fumigant for New Zealand export logs. However, the available examples from elsewhere demonstrate the significant differences in the ability of sulphuryl fluoride to control larvae, pupae and adults compared with eggs. Soma et al. (1996, 1997) tested sulphuryl fluoride against seven species of wood borers and bark beetles, including Cryptomeria [Japanese cedar] bark borer, *Semanotus japonicas* Lacordaire (Coleoptera: Cerambycidae); small cedar longicorn [longhorn] beetle, *Callidiellum rufipenne* (Motschulsky) (Coleoptera: Cerambycidae); Japanese pine sawyer, *Monochamus alternatus* (Hope) (Coleoptera: Cerambycidae); *C*. *fulvus* Niijima (Coleoptera: Bostrichidae; Scolytinae); larch ips, *I*. *cembrae* (Coleoptera: Bostrichidae); thuja bark beetle, *Phloeosinus perlatus* Chapuis (Coleoptera: Bostrichidae: Scolytinae); and a spruce bark beetle, *Sirahoshizo sp.* (Coleoptera: Bostrichidae: Scolytinae). Their results found that *C. fulvus* was the most tolerant species and that the eggs of all seven species were the most tolerant stage to sulphuryl fluoride (Soma et al. 1996). *C. fulvus* eggs were 3.5 times more tolerant to sulphuryl fluoride than larvae, the next most tolerant life stage (Soma et al. 1996).

Mizobuti et al. (1996) studied the toxicity of sulphuryl fluoride to five species of ambrosia beetle forest pests, *Xyleborus pfeili* (Ratzeburg) (Coleoptera: Scolytidae); *X*. *validus* Eichhoff (Coleoptera: Scolytidae); black timber bark beetle, *Xylosandrus germanus* (Blandford) (Coleoptera: Scolytidae); *Platypus calamus* Blandford (Coleoptera: Platypodidae); and *P*. *quercivorus* Murayama (Coleoptera: Platypodidae). Their results were similar to those of Soma et al. (1996) whereby the eggs for all five species were the most tolerant life stage. The eggs of the most tolerant species, *X*. *pfeili*, required 2 to 3 times the sulphuryl fluoride concentrations required to kill the larvae, pupae or adults of all species and twice the exposure period (48 h versus 24 h) to obtain 23.1% mortality of eggs compared with 99.8% mortality for larvae at 15°C (Mizobuti et al. 1996). Moreover, the sulphuryl fluoride tolerance of *X*. *pfeili* eggs was so marked that Mizobuti et al. (1996) could not calculate from their results either the sulphuryl fluoride concentration or the exposure time necessary to obtain an LD_{95}.

Zhang (2006) reported the results of studies on sulphuryl fluoride as a potential fumigant to control *A. tristis* [syn. *ferus*] eggs and adults (larvae were not tested) in New Zealand export logs. Zhang (2006) found that 15.0 g/m^3 for 24 h at 15°C was adequate to kill all adults but that the eggs required 120.0 g/m^3 for 24 h at 15°C, an eight-fold increase in sulphuryl fluoride concentration. Zhang (2006) also found that 15.0 g/m^3 sulphuryl fluoride killed all *H*. *ater* adults and larvae after a 24-h exposure period at 15°C, but no *H*. *ater* eggs were tested.

Barak et al. (2009) and Yu et al. (2010) obtained complete mortality of bamboo borer, *Chlorophorus annularis* F. (Coleoptera: Cerambycidae), larvae (n = 2,424), pupae (n = 90) and adults (n = 3) using 96.0 g/m^3, 80.0 g/m^3, or 64.0 g/m^3 for 24 h at 15.6, 21.1, or 26.7°C, respectively. Although no individual test results were given by Barak et al. (2009) and no *C*. *annularis* eggs were tested, the results were used to recommend a sulphuryl fluoride fumigation schedule for *C*. *annularis* larvae, pupae and adults in bamboo poles (Table 16). Noteworthy is the significantly greater concentration (96.0 g/m^3) required at 15°C to kill the larvae, pupae and adults of *C*. *annularis* (Barak et al. 2009) compared with the concentrations required to obtain complete mortality of *A. ferus* adults (15 g/m^3) (Zhang 2006), of ambrosia beetle larvae, pupae and adults (5 - 15 g/m^3) (Mizobuti et al. 1996), and of the most of the forest pest larvae, pupae and adults (5 - 40 g/m^3) tested by Soma et al. (1996). The exception is *X. pfeili* larvae that required > 80 g/m^3 (estimated) (Misobuti et al. 1996) and the results of Barak et al. (2006) show that there may be significantly wide ranges of insect response to sulphuryl fluoride by life stages other than the egg stage.

Table 16. Proposed sulphuryl fluoride fumigation schedule for *Chlorophorus annularis* F. in bamboo stakes and poles[a]

Temperature (°C)	Concentration (g/m^3)	Minimum concentrations at hour (g/m3)				Min. Target CT (g-h/m3)
		0.5	2	4	24	
15.6 - 21.1	96	103	93	87	63	1826
21.1 - 26.7	80	85	77	73	53	1536
≥ 26.7	64	68	59	53	28	1008

[a]From Barak et al. (2009).

Regardless of the difficulty in killing insect eggs with sulphuryl fluoride, numerous authors suggest that it is a viable fumigant for logs, sawn timber, solid wood packing materials, and wood products (e.g., Banks 2002; Barak 2001; Barak et al. 2002, 2006, 2009, 2010; Jeffers et al. 2012; Messenger et al. 2008; Misumi et al. 2010, Mueller 2009; Rajendran & Kumar 2008; Reichmuth 2002; Thoms 2010a, b; Tubajika & Barak 2007, 2008). Additionally, there are many studies in which sulphuryl fluoride was combined with other fumigants or gases to find fumigant mixtures that would overcome the difficulties in obtaining control of insect eggs (discussed below).

4.15.3 Sulphuryl fluoride combined with other fumigants or compounds

<u>Sulphuryl fluoride combined with carbon dioxide</u> - Following on early studies that showed the toxicity of fumigants could be enhanced by the addition of carbon dioxide (e.g., Cotton 1930, Jones 1938, Bond & Buckland 1978), Scheffrahn et al. (1995), Yue & Zhu (1998) and Muhareb et al. (2009a, b) reported that the addition of carbon dioxide also resulted in synergistic effects to the toxicity of sulphuryl fluoride.

Scheffrahn et al. (1995) obtained a maximum synergism ration of 2.2 (i.e., 2.2 times more efficacy than provided by the fumigant alone) when either 10% or 20% (vol:vol) carbon dioxide was added to sulphuryl fluoride in dose-response tests against the Formosan subterranean termite, *Coptotermes formosanus* Shiraki (Isoptera: Rhinotermitidae) and recommended the addition of 10% (vol:vol) carbon dioxide to methyl bromide for house fumigations to control termites.

Yue and Zhu (1998) reported maximum synergism ratios of 1.8, 2.2 or 2.7 by the addition of 0.5%, 10.0% or 20% carbon dioxide to identical concentrations of sulphuryl fluoride in dose-response tests against the larvae of *T. granarium* in dose-response studies.

Noteworthy is that no studies are reported in the literature specific to the addition of carbon dioxide to sulphuryl fluoride in dose-response studies against insect eggs. Perhaps the addition of carbon dioxide alone to sulphuryl fluoride does not provide synergism that increases the efficacy of the fumigant against the insect egg stage.

Sulphuryl fluoride combined with hydrogen cyanide – Refer to page 47, hydrogen cyanide combined with sulphuryl fluoride.

Sulphuryl fluoride combined with methyl bromide – Refer to page 48, methyl bromide combined with sulphuryl fluoride.

Sulphuryl fluoride combined with methyl isothiocyanate – Refer to page 56, methyl isothiocyanate combined with sulphuryl fluoride.

Sulphuryl fluoride combined with phosphine – Refer to page 64, phosphine combined with sulphuryl fluoride.

Sulphuryl fluoride combined with propylene oxide - Muhareb et al. (2009a, b) reported that the addition of propylene oxide increased efficacy of sulphuryl fluoride against the eggs of *T. castaneum* primarily because propylene oxide is very toxic to the egg stage. Therefore, the increase in efficacy was not a synergistic effect but a cumulative effect of the two fumigants. However, when Muhareb et al. (2009a, b) added 5.0%, 7.0%, 10%, or 15% carbon dioxide, they found that the addition of 10% carbon dioxide was the optimum mixture of carbon dioxide and that it reduced the doses of sulphuryl fluoride and propylene oxide required for complete control of *T. castaneum* eggs by almost 66% in 24-h fumigation tests. Although the efficacy of combining sulphuryl fluoride, propylene oxide and carbon dioxide provided greatly increased efficacy against eggs, no further research on this specific combination of fumigants with carbon dioxide was found in the literature.

Another sulphuryl fluoride and propylene oxide combination called “Flurox” was developed by Specialty Gases, Sydney, Australia (R. Ryan, personal communication). The application provides the efficacy of sulphuryl fluoride against the insect larval, pupal and adult life stages of the target pests while the propylene oxide provides the necessary efficacy against insect eggs that is lacking in sulphuryl fluoride. The mixture is further improved by mixing with carbon dioxide, which has the dual benefits of eliminating the propylene oxide flammability hazard and reducing the amount of sulphuryl fluoride and propylene oxide required for efficacy because of the synergistic effect of carbon dioxide with both sulphuryl fluoride and propylene oxide (R. Ryan, personal communication). Flurox was not registered for use at the time this review was written.

4.15.4 Health issues associated with sulphuryl fluoride

As reported above, the cylinderised version of sulphuryl fluoride marketed as Profume® was intended for use on dried stored products, such as grains, seeds, pasta, dried fruits and tree nuts, cocoa, pet food, dried legumes, and peanuts, and for corn, rice and wheat milling and food processing facilities (Thoms et al. 2010b). Although studies by Scheffrahn et al. (1989) and Sriranjini and Rajendran (2008) found “low to moderate” fluoride residues in the edible commodities they tested, and despite a strong defence of sulphuryl fluoride by Dow AgroSciences (2011), the use of sulphuryl fluoride in the US became problematic because of health issues. Research in the US during the past decade found that the amount of fluoride uptake from a combination of fluoridation of water to enhance the health of children’s teeth and fluoridated toothpastes, the manufacture of beverages using fluoridated water, and other fluoride sources was having an adverse health impact on young children in the form of “dental fluorosis" and a lifetime accumulation of fluoride in bone that could put individuals at greater risk of bone fractures (Tiemann 2013).

The US Environmental Protection Agency began a review process (USEPA 2011) to revise the standards for the amount of fluoride in drinking water and set limits on the amount of fluorine exposure for children. Tsai (2010) reported that replacing methyl bromide with sulphuryl fluoride to meet the demand for the variety of food product uses could create significant impacts on human health and showed that the toxic decomposition products from SO_2F_2 may include S_2OF_{10}, HF, H_2SO_4, F_2O, SO_2, H_2S, NF_3, S_2F_{10}, SF_4 , SF_5 (S_2F_{10}), SF_6, SO_2, SO , SOF_4, and $S_2O_2F_{10}$. Public reaction in the US called for banning the fluoridation of water, historically a highly charged political issue (Tiemann 2013) and for banning the use of sulphuryl fluoride on edible commodities. Consequently, the US Environmental Protection Agency re-evaluated the available science on fluoride and began a phased-down withdrawal of sulphuryl fluoride used in food storage and processing facilities (USEPA 2012a) stating that "*sulphuryl fluoride is currently registered for the control of insect pests in stored grains, dried fruits, tree nuts, coffee and cocoa beans, and for use in food handling and processing facilities. Although sulphuryl fluoride residues in food contribute only a very small portion of total exposure to fluoride, when combined with other fluoride exposure pathways, including drinking water and toothpaste, EPA has concluded that the tolerance (legal residue limits on food) no longer meets the safety standard under the Federal Food, Drug, and Cosmetic Act and the tolerances for sulphuryl fluoride should be withdrawn*" (authors' italics).

Noteworthy is that sulphuryl fluoride is registered in Australia (APVMA 2007a, b) for many of the same uses as the original US registration and that, following the US EPA (2011) decision to withdraw sulphuryl fluoride tolerances, Australia (APVMA 2011) chose to maintain their sulphuryl fluoride registration without change. Also noteworthy is that the Australia regulatory decision to maintain the status quo for sulphuryl fluoride (APVMA 2011) has become a public and political issue in Australia (The Rivermouth Action Group 2013). While the health issues associated with sulphuryl fluoride in the US based on water fluoridation, fluoride residues and decomposition products would seem far removed from its potential use in New Zealand, the amount of sulphuryl fluoride required to replace the significant amount of methyl bromide used for export logs (Armstrong et al. 2011) will need to be thoroughly scrutinised to ensure that New Zealand health standards are maintained.

4.15.5 Sulphuryl fluoride issues with atmospheric gases

Despite the fact that sulphuryl fluoride does not contain either chlorine or bromine and, therefore, does not adversely impact the atmospheric ozone layer (Thoms & Scheffrahn 1994, USEPA 1996b), the results of more recent studies showed that sulphuryl fluoride is a greenhouse gas (Hunt 2009, Mühle et al. 2009, Papadimitriou et al. 2008) and that the half life of sulphuryl fluoride in the atmosphere, originally believed to be about 4.5 years, was found to be 36 years (Mühle et al. 2009, Papadimitriou et al. 2008) and that the data "*indicate that, ton for ton,* [sulphuryl fluoride] *is about 4,800 times more potent a heat-trapping gas* [i.e., trapping infrared radiation] *than carbon dioxide* (Hunt 2009, Mühle et al. 2009)." Although Dow AgroSciences (2009) responded to claims that sulphuryl fluoride was a greenhouse gas , the amount of sulphuryl fluoride required to replace the significant amount of methyl bromide used for New Zealand export logs (Armstrong et al. 2011) will need to be thoroughly scrutinised to determine whether there are adverse atmospheric impacts.

4.15.6 Economics of sulphuryl fluoride fumigation

Adam et al. (2010) completed an exhaustive economic study comparing methyl bromide with sulphuryl fluoride fumigations of food processing facilities, warehouses, and cocoa beans. Although the costs for the two fumigants were comparable (about $15/kg), Adam et al. (2010) found the most important factor affecting relative profitability of the two fumigants was the amount of sulphuryl fluoride required for an effective fumigation because, under typical assumptions and parameter values, a sulphuryl fluoride fumigation required two-thirds more fumigant than methyl bromide. A key issue in the need to use more sulphuryl fluoride than methyl bromide to achieve an effective fumigation (Adam et al. 2010) is sulphuryl fluoride's lack of efficacy against insect eggs.

4.15.7 Sulphuryl fluoride research to control fungi and nematodes

Sulphuryl fluoride is used as both an antifungal fumigant and to control nematodes in logs, sawn timber and wood chips. Research on sulphuryl fluoride to control a range of fungal pathogens was reported by Murdoch (1992), Scheffrahn et al. (1987, 1992), Schmidt and Christopherson (1997), Schmidt et al. (1997, 1998, 2001a, b), Schmidt and Kreber (1998), Tubajika and Barak (2006, 2011), Tubajika et al. (2005), and Woodward and Schmidt (1995). Research on sulphuryl fluoride to control nematodes was reported by Abe et al. 2009; Bonifácio et al. (2013); Buckley (2010); Dwinell et al. (2005a, b, 2006); Flack et al. (2008); Liu et al. (2010); Sousa et al. (2010); and Thoms et al. 2010a.

4.15.8 Rejection by China of sulphuryl fluoride for use on logs exported from the US to China

As of 6 September 2013, China informed USDA that "they will not accept sulphuryl fluoride as a treatment option for softwood logs." The notification to US exporters was issued under "Important Notes" on the US Department of Agriculture Phytosanitary Certificate Issuance & Tracking System (PCIT) website for Phytosanitary Export Database (PExD) for the Commodity Summary for China regarding the export of hardwood and softwood logs from the US to China (USDA 2014a). The use of sulphuryl fluoride as a phytosanitary treatment for logs exported from the US to China was not permitted on the basis of a study by Wang et al. (2003a) that used sulphuryl fluoride against the larvae and pupae of *Anoplophora nobilis* [= *A. glabripennis*], carpenter moth, *Cossus cossus orientalis* Gaede (Lepidoptera: Cossidae), and poplar pole clearwing moth, *Sphecia siningensis* Hsu (Lepidoptera: Sesiidae) (J. Jones, USDA, APHIS, personal communication). Wang et al. (2003a) obtained 100% mortality of the larvae and pupae for all three species at dosages of 104 g/m^3 at 15.5°C, but could not obtain 100% mortality at either 120 g/m^3 at 10°C or 160 g/m^3 at 4.4°C. Whether the survival at the higher sulphuryl fluoride concentrations used at lower temperatures were the result of a narcosis effect from high concentrations or reduced respiration that resulted in reduced uptake of sulphuryl fluoride at lower temperatures was not determined. Regardless, China will not allow the use of sulphuryl fluoride as a quarantine treatment for the export of pine logs from the US (USDA 2014a).

4.15.9 Recommendation for further research with sulphuryl fluoride

Sulphuryl fluoride may be a poor choice as a methyl bromide alternative when considering:

- The rejection by China of sulphuryl fluoride for use on logs exported from the US to China.
- The potential costs associated with log fumigation.
- The potential impact on atmosphere greenhouse gases.

- The lack of efficacy in controlling insect eggs that may require the addition of another fumigant, such as propylene oxide, that increases efficacy against insect eggs.

Regardless, the authors recommend sulphuryl fluoride for further consideration as a potential methyl bromide alternative because:

- Sulphuryl fluoride has good characteristics as a fumigant (good penetration and insect toxicity, easy to apply, and moderate cost for the fumigant).
- Sulphuryl fluoride has substantial literature supporting its use for a wide range of insects.
- Sulphuryl fluoride is already registered for use as a structural fumigant, and approval for its use on logs may be relatively uncomplicated compared with the other major fumigants.

Ultimately, sulphuryl fluoride, with all its negative issues presents the only possible second choice after ethanedinitrile for further study as a methyl bromide alternative. However, sulphuryl fluoride should be considered for further research only if the authors' first choice, ethanedinitrile (refer to 4.5.3, page 39), is rejected as an option based on a technological and economic study.

5 Minor fumigants

There are a number of minor fumigants that were studied on one or two occasions but did not receive further attention in either the research or commercial sectors for a number of reasons, including toxicity, difficulty in handling or dispersal, lack of producer or user interest, environmental concerns, or selection of a more suitable closely-related compound, or for other reasons.

Authors' Note: One author began a research career in the US in the late 1960s at a time when a major transformation occurred in the use of pesticides (including fumigants), and the rather laissez-faire approach towards pesticide research, development and application that was symptomatic of the "Green Revolution" (J. Armstrong, personal communication; Pingali 2012). Rachael Carson's 'Silent Spring (Carson 1962) had resulted in a national debate on the complications arising from the "Green Revolution" that led ultimately to an exposure of the US agro-chemical and agricultural research complex that tended to be driven only by the need to produce and use new and more agro-chemicals. Deaths and other health issues and environmental damage (whether real or perceived) resulting from agro-chemicals, including fumigants, received more press after the publication of 'Silent Spring' (Carson 1962) with the result that the greater attention to these issues increased the public debate (e.g., Allen et al. *1996). Following the establishment of the US Environmental Protection Agency in 1970 and the US Clean Water Act of 1972, the scrutiny placed on the research and development methodology and the application of pesticides resulted in the loss of many "standard" practices in both the research and commercial sectors. New requirements for toxicological and worker safety data, environmental and non-target organism impact studies, and the attendant costs to develop these data for the registration of new pesticides became limiting factors that resulted in the voluntary or forced withdrawal of many pesticides, including fumigants, from approved use (e.g., acrylonitrile) or major changes in how they were used. The changes that occurred may explain why there once appeared to be so many potential fumigant alternatives but so few today.*

Many of the minor fumigants, or references to them in the literature, are the result of fumigant screening trials, primarily in the US, during the late 1940s through the 1970s, that were the natural progression from earlier fumigant successes in the literature (e.g., hydrogen cyanide fumigation of citrus trees to control scale insects reported by Quayle in 1938). These fumigant screening trials were predominantly to find fumigation treatments for stored products and, to a lesser extent, pests on or in harvested fruit. These preliminary studies resulted in a number of compounds that became part of the historical fumigant literature and, although they did not become commercially viable, their "potential" was maintained in the literature as recognised minor fumigants (e.g., Bond 1984, Monro 1969). The minor fumigants include acetaldehyde, acrylonitrile, azobenzene, carbon bisulphide, carbon monoxide, dichloronitroethane, ethylene chlorobromide, methyl allyl chloride, methyl chloroform, methylene chloride, naphthalene, nicotine, methyl formate, paradichlorobenzene, propylene dichloride, sulphur dioxide, and tetrachloroethane (Aharoni et al. 1979; Baker & Wright 1977; Benschoter 1960, 1963; Bond 1984; Calderon & Desmarchelier 1979; Calderon 1991; Dumas & Bond 1977; Eaks & Sinclair 1959; Haring 1946; Hartsell et al. 1979; Kenaga 1961; Leesch 1984; Dibble 1933; Lindgren & Sinclair 1953, 1959b; Madsen & Blair Bailey 1959; McPhail et al.1969; Mostafa et al. 1972; Richardson 1940, 1954; Richardson & Busbey 1937; Richardson & Casanges 1942a, b; Roth 1970; Sanford 1962; Sharp 1946; Sullivan et al. 1941; Wolsky 1938). Other minor fumigants , such as ethyl acetate (Jamieson et al. 2009) or propylene oxide (Isikber et al. 2006), have been studied more recently but have not been proven either cost effective or adaptable to commercial operations. Brief discussions of each of the minor fumigants are provided below.

Other examples can be found in the patenting of various toxic compounds for use as fumigants that never resulted in a commercial product. In one such example, Binker and Binker (1999) applied for a German patent to control pest insect species by fumigation with an ester (methyl, ethyl, allyl, phenyl, benzyl, amyl, propyl, and formic esters were named) combined with sulphuryl chloride that was introduced sequentially into a gas-tight "treatment area". The insects considered in the patent application included stored product and structural pests, but very little or no data were provided to substantiate the patent claims. The patent was rejected in 2002 for reasons unknown. Perhaps fumigation with sulphuryl chloride was considered too hazardous because it is considered extremely reactive, incompatible with moisture, and reacts readily with water to form hydrogen chloride and sulphuric acid (Sciencelab.com 2013).

Minor fumigants that were used decades ago but have disappeared from the literature or found only limited use include:

5.1 Acetaldehyde

Acetaldehyde is a natural plant volatile and a generally-regarded-as-safe compound, acetaldehyde was studied as a fumigant against insect pests found on strawberries and lettuce (Aharoni et al. 1979, Hartsell et al. 1979), but it was eclipsed by ethyl formate because the latter compound had the same attributes but was easier to handle, somewhat less dangerous when used in concentrations required to kill insects, and less expensive (P. Hartsell, personal communication).

5.2 Acrylonitrile

Acrylonitrile was tested in fumigant screening trials against *T*. *confusum*; *T*. *granarium*; walnut husk fly, *Rhagoletis completa* (Cresson) (Diptera: Tephritidae); a gall midge, (Diptera: Cecidomyidae); a seed chalcid (Hymenoptera: Eurytomidae); *S*. *oryzae*; and other insects infesting stored products (Bond & Buckland 1976, Dumas & Bond 1977; 1978; Kenaga 1961; Krohne & Lindgren 1958; Lindgren 1955; Lindgren & Vincent 1959a, b; Richardson & Casanges1942; Richardson & Roth 1968; Ruppel et al. 1960). Although Bond (1984) listed acrylonitrile as a minor fumigant, no research with acrylonitrile was done after the work of Bond and Buckland (1978). Whether the end of research on acrylonitrile as a fumigant was due to its flammability, toxicity, or explosive potential (3-17% by volume in air) or its potential carcinogenicity (IARC 1999) is unknown but the registration for acrylonitrile as a fumigant in the US was voluntarily withdrawn in 1978 (USEPA 1980).

5.3 Azobenzene

Azobenzene was studied only twice as a potential fumigant used against insects (Haring 1946, Sharp 1946) but not further information was found.

5.4 Carbon bisulphide

Mostafa et al. (1972) compared the toxicity of carbon bisulphide to that of methyl bromide and found that methyl bromide was significantly more toxic to 1-, 2- or 3-day-old eggs of four stored-product insect species. Carbon bisulphide also was mentioned as a minor fumigant by Bond (1984).

5.5 Carbon monoxide

Wolsky (1938) demonstrated that carbon monoxide directly affected the oxygen consumption of *T. castaneum* pupae. Richardson (1954) first tested carbon monoxide as a fumigant against insects and Baker and Wright (1977) described the effects of carbon monoxide on insects. Calderon (1991) demonstrated that *T. castaneum* adults and pupae were susceptible to carbon dioxide and suggested that carbon monoxide had potential as a grain fumigant. Calderon and Desmarchelier (1979) found that exposure to carbon monoxide caused *T. castaneum* adults to become more susceptible to organophosphate insecticides. Cross (1994, unpublished data) found that adding carbon monoxide to sulphuryl fluoride did not increased the efficacy of sulphuryl fluoride obtaining mortality of *P. reticularis* eggs. However, Wang et al. (2009a) found that carbon monoxide alone had no effect on the adults of three stored-product insects, and that combining carbon monoxide with carbon dioxide improved mortality more than that obtained by carbon dioxide alone. Based on their results, Wang et al. (2009a) suggested that the addition of carbon monoxide to controlled atmosphere treatments of stored products may be enhanced by the addition of carbon monoxide. Currently, carbon monoxide is used commercially only as a warren and den fumigant to control rabbits and foxes, respectively (Sharp 2012, Sharp & Saunders 2004).

5.6 Dichloronitroethane

Dichloronitroethane was mentioned as a minor fumigant by Bond (1984). Dichloronitroethane was patented in the US by Hass (1942) as a new fumigant for grains with the beneficial characteristic of rapid penetration and high insect toxicity. With the exception of Schmidt (1955) of using dichloronitroethane as one of eight fumigants tested on wheat to determine their effects on germination, no other information on this compound was found in the literature.

5.7 Ethyl acetate

Ethyl acetate is a naturally occurring compound that, like ethyl formate, is considered a generally-regarded-as-safe compound for use in conjunction with food (USFDA 2013). Van Epenhuijsen et al. (2008) used 94-120 g/m^3 ethyl acetate against thrips eggs but obtained ≤ 91.1% mortality. Tests with 5000 ppm ethyl acetate at 25°C or 30°C controlled fifth instar light brown apple moth on apples with no phytotoxic damage (L. Jamieson, unpublished data).

5.8 Ethylene chlorobromide

With the exception of proposed use for control of cadelle beetle, *Tenebroides mauritanicus* L. (Coleoptera: Tenebrionidae) by Bond and Monro (1961) and khapra beetle by Lindgren and Vincent (1959b) in stored grain and aphids in lettuce (Leesch 1984), all other studies of ethylene chlorobromide as a fumigant were for use on fruits to control Tephritid fruit flies and other internal fruit pests of quarantine importance (Benschoter 1960, 1963; Eakes & Sinclair 1955; Lindgren & Sinclair 1953; McPhail et al. 1969; Richardson & Roth 1966; Roth & Richardson1970; Sanford 1962).

5.9 Methyl allyl chloride

Methyl allyl chloride was mentioned as a minor fumigant by Bond (1984) but not further information was found.

5.10 Methylene chloride

Also called dichloromethane, methylene chloride was mentioned as a minor fumigant by Bond (1984) but no further information was found.

5.11 Naphthalene

Naphthalene was proposed for use as a fumigant by Sullivan et al. (1941) and as a fumigant mixture with nicotine by Richardson (1940), but no further references were found.

5.12 Nicotine

Nicotine, known as a 'botanical' insecticide, is a potent parasympathomimetic alkaloid found in the nightshade family of plants. It was mentioned as a minor fumigant by Bond 1984 and tested as a mixture with naphthalene by Richardson (1940). Richardson and Busbey (1937) tested nicotine as a fumigant to control aphids in harvested lettuce. Nicotine sulphate, a common botanical insecticide made by extracting nicotine from tobacco, *Nicotiana spp*. (Solanales: Solanaceae), and sold under such names as 'Black Leaf 40' (40% nicotine sulphate) is no longer recommended for use because of its acute toxicity to humans (Geick 2010).

5.13 Methyl chloroform

Methyl chloroform was tested by Kenaga (1961) as a potential grain fumigant and mentioned as a minor fumigant by Bond (1984). Hole et al. (1985) determined that the toxicity of methyl chloroform was significantly greater than methyl bromide or phosphine on stored product insects that were both methyl bromide and phosphine tolerant. Bell et al. (1988) found that the toxicity of fumigant mixtures containing various concentrations of methyl bromide combined with methyl chloroform was enhanced by the presence of methyl chloroform when tested against nine species of stored-product insects, and that diapausing larvae, pupae and older larvae were the most tolerant life stages when compared with the egg stage.

5.14 Paradichlorobenzene

Paradichlorobenzene, the insecticidal compound in 'moth balls', was tested as a soil fumigant and tree spray to control an insect pests of apricot trees (Madsen & Blair Bailey 1959)

5.15 Propylene dichloride

Propylene dichloride was first identified as a potential fuming insecticide against European corn borer in corn, as a soil drench fumigant to control peach tree borer, and as a soil fumigant against pests of apricot trees (Madsen & Blair Bailey 1959, Snapp 1943).

5.16 Propylene oxide

Propylene oxide, or PPO, has been used for food fumigation as a "sterilisation" method in the US since 1958 where it is the only authorised sterilant allowed for reducing bacteria, mould and yeast in nutmeats and cocoa powder (Griffith 1999, 2006; USDA 2007). Studies found that a 0.1% concentration of propylene oxide was sufficient to obtain complete mortality of all life stages of the *T. confusum* (Griffith 1999) after a 4-h exposure at 26.6°C and under vacuum. Navarro et al. (2004) reported on combinations of propylene oxide with low pressure (13.3 kPa) and/or carbon dioxide that are very similar to the report by Isikber et al. (2004) (the authors of both publications are identical except in different order). The more complete study, Isikber et al.

(2004), found that a 4-h exposure to 4.7-26.1 g/m^3 propylene oxide was required at 30°C and 13.3 kPa pressure to obtain 99% mortality of the life stages of four stored-product insects. Based on their results, Isikber et al. (2004) suggested that propylene oxide showed "high and rapid toxicity to insects", and was "a fumigant [that] should have a reasonable sorption by the commodities, rapid penetration into bulk commodities, and no adverse impact on commodity quality," and that "although these toxicity tests indicate that the combination PPO with low pressure is a rapidly acting treatment for disinfestation of commodities, it is clear that further studies are needed to obtain data on phytotoxicity of PPO on seeds and fresh commodities, on its absorption by different commodities, and on its power of penetration into bulk commodities. Additionally, because most quarantine treatment schedules include temperature scales much lower than that used in this study (30°C), further toxicity tests of PPO with low pressure at other temperatures need to be done to determine its potential as a fumigant for quarantine treatment under a wide range of conditions." Perhaps the low pressure Iskiber et al. (2004) used in their tests was an important factor in obtaining mortality because Zettler et al. (2002) reported fumigation studies with propylene oxide in which a concentration of 45 g/m^3 for a 48-h exposure period at 38°C were required to obtain 100% mortality of the life stages of seven stored-product insects, including the four species Isikber et al. (2004) used in their tests. Moreover, Zettler et al. (2002) reported that reducing the exposure time to 24 h and the treatment temperature to 26.7°C resulted in survivors. Zettler et al. (2002) also showed that "sorption was significant and rapid in dried fruits and nuts, and was independent of dose." Although Muhareb et al. (2009a, b) reported on using a mixture of sulphuryl fluoride and propylene oxide with and without the addition of carbon dioxide as a method for overcoming the insufficient toxicity of sulphuryl fluoride to insect eggs, no further work has been done on propylene oxide alone or in combination with carbon dioxide, low pressure, or mixed with other fumigants since 2009 which is indicative of issues not readily apparent from the publications. The latest Report of the Technology and Economic Assessment Panel (TEAP 2013a) mentions in a footnote to Table 1-6 [*in the TEAP report*] that "a combination treatment of SF [*sulphuryl fluoride*], carbon dioxide and propylene oxide continues to be researched as preliminary results were positive for dried fruits, but the registration approval scenario for this combination treatment indicates it would only be a longer term proposition." Whether the TEAP (2010) footnote is in reference to the Navarro et al. (2004), Isikber et al. (2004), and/or Muhareb et al. (2009a, b) studies is unknown because no references are provided. Regardless, no further research using propylene oxide could be found reported in the literature after the report of Muhareb et al. (2009a, b). Additionally, the TEAP (2013a) footnote indicates that registration of mixtures of sulphuryl fluoride and propylene oxide may be an issue but provided no supporting information.

Also refer to page 70, sulphuryl fluoride combined with propylene oxide.

5.17 Sulphur dioxide

Sulphur dioxide is one of the oldest fumigants, purportedly obtained by ancient Greeks by burning sulphur and used to fumigate homes and as a wine preservative (ICFI 2011). Winkler and Jacob (1929) first described the use of sulphur dioxide to reduce losses from fungal decay during the shipping of grapes, which became a recommended procedure (Jacob 1929) that remains in use today (Feliziani & Romanazzi 2013) but instead of direct fumigation the sulphur dioxide is released from slow-release sulphur dioxide pads that can control both decay and insects (Yokoyama et al. 1999, 2001). Swisher (1944a, b) studied the combination of sulphur dioxide combined 1:1 vol:vol with acetone as a potential fumigant to control bedbugs when applied to mattresses as a liquid. Swisher (1944b) also tested sulphuryl fluoride in combination with acetone or ethylene oxide as a potential fumigant combination to control stored-product insects. The results of these studies (Swisher 1944a, b) apparently failed to progress further than the initial publications. Kenaga (1956) evaluated the use of sulphur dioxide, which the author claimed was a synergist when used with other fumigants, in fumigant mixtures for grain treatments to control stored-product insects. However, the use of sulphur dioxide for grain fumigation was found impractical because (1) the fumigant “was highly sorbed and/or reacted in grain,” (2) there was no appreciable penetration below the surface of the grain, and (3) mixtures of sulphur dioxide with acetone or ethylene oxide provided no additional penetration or insect control (Kenaga 1956). No further research was found in the literature pertaining to sulphur dioxide fumigation of durables, probably for the reason the fumigations tested by Kenaga (1956) failed to control insects. Sulphur dioxide remains a niche fumigant used to control postharvest decay in fresh fruits under controlled conditions (Cantin et al. 2011).

5.18 Tetrachloroethane

Tetrachloroethane was tested as a soil and tree fumigant to control insect pests of apricot trees (Madsen & Blair Bailey 1959) but no additional information was found.

These minor fumigants are mentioned here to ensure that all fumigants named in the literature have been included in this review. None of the minor fumigants identified above has been tested as a potential fumigant for logs, timber or wood products in the literature. Moreover, the authors found no substantial evidence in the literature that any of the minor fumigants had any potential that merited further consideration for use on export logs.

6 Chemical treatment methods – miscellaneous

6.1 Pesticide drenches

Contact pesticides can be applied quickly and easily as a postharvest chemical dip or an inline, low-volume spray application but, in the case of toxic compounds, residues need to remain below maximum residue limits for export markets and there may be health, safety and environmental concerns associated with application and disposal and potentially high costs for registration (Jamieson et al. 2009). Pesticide drenches are used against insect pests in quarantine programs (USDA 2010) and are commonplace in the nursery industry where plants growing in containers can be easily immersed (Dennis et al. 2004). However, these pesticide drenches have a number of problems that include being hazardous to labour, very time consuming, must be subjected to lengthy environmental assessments, and later require the disposal of large volumes of pesticide solution and clean-up of treatment areas (Dennis 2004, USDA 2010).

The authors chose to eliminate chemical drenches from consideration in this review because of New Zealand's unique environment and because chemical drenches have implied potential issues related to worker safety and health, soil and ground water contamination, insect resistance, non-target species impact, and residue and handling; issues that could result in lengthy and costly approval processes with no assured outcome and that could become a flashpoint for environmental politics.

6.2 Aerosols and fogging

In agriculture an aerosol or fog may be used in glasshouses, 'polytunnels' and warehouses to treat a space rather than spray surfaces. As the pesticide particles are intended to remain airborne for as long as possible, deposition is limited so a long residual action is not expected; where a more residual effect is needed, it is better to apply a spray or mist (Thornhill & Matthews 1995).

The application of a prophylactic insecticide treatment is one potential option for extending the Post Fumigation Exposure Period (PFEP) to maintain the pest-free status of wood products after fumigation. The PFEP is a requirement imposed by MPI to provide assurance that the phytosanitary requirements of our trading partners are not compromised by reinfestation with flying insects, in particular *H. ater* and *H. ligniperda*, *A. ferus* and *P. reticularis*. A review of the insecticide cypermethrin (a synthetic pyrethroid) suggested that it to be a fit for purpose chemical to control reinfestation by phytosanitary pests (Rolando et al. 2011). Subsequent bioassays confirmed that the cypermethrin was effective against the target pests although there was considerable variability in control survival. Test results showed that an application of ~0.5 mg cypermethrin/cm^2 bark would be sufficient to cause mortality of pests attempting to re-infest log stacks after fumigation (Rolando et al. 2013). Self (2007) identified fogging as a potential application method to apply insecticide to a log stack. Rolando et al. (2013) attempted three cypermethrin fog applications to commercial log stacks (650 - 950 m^3) that were under a commercial fumigation tarpaulin using a concentration rate of 40 - 360 g active ingredient per 1,000 m^3 of surface area. The cypermethrin application rates Rolando et al. (2013) used were 4-36 times greater than the manufacturer's recommended application rate to fog an empty storage facility. However, neither an effective cypermethrin concentration was obtained on the logs in the stack nor was complete insect control obtained, thereby indicating that fogging would not be an effective insect control treatment at application rates significantly greater than that recommended by the manufacturer. Furthermore, fogging at extremely high rates of application probably would be unacceptable from an environmental perspective (especially marine life), given the lack of bundling of timbers and the large numbers of log stacks at the ports (Rolando et al. 2011).

The use of insecticidal fogs as an effective phytosanitary measure, as opposed to a post-treatment product security, is a different concept that requires an understanding of the pest biology. New Zealand treats export logs for specific regulated pests that include bark beetles, wood borers and a Siricid wood wasp, *S. noctilio* (Pawson et al. 2012). All of these adult pests either bore under the bark to lay eggs, oviposit directly into the wood, or lay eggs in bark crevices that subsequently hatch and the larvae bore into the wood (Pawson et al. 2012). Therefore, when the logs reach a central treatment point at a port before they are exported, any infestations of the logs are internal and fogging with a compound with an aerosol size of <15 μm (Matthews 1979) is unlikely to penetrate and reach the target pest, even where insect entry holes are present (although no studies have been done to test the penetration of fogs into insect entry holes).

Fogging was approved as an off-shore phytosanitary treatment for timber exported from New Zealand to Australia (MPI 2014b). The regulations include:

1. Prior to consignments arriving into Australia, consignment must:

a. Meet the requirements of the MPI Secure Pathway Official Assurance Programme (available for containerised consignments only), or

b. Be treated with one of the following:

   i. Methyl bromide at 48g/m³ for 12 hours at a minimum temperature of 15°C

   ii. Methyl bromide at 56g/m³ for 12 hours at a minimum temperature of 10°C

   iii. Insecticidal fog (e.g. Pestigas, Permigas, Pybuthrin 33) containing a synthetic or natural pyrethroid(s) applied as per label instructions. This treatment must be undertaken in an enclosure (e.g. under tarpaulin, container or an enclosed building) it must not be applied to goods standing in the open, or

   iv. Spray containing synthetic pyrethroid(s) (e.g. Cislin 25) registered for the control of crawling pests in workplace environments is applied to surfaces as per label instructions. This treatment can be applied to goods standing in the open.

Noteworthy is that the fogging treatments were approved without any supporting data. Hence, it must be assumed that, regardless of any fogging that was done before timber was exported, the interception of live insects at the port of entry by Australia would result in some form of regulatory action.

Fogging is not considered to be applicable as a methyl bromide alternative because of the lack of efficacy at significantly high concentrations of applied pyrethroid (Rolando et al. 2011). Even if the studies of Rolando et al. (2011) had been successful in obtaining uniform coverage of log surfaces and complete insect control, the potentially deleterious environmental effects from pyrethroid run-off at the ports where treatments occurred would preclude the use of this technology.

7 Non-chemical treatments and methods

7.1 Controlled and modified atmospheres

Following on the reports of AliNiazee and Lindgren (1969), Blickenstaff (1973), Dcstan (1963), Hooper (1970), and White et al. (1970) on the effects of elevated carbon dioxide and/or low concentrations of oxygen on insects, the use of controlled or modified atmospheres as a “non-toxic fumigation” method gained serious attention. Since then, the use of low oxygen and elevated carbon dioxide atmospheres have been researched and used commercially to control stored-product pests in grains (De Lima 1990) and other commodities, such as fresh produce (Jamieson et al. 2009).

The terms ‘controlled atmosphere’ and ‘modified atmosphere’ are often used to describe these types of atmosphere modifications. Modified atmosphere treatments for pests of fresh horticultural products and dried stored products consist of altering the normal atmospheric gas composition to one that will kill insects (Hallman 1994). Modified atmosphere is a general term which includes all changes in the normal atmospheric composition (Calderon 1990) and controlled atmosphere is a modified atmosphere that is maintained with little adding or removing gases as needed (Hallman 1994). Stated in another way: in controlled atmospheres, gas concentrations are controlled to within a few percent of set-points through the addition of nitrogen or air or scrubbing of carbon dioxide, and modified atmospheres are when the respiration of the commodity sealed in a container is used to alter the ratio of oxygen and carbon dioxide during storage (Mitcham et al. 2006). An example of a controlled atmosphere treatment is the work by Soderstrom et al. (1990) where a 0.5% oxygen, 10.0% carbon dioxide and 89.5% nitrogen atmosphere was used to control codling moth life stages in 7-19 d at 25°C and either 60% or 95% RH. An example of a modified atmosphere treatment is the work by White et al. (1995) that determined naturally produced concentrations of carbon dioxide from the biological respiration of stored wheat could both delay population growth and kill the life stages of rusty grain beetle, *Cryptolestes ferrugineus* (Stephens), red flour beetle, *T. castaneum* (Herbst), and flat grain beetle, *C. pusillus* (Schönherr) (Coleoptera: Tenebrionidae).

Today, most controlled or modified atmospheres are used in the storage of fresh produce to delay ripening, decrease losses from postharvest decay organisms, and maintain quality and shelf life (Navarro et al. 2012). However, the use of controlled or modified atmospheres has been studied for use against a number of pests found on or in fruit or root crops, including examples such as:

- Apple maggot, *Rhagoletis pomonella* (Walsh) (Diptera: Tephritidae) and plum curculio, *Conotrachelus nenuphar* (Herbst) (Coleoptera: Curculionidae), larvae in cold-stored plums using 3% oxygen and 2-8% carbon dioxide at 3.3°C required 33 d to kill all larvae of both species (Glass et al. 1961).
- Apple maggot eggs and larvae in apples using 7 d or 14 d cold storage at 10°C and 10.6-19.0% carbon dioxide (Agnello et al. 2002). Although larvae were controlled by the controlled atmosphere, complete control of the egg stage was not obtained at either the 7-d or 14-day holding periods.
- Caribbean fruit fly, *Anastrepha suspensa* (Loew) (Diptera: Tephritidae), eggs and larvae in citrus using 2, 10 or 20% oxygen and 20, 50 or 80% carbon dioxide at 15.6°C or 10.0°C for 3, 5, 7, or 10 d (Benschoter 1987). None of the treatment combinations were able to control the egg or larval stages and extended treatment times caused unacceptable damage to the citrus quality (Benschoter 1987).

- Delate et al. (1990) were able to control the life stages of sweetpotato weevil, *Cylas formicarius elegantulus* (Summers) (Coleoptera: Curculionidae), using 2% oxygen and 60% carbon dioxide at 25°C and 75% RH for 7 d.
- Soderstrom et al. (1990) exposed eggs, mature larvae, diapausing larvae, pupae, and adults of codling moth to either 0.5% oxygen and 10% carbon dioxide and nitrogen balance or 60% carbon dioxide in air at 25°C and 60 or 95% RH. The trend from least to most tolerant stage was eggs, adults < pupae < mature larvae < diapausing larvae. Mortality occurred more quickly at 60% RH than at 95% RH, except in eggs where there was no significant difference, and 60% carbon dioxide atmospheres killed more quickly (<2 to 19 days) than the low oxygen atmosphere (18-42 d).

These five examples demonstrate several important issues encountered with the use of controlled or modified atmospheres to eliminate insects from commodities:

- Lengthy treatment durations (e.g., 7 d for sweetpotato weevil, 33 d for apple maggot or 42 d for codling moth diapausing larvae) are needed to obtain insect mortality.
- Insect species and life stages react differently (e.g., sweetpotato weevil life stages compared with those of Caribbean fruit fly eggs or codling moth diapausing larvae or eggs).
- Very low oxygen concentrations are needed to kill insects (e.g., apple maggot and sweetpotato weevil).

Regarding the issue of low oxygen concentration, Banks (1978) found that oxygen levels must be <2% to be lethal to stored-product insects. It is important to note here that the studies of Glass et al. (1961), Agnello et al. (2002), Benschoter (1987), and Delate et al. (1990) were seeking to obtain efficacy at levels required for quarantine security while Soderstrom et al. (1990) were seeking to control codling moth in walnuts at economic levels to reduce damage during storage. Whereas quarantine security requires significantly high probabilities that all target insects will be killed (Robertson et al. 1994a), controlling insects to prevent economic losses allows for some survival to occur (Banks et al. 1990, Jay 1984). Because 100% mortality is not required, the most successful controlled and modified atmosphere storage for insect control has been in the commodity area of stored products (e.g., Banks et al. 1990, Soderstrom and Brandl 1984, Wang et al. 2010).

Two additional issues with controlled or modified atmospheres include:

- Cost of application - The technology must be applied to products sealed in air-tight or nearly air-tight containers or structures and the gas concentrations must be maintained at the desired levels to achieve insect control. The principal limitation in the widespread use of controlled or modified atmospheres to control insects in stored products is the cost of obtaining or producing the atmospheres (Collins 2010).
- Sub-lethal effects - According to Carpenter et al. (2001) the sub-lethal effects of controlled atmospheres are usually detected only when they are specifically designed experimentally to do so. For many commodities that could be disinfested with controlled atmospheres for quarantine purposes, the effective treatment is close to levels that would damage the commodity, although this depends on the durability of the commodity to be treated. For other insects where natural biological variation provides for sub-lethal effects to occur, the issue eventually will result in the interception of survivors on the treated produce. Until more is known about the mode of action of controlled atmospheres in causing insect death and the occurrence of sub-lethal effects that can be predicted and detected, it is unlikely that controlled atmospheres will be acceptable as quarantine treatments (Carpenter et al. 2001).

Although there is a significant amount of literature on the mortality of insect pests in response to various controlled atmosphere treatments, there is considerably less information on the mode of action of controlled and modified atmospheres on insects (Mitcham et al., 2006). The reviews in this area include Carpenter & Potter (1994), Fleurat-Lessard (1990) Mitcham et al. (2006), and Navarro et al. (2012).

A succinct overview of pest responses to controlled or modified atmospheres was provided by Mitcham et al. (2006): “Arthropods cope with reduced oxygen and elevated carbon dioxide atmospheres with a reduction in metabolic rate, also called metabolic arrest. The reduction in metabolism lessens the pressure on the organism to initiate anaerobic metabolism, but also leads to a reduction in ATP production. The natural permeability of cellular membranes appears to be important for the survival of the arthropod under low oxygen or high carbon dioxide atmospheres. Despite the similarities in response, arthropod mortality is generally greater in response to high carbon dioxide as opposed to low oxygen atmospheres. There appears to be a greater decrease in ATP and energy charge in arthropods exposed to high carbon dioxide as compared with low oxygen atmospheres, and this may be due to greater membrane permeability under carbon dioxide leading to an inefficient production of ATP. Reduced oxygen and elevated carbon dioxide atmospheres can have an additive effect in some cases, depending on the concentrations used. The effect of these atmospheres on arthropods depends also on temperature, species and life stage.”

The application of temperature to controlled or modified atmospheres led to more rapid insect control, especially in the development of quarantine treatments. The controlled atmosphere and temperature treatment system became known as CATTS (Neven & Mitcham 1996). CATTS has been successful in reducing the amount of treatment time required to eliminate target insects life stages when compared with either heat treatments or controlled atmospheres alone. Neven and Mitcham (1996) treated codling moth fifth instars with a controlled atmosphere of 1.0% oxygen and 15% carbon dioxide in combination with high temperature at 45°C or 47°C to obtain 100% mortality in 64 or 44 minutes, respectively, compared with 124 or 72 minutes for heat treatments alone of 45°C or 47°C, respectively. Examples of the effects of CATTS on different insects include:

- Whiting et al. (1991) found that a controlled atmosphere of 0.4% oxygen and 5.0% carbon dioxide at 40°C gave a mean LT_{99} of 4.2 h to provide 100% mortality of fifth instar light brown apple moth.
- Whiting and van den Huevel (1995) achieved a lowest mean LT_{99} of 133 h for 100% mortality in diapausing adult two-spotted spider mite using an atmosphere of 0.4% oxygen and 20.0% carbon dioxide at 20°C and found that by increasing the treatment temperature to 40°C the mean LT_{99} was reduced to 15.5 h.
- Neven (2005) developed a quarantine treatment to control codling moth in sweet cherries using a controlled atmosphere of 1.0% oxygen and 15.0% carbon dioxide in a - 2°C dew point environment and a treatment time of 45 minutes using a treatment temperature of 45.0°C or 25 minutes using a treatment temperature of 47.0°C.
- Neven et al. (2006) showed in efficacy and confirmatory tests that combining a high-temperature forced-air treatment (Armstrong et al. 1989) using linear heating rates of either 12 or 24°C/h to a final chamber temperature of 46°C with a controlled atmosphere of 1% oxygen and 15% carbon dioxide in a >90% RH atmosphere provided quarantine security against codling moth and oriental fruit moth, *Grapholita molesta* (Busck) (Lepidoptera: Tortricidae), in peaches and nectarines exported from the US.

- Son et al. (2012) developed a controlled atmosphere high-temperature forced-air treatment system similar to Neven et al. (2006) to disinfest fruit moth, *Carposina sasakii* Matsumura (Lepidoptera: Carposinidae), from apples before export using a heating rate of 16°C/h to a chamber temperature of 46°C in an atmosphere of <1% oxygen and 15% carbon dioxide with a 60 minute treatment time.

Schroeder and Eidmann (1986) reported the results from controlled atmosphere studies with spruce bark beetle, *Ips typographus* L.; *Pityogenes chalcographus* [*no common name*]; and pine shoot beetle, *Tomicus pineperda* (L.) (Coleoptera: Scolytidae), that showed that the beetles were more susceptible to controlled atmospheres with higher concentrations of carbon dioxide than higher concentrations of nitrogen. However, Schroeder and Eidmann (1986) did not develop any treatments against the three Scolytid species.

Of specific interest to the issue of New Zealand export logs, Dentener et al. (1997) tested the effects of controlled atmospheres alone and in combination with heat against "small, medium and large" sized *P. reticularis* larvae (size was based on larval weight). Preliminary experiments at 20°C and 30-50% RH showed that the larvae were tolerant to low oxygen conditions and exposure for 10 d to >99% carbon dioxide with only 72%, 15% and 0% mortality in small, medium and large sized larvae, respectively. Similarly, exposure to a 99% nitrogen atmosphere for 10 d resulted in 88%, 30% and 8% mortality in small, medium and large sized larvae, respectively (Dentener et al. 1997). However, when the same controlled atmospheres were tested against the three sizes of larvae at 40°C, larval mortality was greatly increased and the mortality between the three larval sizes were not significantly different (the mortality data was combined for all larval sizes). The >99% nitrogen atmosphere at 40°C resulted in an LT_{99} of 8.3 h; the >99% carbon dioxide atmosphere at 40°C resulted in an LT_{99} of 6.9 h; an atmosphere of 50% each carbon dioxide and nitrogen resulted in an LT_{99} of 6.9 h (Dentener et al. 1997). Further research suggested by Dentener et al. (1997) was never realised and no further work was done with controlled atmospheres as potential treatments against New Zealand forest pests.

7.1.1 Controlled atmospheres combined with high pressure

Following the initial publication of Nakakita and Kawashima (1994) on a "new" method to control stored-product insects using carbon dioxide with high pressure followed by sudden pressure loss there was a flurry of reports on the use of carbon dioxide, nitrogen and mixtures of both gases at high pressure (1500 to 2000 kPa) for insect control. The "high pressure" used in the treatment is supplied by the pressure of the carbon dioxide released into the treatment chamber (Nakakita & Kawashima 1984). Research using high-purity carbon dioxide combined with high pressure followed by sudden decompression release of the carbon dioxide as an insect control method was reported by Caliboso et al. (1994), Kutbay et al. (2011) Locatelli et al. (1998), Prozell et al. (1997), Reichmuth (1997), Reichmuth and Wohlgemuth (1994), Riudavets et al. (2010), Sabine and Reichmuth (1991), Ulrichs (1995), and Wei et al. (1998). The primary benefit from using the carbon dioxide combined with high pressure was that the treatment time was short, generally 15-60 minutes. However, there are time-related issues with loading the carbon dioxide required to reach the desired pressure (Kutbay et al. 2011).Although many of the research reports suggest further research is needed to construct commercial treatment facilities (e.g., Wei et al. 1998), there was no evidence found in searches of the literature or the internet that actual commercial facilities were available.

Studies of atmospheres in closed systems, including fumigation chambers in the laboratory and ship holds (B. Bycroft and S. Olsson, unpublished data) found that log respiration caused carbon dioxide concentrations to increase to >10% and oxygen to decrease to <1%. Following on the work by Dentener et al. (1997) and using the natural increase in carbon dioxide concentration by log respiration it may be possible to elevate the carbon dioxide concentrations in closed systems, e.g., ship holds, then add heat from either an external (e.g., Biovapor NZ Ltd., see www.biovapor.com) or internal (e.g., heat from ship engines) source to increase the log surface temperature to ≥ 40°C. Hence, the authors consider that a limited investigation to determine the carbon dioxide concentration and temperature combination that is required to kill New Zealand forest insects to be a feasible research approach.

7.2 Energy treatments

Energy treatments covered in this section include irradiation, microwave, radio frequency, and ohmic (joule) heating. Dielectric heating is a term that covers radio frequency and microwave heating. Radio frequency and microwave are high-frequency electromagnetic waves generated by vacuum tubes, magnetrons or klystrons. The rotational responses of polarised molecules to an alternating electric field (electronic polarisation) and migration of charged ions (ionic polarisation) are the main contributing mechanisms for heat generation in a material (Barber, 1983).

Generally, a distinction is made between radio frequency dielectric heating (1-300 MHz) and microwave dielectric heating (300-30,000 MHz) (Orfeuil 1987), not only in the frequency ranges, but also in the dielectric properties of generators, applicators and related materials (Tang & Wang 2007).

Radio frequency and microwave treatments have particular advantages over conventional hot air in treating commodities. In the case of in-shell walnuts, for example, the shell and the air spaces within the shell act as layers of insulation and slow down heat transfer with conventional heating methods, while electromagnetic energy directly interacts with the kernel inside the shell to generate heat.

Ohmic (or joule) heating consists of heating an object by passing an electrical current through it due to the object's electrical resistance in the same fashion that an electric stove element heats (Kamonpatana 2012). Irradiation differs significantly from radio frequency, microwave or ohmic heating because the gamma rays, electron beams or x-rays that constitute an irradiation treatment kill by destroying the genetic material of the target pest. Pulsed electrical field differs from the other treatments because the mode of action is thought to be related to increased permeability of the cell membrane due to compression caused by an electrical potential across the membrane when an external electrical field is applied. In contrast, radio frequency, microwave and ohmic heating kill the target pest by elevating the temperature of the substrate beyond the thermal tolerance of the pest. Irradiation (electron beam and x-rays only), radio frequency, microwave, ohmic heating, pulsed electrical field were combined arbitrarily on the basis that they all may require significant energy (and energy costs) to carry out treatments that could be considered herein as alternatives to methyl bromide fumigation. Because they heat the substrate in and/or on which the target pest is found, radio frequency, microwave and ohmic heating also could be placed in Section 7.3.2 Heat treatments.

7.2.1 Irradiation

Physicists credit French physicist Henri Becquerel with discovering gamma radiation. In 1896, he discovered that uranium minerals could expose a photographic plate through a heavy opaque paper. Roentgen had recently discovered x-rays, and Becquerel reasoned that uranium emitted some invisible light similar to x-rays. He called it "metallic phosphorescence" but in reality he had found gamma radiation being emitted by radium-226 that is part of the uranium decay chain and commonly occurs with uranium (USEPA 2014a). The most common gamma ray emitters in use today are cobalt-60, caesium-137 and technetium-99m, the latter being most widely used in diagnostic studies and during the production of cobalt-60 and caesium-137 to improve their physical characteristics (USEPA 2014a). The gamma rays emitted by caesium-137 have less penetrating gamma beams than cobalt-60. Gamma rays and x-rays, like visible, infrared, and ultraviolet light, are part of the electromagnetic spectrum but they differ in their origin. Gamma rays originate in the nucleus of a “radioactive” or gamma-emitter material, x-rays originate in the electron fields surrounding the nucleus or they are machine-produced (USEPA 2014a).

Caesium-137 is one of the most common radioisotopes used in industry. Thousands of devices use caesium-137, such as moisture-density gauges that are widely used in the construction industry, levelling gauges that are used in industries to detect liquid flow in pipes and tanks, in thickness gauges for measuring thickness of sheet metal, paper, film and many other products, and in well-logging devices in the drilling industry to help characterise rock strata. Cobalt-60 is used primarily in industry to sterilise medical equipment in hospitals, pasteurise certain foods and spices, and as a disinfestation treatment for fresh fruits before exports. Both caesium-137 and cobalt-60 are used in industry in thickness gauges for measuring thickness of sheet metal, paper, film and many other products, and in the medical field for the treatment of cancers (USEPA 2014a).

Food irradiators include two source types: gamma sources and x-ray sources. X-ray sources include electron beam generators that generate e-beams and work on the same principle as a television tube, and x-ray generators that use an electron beam accelerator to target electrons on a metal plate (e.g., tungsten) to convert the e-beams to x-rays. Whereas e-beams have only a shallow depth of penetration, both gamma rays and x-rays have deep penetration characteristics (USEPA 2014a).

The particles composing “ionising radiation” (e.g., electrons and x-rays) are sufficiently energetic as to be capable of ejecting electrons from atoms and molecules (Miller 2005). The biological effects caused by ionising radiation are primarily the result of disruption of the deoxyribonucleic acid (DNA) molecules in the nuclei of cells in living organisms. The damage to the DNA caused by ionising radiation, either the complete or incomplete severing of the DNA strands, results in immediate death or prevents the normal replication of the correct DNA codes necessary for survival and results in eventual death (Miller 2005).

The international standard for measuring ionising radiation is a unit called a “Gray” (symbol = Gy) and it is a measure of the absorbed dose that is defined as the absorption of one joule of radiation energy by one kilogram of matter (IBWM 2006). A Gy is a physical quantity that does not take into account any biological context and is defined independently for any target material (WHO 1999).

Soon after ionising radiation was discovered in the late 19th century it was found that organisms could be reproductively sterilised with relatively low doses that showed no other gross effects to the organisms (Hunter 1912). Irradiation as a commercial insect control technique was applied for the first time in 1929 to cigars to control *L. serricorne* although the x-ray machine used turned out to be unsuitable for continuous processing (Diehl 1995).

There are three types of irradiators available today based on the source for irradiation: cobalt 60, electron beam generators, and x-ray accelerators. The following information was provided by the US Environmental Protection Agency (USEPA 2014a):

Cobalt-60 Gamma Source - emits ionising radiation in the form of intense gamma rays. Gamma facilities store cobalt-60 in stainless steel capsules (called "pencils") in underwater in tanks (called "pools") because the water rapidly attenuates the gamma rays and acts as a shield. The cobalt-60 source containing the pencils is either lifted mechanically from the pool to irradiate the target or the target (usually in a container) is exposed to the gamma rays by submerging it in the pool. The dose received by the target is a factor based on the energy (gamma ray emissions) of the cobalt-60 and exposure time measured in Grays. Cobalt-60 facilities have several advantages that include:

- Up to 95% of the energy emitted is available for use
- Deep penetration
- Yields substantial uniformity of the dose in the target
- Decays to non-radioactive nickel
- Considered to pose low risk to the environment

Several disadvantages of cobalt-60 facilities include:

- Cobalt-60 pencils require frequent replenishment
- Target cannot be irradiated in its final shipping container if it must be submerged into the pool. In the case where the source is raised from the pool, the final shipping container may pose an additional constraint on penetration and overall dose acquisition.
- Treatment process may be slow depending on the source size and target density

Electron Beam Generators - the generated e-beams are concentrated and accelerated to 99% of the speed of light and energies up to 10 MeV (10^{-14} joules). Because e-beams are generated electrically, they offer the advantages of:

- They can be turned on only as needed
- They do not require replenishment of the source as does cobalt-60
- There is no radioactive waste
- Target can be irradiated in its final shipping container

Several disadvantages of electron beam facilities include:

- Shallow depth of penetration
- E-beams must be converted to x-rays to penetrate large items
- High electric power consumption
- Complexity (with potentially high maintenance)

X-ray Accelerators - share the same advantages and disadvantages with electron beam generators except that the x-rays are immediately available and have deep penetration characteristics.

Irradiation is a quarantine treatment option for fresh and durable commodities (IAEA 1999). During the past 10 years, this technology has been used as a phytosanitary treatment for control of quarantine insect pests in tropical fruits exported from Australia to New Zealand and Malaysia, and from Hawaii, India, Thailand, Vietnam, and Mexico to the mainland United States (Follett 2009, Follett & Weinert 2012). Australia and New Zealand have approved generic doses for tropical fruits of 150 Gy for Tephritid fruit flies, 250 Gy for other insect pests and 300 Gy for mites (Follett & Neven 2006). The United States has approved generic radiation doses for all fresh horticultural commodities of 150 Gy for any Tephritid fruit fly and 400 Gy for all other insects except the pupa and adult stages of Lepidoptera (moths and butterflies) (USDA 2006).

Similar generic radiation doses have not been approved for stored-product pests for two reasons, which, according to Donahaye (2000) have been perceived historically as problematic because:

- Irradiation does not kill insects immediately. Hence, they continue to feed and damage the commodity.
- No routine tests to determine whether surviving insects are sterile are available. Therefore, treated insects may continue to reproduce.

The approvals for phytosanitary irradiation to control quarantine insect pests of fresh horticultural commodities for export and the rapidly expanding use of the technology for this purpose (Follett, 2009), demonstrate that the presence of live but sterile or non-viable insects is acceptable to regulatory authorities, and facility certification and proper documentation can be used to ensure treatment at the required dose. Many other reports can be found in the literature showing the efficacy of irradiation for the control of quarantine pests on fresh commodities, e.g., Ravuiwasa et al. (2009) reported that irradiation with 150-250 Gy had a significant effect on all life stages of the passionvine mealybug, *Planococcus minor* (Maskell), (Hemiptera: Pseudococcidae), by decreasing its survival rate, percentage of adult reproduction, oviposition, and fertility rate.

Hoedaya et al. (1973) irradiated stored rice infested with *S. oryzae* and 99% were killed at 200 Gy after three weeks; Tilton et al. (1966) found 100% mortality of *S. oryzae* treated at 175 Gy after three weeks; and Tuncbilek (1995) irradiated adult *S. oryzae* at 90 Gy and mortality was 100% after three weeks. Ignatowicz (2004) irradiated immature *S. oryzae* (eggs, larvae and pupae) at 80 and 100 Gy and observed no development to the adult stage. Radiation treatment of adults of the closely related weevil, *S. granarius*, required 100 Gy to achieve sterility (Aldryhim & Adam, 1999). Immediate kill of *S. oryzae* and other stored-product insects may require much higher doses, in the range of 1-3 KGy (Ignatowicz, 2004). Follett et al.(2013) found that a 120-Gy radiation dose would ensure that *S. granarius* adult weevils are sterilised and, therefore, could not propagate, and that larval feeding was arrested and would result in no further damage to the rice by larval feeding. Follett et al. (2013) suggested that their irradiation treatment could be particularly helpful in controlling phosphine-resistant populations, and help manage resistance to phosphine by preventing the spread of resistant insects in exported grains.

A key technical disadvantage of using irradiation as a quarantine treatment is that it is the only commercially applied treatment that does not result in death of the pest immediately after the treatment has been applied, thereby providing no direct verification of treatment efficacy. The measure of irradiation efficacy is prevention of development and/or reproduction, rather than acute mortality (Hallman & Thomas 2010). Consequently, the discovery of live quarantine pests on inspection of the commodity for which a certified irradiation treatment is applied does not indicate treatment failure. For virtually every other treatment, when live quarantine pests are found at inspection, the consignment is rejected or retreated regardless of treatment certification. In such cases it is assumed that the treatment was not properly done or did not work or that the shipment was contaminated with untreated, infested commodity or a treated commodity that was reinfested after treatment. Because there is no independent confirmation of efficacy, greater validation of the research process may be advisable for irradiation treatments compared with those treatments where acute mortality is the endpoint (Hallman & Thomas 2010).

Another disadvantage is the cost of an irradiation facility. Typical food irradiators can cost from US$1-3 million depending on size, processing capacity, and other factors (ISU 2010). The size and source type (cobalt versus electron beam) also impact costs with increased costs for safety and other issues specific to cobalt-source irradiators. However, technological advances may impact the cost of irradiation facility construction, such as semi-unitised irradiators with predesigned facilities (e.g., Gray*Star Genesis II, see http://www.graystarinc.com/genesis.html). Construction of a Sure Beam® e-beam (x-ray) irradiator was constructed in Hilo, Hawai'i and completed in 2000 at a cost of US$6.5 million for the irradiation of papaya and, eventually, other fresh produce including tropical fruits and sweet potatoes for export to the US mainland (Follett and Weinert 2012). In comparison, construction of a cobalt-60 Gray*Star irradiator was constructed at Kunia, Hawai'i in 2013 at a cost of US$4 million to treat 32.8 million kg of papaya along with other tropical fruits, vegetables and herbs (Gomes 2012).

According to a USDA Forest Service review of potential treatments for export logs from the [then] Soviet Russia (USDA 1991), speculative estimates for irradiation treatment for logs and prepared timbers provide cost figures competitive with those for fumigation, but until a specific proposal is made these costs can only be used to indicate an order of magnitude. For example with cobalt-60 at US$0.50/Curie and timber of density 0.5 g/cm^3, treatment with a dose of 2500 Gy would cost US$2.12/m^3, assuming 10% efficiency and continuous operation. This compares with present-day (1991) fumigation costs for timber in large batches (> 1416 m^3) of US$0.03-$0.04/m^3 ($\approx$ 60-fold difference). Hence, the margin is not sufficiently large to provide an incentive but the economics and the commercial exploitation interest in the application would be somewhat different if there was a mandatory requirement by Quarantine authorities to treat all timber, or a species of timber (USDA 1991).

Whereas irradiation can be carefully controlled for wood treatment, the dosages needed to eliminate pests would require constructing large irradiators capable of rapidly treating significant quantities of logs. At this level, both the cost of the irradiator and the potential safety problems associated with the source become a concern (Morrell 1995). Given these constraints, irradiation has severe economic drawbacks and is probably not feasible for mitigating pest risks in logs because they are a relatively low-value, high-volume commodity. Cornwell (1966) suggested that irradiation costs were up to 60 times those for conventional fumigation (see preceding paragraph); however, these results must be viewed with caution because both treatments were evaluated for eliminating pests near the wood surface. Costs might differ dramatically for control deeper in the wood. Unfortunately, the subject of economic viability remains speculative because no current (after the USDA 1991 figures in the previous paragraph) cost analysis for the irradiation treatment of logs to control quarantine pests could be found in the literature.

Radiation could be considered for the treatment of logs and prepared timbers, but it would be virtually impossible to engineer a plant capable of treating effectively the wide variety of sizes and shapes of imported packing cases. Thus, if irradiation were used, it would have to be employed in the exporting country where disinfestation is already often carried out; such packing cases are stamped, "Fumigated for Sirex wasp," and are certified and accepted by quarantine authorities (USDA 1991).

A final consideration in the use of irradiation is the potential for effects on wood structure. Older data suggest that irradiation will have little or no effect on mechanical strength of the wood, nor will it affect durability (Becker 1962; Kenaga & Cowling 1959; Scheffer 1963; Shuler 1969, 1971;

Shuler et al. 1975; Smith & Sharman 1971); however, these reports used wood that was irradiated while dry. Logs will be irradiated while green and the added moisture will require longer irradiation periods to produce a similar dosage at the centre of the log. The effects of these higher dosages on wet wood need to be thoroughly investigated before irradiation treatments are considered (Morrell 1995).

The development of any large-scale cobalt-60-based irradiator would be very problematic in New Zealand because of the country's non-nuclear policy (MFAT 2013). Hence, only electron beam or x-ray accelerators would be viable options. In June 2014, the National Centre for Radiation Science - Institute of Environmental Science and Research, Ltd., initiated the process to acquire an electron beam irradiator for research and commercial purposes (A. Pinkert, personal communication). Regardless, studies on the use of radiation to control pests of wood products, timber and logs has been ongoing for over 50 years, as shown by the following examples from the literature:

- The efficacy of irradiation for treating wood has been investigated to some extent for insects, fungi, and nematodes (Hansen 1972, Smith & Sharman 1971). Limited studies suggest that ambrosia beetles succumbed following 73-to 130-krad exposures (Yoshida et al. 1974, 1975); however, a major advantage of irradiation with respect to insects is its ability to disrupt reproductive capabilities. Irradiation has a long history of application to sterilise insects, which are then introduced into a region as a pest management strategy. The sterilised pests compete with fertile males for potential mates and, if released in sufficient number, outcompete with the fertile population. Sterilising dosages for irradiation appear to range from 20-40 Gy for the three ambrosia beetles tested (Yoshida et al. 1974, 1975). The pinewood nematode appears to be similarly susceptible to irradiation (Eicholz et al. 1991).
- Because irradiation functions by wholesale disruption of ongoing metabolic activities, insects and nematodes are susceptible to exposure throughout most of their life cycles. In contrast, fungi are often dormant for many parts of the year and produce resistant survival structures. Thus, these structures may be less sensitive to irradiation. In addition to this diminished sensitivity, fungi in wood may not be easy to sterilise with lower dosages, because many wood-inhabiting fungi produce asexual stages that might be unaffected by irradiation (Morrell 1995). The ability of most fungi to regenerate from hyphal fragments would permit fungi that survived sublethal dosages to spread later from the wood through dissemination of fragments by wind, water, or insect vectors. As a result, mitigation of potential fungal pests through the use of gamma irradiation will probably require the application of higher dosages than would typically be used to control insects or nematodes (Morrell 1995, Shuler 1969).
- Gamma irradiation was investigated as a possible method for disinfestation of *P. reticularis* in *P. radiata* logs by Lester et al. (2000). Larvae of four representative size classes were irradiated at six doses, and the lethal dose (LD99) calculated from mortality data 3 d and 10 d after treatment. All larval size classes showed a similar sensitivity to gamma irradiation and required 3677 Gray (Gy) and 2476 Gy for a LD_{99} 3 and 10 d after treatment, respectively. The penetration of gamma irradiation into pine wood was found to be lowest in freshly cut logs, and decreased linearly at a rate of 0.698 Gy mm^{-1} of wood. The penetration was greatest in wood that had been stored for 2 years, and decreased 0.512 Gy mm^{-1} of wood. These results were likely correlated with wood moisture content. Based on their results, Lester et al. (1999) suggested that gamma irradiation was a potential alternative method to fumigation for quarantine treatment of *P. reticularis*.
- Krcmar et al. (2010) used gamma irradiation to control the wood-feeding larvae of lesser stag beetle, *Dorcus parallelopipedus* (L.) (Coleoptera: Lucanidae). They found that 3.6 Gy

min^{-1} constant dose rate provided complete mortality after 55 d and a minimum dose of 360 Gy and that the instant lethal dose was 4238.3 to 2,784.9 Gy depending on larval size.

- Chmielewska et al. (2011) used irradiation treatments to control the developmental stages of *L*. *serricorne* and drugstore beetle, *Stegobium paniceum* (F.) (Coleoptera: Anobiidae) to preserve cultural heritage items (including wood artefacts) in museums. Their results found that the most susceptible life stage to irradiation was the egg followed by the larvae and pupae. Chmielewska et al. (2011) also found that 120 Gy completely inhibited the development of immatures to the adult stage in both species; and that 125 Gy caused complete sterility in both sexes of *L*. *serricorne*.

Whether irradiation could be used as a quarantine treatment against forest pests on export logs is doubtful because of the costs of providing enough irradiator capacity to handle the volume of logs exported from New Zealand. Whether other factors, such as energy costs, are prohibitive to the use of irradiation must be considered on both technological and cost-benefits levels. Although the authors considered it worthwhile to provide a complete overview of irradiation as a potential treatment, irradiation is not a viable option for logs at this time. However, irradiation is an approved treatment for timber under ISPM 18 (IPPC 2005), but whether the value and volume of timber exported from New Zealand would make the use of irradiation an economically viable quarantine treatment for timber is questionable.

7.2.2 Microwave treatments

Microwaves have been applied to a wide range of products, from soil and museum artefacts to fresh fruits (Hansen et al. 2011). However, the predominant efforts of current microwave technology have been to control pests of grain and stored products (Nelson 1973; Roseberg & Bögl 1987; Nelson et al. 1998; Wang et al. 2001a; Wang & Tang 2001).

Hamid and Boulanger (1971) described a microwave system to dry wheat and obtained complete control of *T*. *confusum* at 65°C for >30 min. While examining a microwave unit for drying grain, Boulanger et al. (1971) reported complete control of larvae and adults of *T*. *confusum*, granary weevil, *Sitophilus granarius* (L.) (Coleoptera: Curculionidae), and rusty grain beetle, *Cryptolestes ferrigineus* (Stephens) (Coleoptera: Cucujidae), within 15 min at 45°C. Kirkpatrick et al. (1972) found microwave treatments were less effective than infrared treatments for *S*. *oryzae*. Kirkpatrick (1975a) found that mature larvae and pupae were more resistant to microwaves than either larvae or eggs of Angoumois grain moth, *Sitotroga cerealella* Olivier (Lepidoptera: Gelechiidae); *S*. *oryzae*, and *R*. *dominica*. Watters (1976) reported that mortality of different life stages of *T*. *confusum* exposed to microwaves was a function of time and wheat moisture content.

Nelson (1976, 1977) measured the microwave dielectric properties of adult *S*. *oryzae* and hard red winter wheat. Tilton and Vardell (1982a) obtained 49% control of *S*. *cerealella*, *R*. *dominica*, *S*. *oryzae*, and *S*. *zeamais* in rye, corn and wheat after a microwave treatment at a partial vacuum of 35 torr for 10 min. Tilton and Vardell (1982b) went on to describe a pilot scale microwave/vacuum grain dryer that completely controlled *S. oryzae* in wheat. Langlinais (1989) demonstrated that *T*. *confusum* and *C*. *pusillus* can be economically controlled with microwave exposures. In Italy, Locatelli and Traversa (1989) found that beetles were more resistant than moths when using microwave treatments of rice, with *R*. *dominica* being the most tolerant; and that temperatures had to be greater than 80°C to assure complete control. In Canada, Shayesteh and Barthakur (1996) determined that 80°C, generated by microwaves, was needed to kill the most resistant life stage of *T*. *confusum* and Indian meal moth, *Plodia interpunctella* (Hübner) (Lepidoptera: Pyralidae). Using a 4-second microwave exposure, Halverson et al. (2000) treated soft white wheat infested with different life stages of *T*. *castaneum* and *S*.

zeamais and obtained 45.8°C grain temperatures and 49.5% insect mortality. Halverson et al. (2000) provided efficacy data for a microwave applicator against immature life stages of *S. oryzae*, *T*. *castaneum*, and *R*. *dominica*. Nelson and Payne (1982) described the reduced effectiveness in the control of pecan weevil, *Curculio carya* (Horn) (Coleoptera: Curculionidae), in pecan nuts while using microwaves. In England, Wilkin and Nelson (1987) used microwaves to kill adult *T*. *castaneum* and *O*. *surinamensis*, as well as larvae of *P*. *interpunctella* and *E*. *cautella*, *Ephestia cautella* (Walker) (Lepidoptera: Pyralidae), in walnuts at 60°C for 15 min. In Turkey, Baysal et al. (1998) used 90-second microwave exposures to control *E*. *cautella* on sun-dried figs.

A vacuum microwave grain dryer was found to disinfest product rapidly of four stored-product insect species (Tilton & Vardell 1982a). Phillips et al. (2001) confronted severe arcing when treating flowing grain, but reported 49.9% control of three species of stored-product beetles with static infested grain samples when treated with 2.45 GHz at 30 kW.

Microwave energy has been explored to treat wood and wood products. Watanabe et al. (2011) investigated the heating rate of *P*. *contorta* and western red cedar, *Thuja plicata* Donn *ex* D. Don (Pinales: Cupressaceae), during radio frequency heating. Wood blocks of the two species with various moisture contents and power densities were heated using a laboratory-size radio frequency dryer at a 40.7 MHz until temperature reached the 56°C that is approved as a lethal temperature for phytosanitary purposes (IPPC 2005). Heating rates were positively correlated with power density of the wood and negatively correlated with moisture content. The ratio of heating rate to power density had a negative correlation with moisture content and density in both the pine and cedar blocks (Watanabe et al. 2011). Based on their work, Watanabe et al. (2011) developed a one-dimensional mathematical model to describe the heating rate of wood during radio frequency heating that accurately predicted the heating rate of wood of different moisture content.

Hightower et al. (1974) recommended microwave radiation for raising temperatures to 50°C for controlling exotic beetle larvae in hardwoods imported from Africa and South America. Burdette et al. (1975) conducted tests using microwave energy against beetle larvae in hardwood and concluded that this treatment was economically promising. However, Crocker et al. (1987) found that microwave treatments were unsuccessful against weevils in oak acorns. Lewis and Haverty (1996a, b) compared microwave treatments to five other methods to control drywood termites and obtained 99% mortality at 4 weeks after treatment. To control *A*. *glabripennis*, Fleming et al. (2003) found that microwaves heated wood to the controlling temperature of 60°C within 5 min compared to 123 min from conventional heating, and recommended microwave treatment to eradicate *A*. *glabripennis* in solid wood packing materials. Fleming et al. (2004) identified the variables for scaling up a microwave treatment for Asian longhorned beetle control in solid wood packing materials based on moisture content. Fleming et al. (2004) found that wood temperatures 46.2°C sufficient to control *A*. *glabripennis* and *B*. *xylophilus*.

Henin et al. (2008), in examining microwave treatments to control *H*. *Bajulus,* concluded that wood surface temperature of 46°C guaranteed lethal conditions within wood, regardless of moisture content. Later, Makoviny et al. (2012) used 2.45 GHz and a surface heating power density of 1.0 $W.cm^{-2}$ to kill all *H*. *bajulus* in pine (*P*. *sylvestris*) blocks when the average temperature inside the wood near the larvae was 50°C and was held at that temperature for 34 min or 65°C and held at that temperature for 19 min. Nzokou et al. (2008) examined microwave to control *A*. *planipennis*, but concluded that the kiln treatment was better and recommended further research with radio frequency.

Dwinell et al. (1994), Jiang et al. (2006) and Lai et al. (2010) demonstrated that microwave heating could be used to kill *B*. *xylophilus* and *M*. *alternatus* in wood samples. Zona et al. (2010) used wet timber pieces (20 cm x l0 cm x 20 cm) that were artificially infested with *H*. *bajulus* larvae at different depths inside the wood and used both overlapping and homogenous microwave heating. They reported that the heating of the wood is more homogeneous when the microwave irradiation is overlapped by several microwave generators than by one central microwave generator, particularly at a 10-cm depth. The treatment effectiveness at depths less than 10 cm was homogenous. Their work (Zona et al. 2010) also showed that the treatment duration was related to the timber thickness. When the thickness or depth is small, it is possible to keep the effectiveness and save energy, reducing the treatment duration. The thickness of logs would certainly be disadvantageous to obtain a homogenous treatment of brief duration. Although Zona et al. (2010) demonstrated efficacy against *H*. *bajulus* larvae, few larvae were used in the treatments, which Zona et al. (2010) stated was necessary because of the high cost of obtaining the larvae.

According to ISPM No. 28:2007, Annex X (Heat treatment of wood packaging material using dielectric heat) was submitted as a treatment for wood packaging material using microwave heating to reduce the risk of introduction and spread of *A*. *glabripennis* and *B*. *xylophilus* to meet the criteria for treatment as prescribed in ISPM 15 (IPPC 2005). However, according to the ISPM 28:2007, Annex X report, the submission did not provide information on the effectiveness of microwave heating against *B. xylophilus* under operational or simulated operational conditions. As a result the efficacy level of the treatment against this pest could not be determined. In addition, the most resistant life stage was not established and the life stages most likely to be present at the time of treatment were not determined. No statistically supported comparison of the relative susceptibility of representative arthropods from the families listed in Annex 1 of ISPM No. 15 was provided in the submission. Issues with heat-up time specification and fire risks (moisture content lower limit) also need further clarification (IPPC 2005, 2006).

Microwave heating eventually may be applicable for use on solid wood packing materials and other wood products but the physics for using the technology did not appear to have come of age in the literature. Although many authors report success in using microwave heating, all of the research used small microwave heating systems (e.g., Zona et al. 2010). The authors do not recommend considering microwave heating as a viable methyl bromide alternative for logs.

7.2.3 Radio frequency

Radio frequencies generate internal heat by resistance from the very rapid change in molecular polarity. The advantages of radio frequency heating are that it is very fast, can penetrate deep into the target material because of its longer wavelength, may produce possible differential heating between the product and the pest, and does not produce toxic residues (Tang & Wang 2007). The lethal thermal effects on insects caused by radio frequency exposures were first reported by Lutz (1927) and Headlee and Burdette (1929). McKinley and Charles (1930) killed all adults of a parasitoid wasp, *Bracon hebetor* (Say) (Hymenoptera: Braconidae), with 30-second exposures of radio frequency 86 MHz. McLennan (1931) investigated heating from induced fields caused by radio frequency exposures on objects of different conductivities, dielectric properties and shapes, all which are important for applying radio frequency technology to a wide range of commodities. Hadjinicolaou (1931) attributed the death of a variety of stored-product pests, after exposure to high frequency radio waves, to internal heat generated within the body of each insect. Whitney (1932) attributed insect death caused by radio frequency exposures to overheating. Davis (1933) described how radio frequency energy can kill stored-product pests. Pyenson (1933) examined the protective properties of various shielding materials, such as cloth and cereals, surrounding insects, and concluded that insects could be effectively killed when treated in dry soil, woody materials and paper, clothes, tobacco, seeds and grains, flours, cereal breakfast foods, and nuts because these items have low moisture content. Shaw and Galvin (1949) examined heating characteristics of vegetative tissues including those from potato, carrot, apple, and peach. Thomas (1952) produced a comprehensive review of the use of high frequency to control pests in a wide assortment of situations.

Although Mack (2011) suggests that radio frequency heating may be a viable option for carrying out heat treatments under ISPM 15, the size of the equipment shown is simply too small for use with large materials, such as logs. Wang and Tang (2001) and Wang et al. (2001a, 2002) discuss the use of radio frequency heating of fruits and walnuts. Noteworthy are the effects of fruit sizes on heat transfer to a fruit centre and the effect of the walnut shell on heating time. Considering the effect that fruit size and walnut shell have on prolonging heating by radio frequency (Wang and Tang 2001, Wang et al. 2001a, 2002) and the relatively small scale of the equipment used to carry out the radio frequency heating process that is shown in Wang et al. (2002), the authors do not foresee any possibility of using radio frequency heating as a methyl bromide alternative for logs.

7.2.4 Pulsed electrical field

High-voltage electric field pulses delivered in microseconds can deactivate vegetative stages of microorganisms (Grahl & Märkl 1996). Pulsed electric field was studied as a non-thermal means of fluid food preservation by inactivating microorganisms in liquid prepared foods to prolong shelf life and prevent food poisoning. Pulsed electric field is thought to inactivate microbes by making their non-permeable cell membranes permeable and has less adverse effects on nutritional quality and flavour of the food than traditional thermal pasteurisation or sterilisation methods (Hallman & Zhang 1997). The mode of action of pulsed electric field is thought to be related to increased permeability of the cell membrane due to compression caused by an electrical potential across the membrane when an external electrical field is applied. Electrical pulses of 25 kV or more may be needed to inactivate bacteria (Zhang et al. 1994). According to pulsed electric field theory, smaller voltages should suffice to inactivate organisms with larger cells, such as insects, because the electrical potential between the interior and exterior surfaces of the cell membrane is positively related to the size of the cell (Hallman & Zhang 1997).

Hallman and Zhang (1997) studied pulsed electric field to control Mexican fruit fly, *Anastrepha ludens* (Loew) (Diptera: Tephritidae), eggs and feeding third instars. The treatment disintegrated some of the eggs. Percent egg hatch was progressively reduced to a minimum of 2.9% as voltage was increased to a maximum of 9.2 kV/cm^2 delivered in ten 50-ms pulses. Nevertheless, no first instars hatching from eggs treated $\geq$ 5.0 kV (ten 50-ms pulses) survived to the third instar. Although pulsed electric field did not kill third instars immediately, the third instars displayed a variety of pathological symptoms including sluggishness, incomplete pupation with elongated, larviform puparia, and development of necrotic spots throughout their bodies. No third instars treated with >2.0 kV survived to the adult stage. Therefore, pulsed electric field has been shown to control insects, although considerable entomological and engineering work would be needed before a pulsed electric field-based treatment might become practical (Hallman & Zhang 1997).

7.2.5 Electrical energy (ohmic or joule) heating[5]

Around 1898, researchers in Massachusetts, USA, attempted to electrocute root knot nematodes in soil and they were successful when the soil temperature reached 49°C, the nematode's thermal death point (Newhall 1955). In England, Viscount Elveden (1921) compared productivity of soils treated with electricity, steam, and flame, and found that electric resistance heating gave better results than steam. In the state of Washington, USA, entomologist C.F. Doucette demonstrated that soil could be heated with alternating current and showed that the amount of heat generated directly related to the amount of soil moisture (Anonymous 1932). Studies on soil heating using electrical resistance were also done in Holland about 1931 (Newhall 1955), and in Germany using a three-phase circuit (Dix & Rauterberg 1933). After extensive testing, Fee (1933) recommended that resistance heating was more practical than steam for soil sterilisation of flats and benches in greenhouses. Tavernetti (1935) designed a cabinet for sterilising soil on greenhouse benches using electrical current, with soil temperature variations according to differences in soil characteristics, while adjusting voltages was the best method for controlling electrical demand. In Holland, Muyzenberg and Roghair van Rijn (1937) did extensive testing of resistance heating using electricity.

Carney (1932) reported on a method for soil sterilisation by using electrical heating elements (dry heat). Horsfall (1935) developed an improved soil steriliser using electrical heating elements and referred to its advantages over steam. Blauser (1935) also presented a design to sterilise soil using dry heat from electricity. Newhall and Nixon (1935), who compared heating by electrical elements with resistance heating, listed the factors needed for uniform temperature, and they concluded that both these methods were at least as effective as steaming. Newhall (1940) itemised the limitations of resistance heating (including operator safety, high demand on the service line, care in loading the chamber to get uniformity, and the need to increase conductivity by adding an electrolyte solution), while further developing the heating element procedure. Tavernetti (1942) described a continuous process using a screw conveyor and heating elements. The most limiting factor for all these electrical methods was the amount of energy needed to treat a relatively small volume of soil (Newhall 1955).

Ohmic heating is a non-conductive thermal technique which may show promise as a quarantine treatment. Considerable research and substantial commercial application have been done with ohmic heating as a means of sterilising foodstuffs that is less damaging to the nutritive quality of the food than alternative heating methods (Zoltai & Swearingen 1996, Kamonpatana 2012). In ohmic heating, an object heats when an electrical current is passed through it due to the object's electrical resistance in the same fashion that an electric stove element heats, and a number of studies have addressed modelling of ohmic heating in static as well as continuous systems (Kamonpatana 2012). Hallman and Sastry (unpublished data) did preliminary work with ohmic heating as a quarantine treatment for fruits and found that it is possible to heat a small batch of whole fruits rapidly and kill fruit fly larvae inside of fruits when the fruits are immersed in a dilute salt solution (Mangan & Hallman 1997). Ohmic heating has been investigated for preparing veneer logs for peeling (Fleischer & Downs 1953, Perré 2004). It has also been suggested for other purposes, including sterilisation (Reznik 2003). Additionally, there are some published data available regarding thermal properties of green timber (Yu et al. 2011, Dupleix et al. 2013), including several softwood species, but not *P. radiata*, and there is no available information regarding the electrical conductivity of green logs.

[5] Information on ohmic heating provided by W. Heffernan, Canterbury University, personal communication.

At the time of this literature review, research is in progress at the EPECentre, Canterbury University, Christchurch, to determine the technical and economic feasibility of using ohmic heating as a quarantine treatment for export logs. Studies demonstrated that by using 100kW of power, 0.5-0.6-m^3 logs could be heated to the international heat-treatment standards (ISPM-15) for solid wood packing materials (IPPC 2005). A number of important developments have occurred, such as non-invasive instrumentation to monitor temperature in logs, measurements of electrical conductivity, and rugged segmented electrodes to ensure good electrical contact to the log-ends. However, a number of issues need to be resolved by the ohmic heating research program, including:

- Optimal electrical power and frequency to achieve the desired heating parameters
- Elimination or reduction in the potential for 'hot spots' to occur in the log during heating
- Quality of logs and timber after ohmic heating
- Application of ohmic heating under commercial conditions (e.g., on the wharf)
- Costs of equipment and electricity for commercial ohmic heating treatment

Although ohmic heating may be a potential methyl bromide alternative, it is not given further consideration here (except to explain how it works) because it is covered by a funded ongoing research programme.

7.2.6 Infrared

The frequency of the infrared region of the electromagnetic spectrum is from 0.3 to 430 THz, between visible light and microwaves. Infrared radiation is strongly emitted by hot substances and is readily absorbed by living tissue. Thus, it is logical that infrared radiation has been examined as a thermal treatment (Hansen et al. 2011). Schroeder and Tilton (1961) reported complete control of *S. oryzae* and *R. dominica* with infrared exposures of less than a minute and at mean temperatures of 568°C and 688°C, respectively. Tilton and Schroeder (1963) examined the rate of adult emergence of *S. oryzae*, *R. dominica*, and Angoumois grain moths from rice by temperatures produced by infrared radiation. Kirkpatrick et al. (1972) found greater control of *S. oryzae* with infrared radiation than with microwave exposures. Kirkpatrick and Tilton (1972) measured mortalities of 12 species of stored-product beetles in soft winter wheat and obtained >99.5% mortality for all when treated at 658°C for less than a minute. Kirkpatrick (1975a) reported that eggs and early instars of the *R. dominica* and Angoumois grain moth were more resistant to infrared treatments than eggs and early instars of *S. oryzae*. Kirkpatrick (1975b) treated wheat infested with *S. oryzae* and *R. dominica* in bulk with infrared radiation and obtained ≥93% mortality after exposure to a maximum of 48.6C after 24 hours. More recently, Subramanyam (2004, 2005) reported mortality from flameless catalytic infrared heaters on adults of the *O. surinamensis*, *S. oryzae*, *T. castaneum*, *R. dominica*, and merchant grain beetle, *Oryzaephilus mercator* (Fauvel) (Coleoptera: Silvanidae). However, research and application of infrared technologies for the control of insects have not been popular in recent decades (Hansen et al. 2011).

7.3 Physical treatments

Physical treatments consist of using either heat or cold to disinfest commodities of target organisms. Most physical treatments in use today have been developed or refined over the past four decades, which at the time of this writing include refrigeration (or cold) treatment, vapour heat and forced hot-air, and hot-water immersion treatment methods, which are used primarily to disinfest fresh produce (Armstrong & Mangan 2007, Jamieson et al. 2009). Simply put, cold treatments consist of reducing the temperature of the host commodity or infested substrate below the thermal tolerance limits of the target pest, while heat treatments consist of heating the host commodity or infested substrate beyond the thermal tolerance limits of the target pest (Armstrong & Mangan 2007).

7.3.1 Cold treatments

Extreme temperatures were the first quarantine treatments. Ironically, cold storage was initially implicated in the spread of insect pests before it was used as a quarantine treatment (Mangan & Hallman 1997). Fuller (1906) found that Mediterranean fruit fly larvae survived 124 d in peaches stored at about 4.5°C and considered this evidence that international shipment of cold-stored fruit was responsible for the spread of pests. The following year, Hooper (1907) and Lounsbury (1907) reported that Mediterranean fruit fly survived temperatures above 3.3°C, but that storage at temperatures between 0.5-1.7°C for three weeks killed all fruit fly eggs and larvae in various fruits (Quaintance 1912).

According to Lee (1991) many insects and related terrestrial arthropods from temperate and tropical areas are immobilised and enter a state of chill coma when exposed to temperatures between 0°C and 10°C. The chill coma is reversible if the duration of exposure is not prolonged. The conditions under which insects carry out their life cycle, either once or over a number of generations, may alter the effects that sudden temperature changes may have on their survival (Denlinger & Lee 1998, Lee 2010).

As with many treatments, efficacy of cold treatment may be positively related to treatment rate. Gould and Hennessey (1997) found a faster rate of mortality of *A. suspensa*, large third instars in carambolas cooled in 40-45 min to a holding temperature of 1.1°C versus those cooled to 1.1°C in over 24 h. Although rapid cooling may not be commercially feasible, it may indicate a problem when cold treatments are applied on a commercial scale. The faster cooling rate may have prevented cold hardening by the insect. Because the cooling rate of fruit in large, commercial coolers is slower than that usually achieved in small research coolers, it is possible that a cold treatment applied on a commercial scale may have lower mortality than that same treatment when performed on a research scale (Mangan & Hallman 1997).

Although temperatures at or slightly above 0°C are effective for controlling a variety of insects such as fruit flies in host fruits, the major drawback of low temperature treatment is the length of time necessary for adequate control. While high temperatures can kill most insects in a matter of minutes, low temperature treatments may require several weeks or months to achieve the same level of control (Fields 1992). Low-temperature treatments conducted in transit are not as limited by the time requirements needed for control and have been effective for many years. Recent failures of low temperature in-transit treatments, however, have resulted in a re-evaluation of the treatment with an emphasis on adequate distribution of the treatment temperature throughout the container or ship hold (Dowdy 2009).

The authors do not consider cold treatment to be an methyl bromide alternative for export logs because of the energy requirements to cool logs to 0°C, because the length of time required for cold treatments to be efficacious against target pests would impede exports even if consideration is given to ship hold cold treatments, because the requirement to move air to ensure equilibration of temperatures during a cold treatment would be difficult unless the logs were in a fixed cold-storage facility. Moreover, the cold-tolerance of New Zealand's forest pests is unknown (they may be cold tolerant because of the temperate conditions in the forests during winter months).

7.3.2 Heat treatments

Heat is an environmentally acceptable but energy-intensive treatment. Temperatures applied are usually from 40 to 50°C for durations from minutes to hours. The temperature, duration and application method must be precise and uniform to kill pests without damaging the commodity (Jamieson et al. 2009). Heat (thermal) treatments to control insect pests in agricultural commodities must satisfy three criteria to be commercially successful: (1) provide adequate insect mortality to meet quarantine or phytosanitary requirements; (2) cannot adversely affect commodity quality; and (3) be technically and economically feasible to use in commercial operations (Tang et al. 2007). Conventional heating consists of convective heat transfer from the heating medium to the fruit surface and then conductive heat transfer from the surface to the fruit centre. A common difficulty with hot air or water heating methods is the slow rate of heat transfer, resulting in hours of treatment time (Hansen 1992; Opoku et al., 2002). Generally, thermal energy delivered to the interior of a target substrate is significantly influenced by the size, heating medium (e.g., hot air or water) temperature and heating methods (Tang & Wang 2007).

According to Hansen et al. (2011) a major factor in implementing heat treatments is cost. Unless the benefit exceeds the investment required for using heat, the treatment will not be employed, regardless of how effective it is. Small-scale tests, such as those done in the laboratory, may appear promising, but constraints increase when they are expanded for commercial use, such as in time, cost, and complexity of equipment.

Hot-water immersions of seeds to prevent bacterial diseases of plants were described by Jensen (1888). Steam was first reportedly used for soil sterilisation in 1893 by placing soil in a chamber with perforated steam pipes (Beachley 1937). Heat, in the form of a hot-water immersion, was first described as a method of control for postharvest storage decay in papayas by Akamine and Arisumi (1953) and was thereafter studied as a potential quarantine treatment for fruit fly infestation in bananas, mangoes and papayas (Armstrong 1982; Seo et al.1972, 1974).

Although heat treatments must be precise because of the narrow margin between efficacy and commodity tolerance to heat when used on fresh produce, numerous heat treatments have been accepted for fruits and vegetables exported from or entering the USA, for interstate shipments within the US, and in international trade (Armstrong & Mangan 2007, Hansen et al. 2011,USDA 2014c). Reviews of heat treatments can be found in Stout and Roth (1983), Armstrong (1994), Sharp and Hallman (1994), Mangan and Hallman (1998), Burks et al. (2000), Vincent et al. (2003), Yahia (2006), Beckett et al. (2007), Hansen and Johnson (2007), Armstrong and Mangan (2007), Tang et al. (2007) and USDA (2014c).

According to Hansen et al. (2011) little is known about what causes thermal death and most literature on the lethality of heat often provides elaborate mathematical models (e.g., Armstrong et al. 2009) that correlate the duration of exposures to temperatures to the mortality of a target population. The mechanisms of thermal death are believed to involve denaturation or coagulation of proteins (Larsen 1943; Rosenburg et al. 1971; Kampinga 2006) or damage to the cell wall (Bowler 1987). Toxic products may accumulate because of a metabolic disturbance (Fraenkel & Herford 1940; Cloudsley-Thompson 1962). The exact process varies with the conditions and does not apply to all situations. The thermal death point may be affected by humidity (Mellanby 1932), degree of starvation (Mellanby 1934), temperature acclimation (Mellanby 1954), or age (Bowler 1967; Boina & Subramanyam 2004). Other physiological effects of overheating (or hyperthermia) include increased metabolic rate, which also increases respiration and a rapid depletion of food reserves. If there is insufficient available atmospheric oxygen then the pest essentially asphyxiates (Hansen & Sharp 2000).

Heat can adversely affect insects in several different ways. Temperature exposure can be so severe as to cause immediate death (or acute mortality). This is essential for situations where pest elimination needs to be demonstrated before commercial transaction or movement across political boundaries, such as with meeting quarantine regulations (Hansen et al. 2011, Hansen et al. 2000a, b). If the intent is the eventual reduction of the pest population where time is not an important factor, such as with soil sterilisation (Nelson 1996a, b) or sanitising fruit bins to reduce reinvasion by tree fruit pests (Hansen et al. 2006), then the long-term lethal effect (or chronic mortality) is desired (Hansen et al. 2011). Similarly, heat can cause sterility whereby mating pairs continue to expend time and energy without benefit of reproduction (Isely 1938; Proverbs & Newton 1962; Okasha et al. 1970). Heat may affect behaviour so that the targeted pest becomes susceptible to pathogens and natural enemies such as predators and parasites. When some insects are exposed to sublethal high temperatures, they cease activity by going into a heat stupor (El Rayah 1970; Klok & Chown 2001; Slabber & Chown 2005), which would make them susceptible to predation and other causes of mortality. Heat could encourage the pest to move to another location and out of the treatment area, which may be useful when managing structural pests.

Regardless of the mode of action that causes the target pest to die from an exposure to heat at a temperatures and exposure durations that result in death, the ultimate goal of the heat treatment is to get the heat to the target pest. If that cannot be done, survival will occur and the heat treatment will not be efficacious. There are a number of technologies that can be used to develop and apply heat treatments, including hot water immersion, vapour heat, forced hot air, microwave, radio frequency, infrared, and even solar energy (Hansen & Johnson 2007).

Regardless of the heat treatment considered herein, Haack and Petrice (2009) found that residual bark is an impediment to the quarantine security of heat treatments carried out under ISPM 15 (IPPC 2005). Similarly, bark on logs could be expected to impede the quarantine security of any treatment using heat as a disinfestation treatment before exports.

7.3.2.1 Dry heat

Dry heat treatments are generally based on maintaining an interior commodity or structural temperature for a prescribed period at a temperature beyond the thermal limits the targets can survive. Relative humidity is not a factor in the use of dry heat treatments and no additional water vapour is added as in the case of vapour heat treatments. Much of the earliest and most extensive use of dry heat as a commodity treatment was to control stored-product insects in stored grains (Hansen et al. 2011). Dry heat treatments against *S. cerealella* were used in France for stored grains as early as 1792 (Fields & White 2002) and, by 1883, machines for heating infested grain to 49°C for 4 h to kill the larvae and pupae of *S. cerealella* were commonplace in France (Dean 1911, 1913). In the US, Lintner (1885) reported the use of dry heat treatments for grains that consisted of 49-55°C for a few hours to kill the immatures of *T. castaneum*.

Dry heat treatments provide an alternative to methyl bromide fumigation for a variety of structures from residential homes to large flour mills (Hulasare et al. 2010; Lewis & Haverty 1996a, b; Woodrow & Grace 1998) by raising the temperature of a room, equipment, or an entire facility to 50 to 60°C to kill insects, primarily stored-product insects (Heaps 1996; Heaps & Black 1994;Mahroof et al., 2003a, b; Roesli et al., 2003; Beckett et al., 2007). The duration of the heat treatment depends on the area and site being treated with a whole facility (e.g., flour mills) heat treatment typically lasting from 24-36 h (Hulasare et al. 2010).

Dry heat treatments have been developed for several wood pests in timber, wood packing materials and other wood products (Hansen & Johnson 2007). Dry heat treatments for timber is often called ‘kiln treatments’ or ‘kiln drying’ because of the specific equipment used in the dry heat process. The international standard for dry heat treatment of wood packaging materials is ISPM 15 (IPPC 2005) which states that wood packing material should be heated in accordance with a specific time-temperature schedule that achieves a minimum wood core temperature of 56°C for a minimum of 30 min. ISPM 15 allows the user to determine the actual dry-heating process, i.e., the duration from ambient to 56°C based on kiln temperatures. Although this treatment is now the standard for international trade (IPPC 2005), Ramsfield et al. (2010) reported that this treatment did not completely control all of the fungi species they evaluated. Because ISPM 15 heat treatment was designed to kill pest organisms that reside in the wood at the time of treatment, the original version did not require the removal of bark before treatment. Concerns were raised that insects could infest wood packing material after treatment, especially when bark was present given that many borers require bark for successful oviposition (Evans 2007). A requirement that the wood packaging material must be debarked was added in 2009 (IPPC 2010).

Eichemberg (2010) was granted an international patent on a portable inflatable structure fitted with a heating module containing a microprocessor that carried out dry heat treatments that would comply with ISPM 15 heat treatment requirements.

McCullough et al. (2007) examined heat treatments against *A. planipennis* and found that 50°C for 120 min was necessary to control the larvae and prepupae in wood chips. Nzokou et al. (2008) successfully controlled *A. planipennis* in logs with a kiln treatment of 65°C throughout for 30 min. Myers et al. (2009) examined oven treatments against the *A. planipennis* in firewood and concluded that an internal wood temperature of 60°C for 60 min was the minimum temperature and time required for heat sterilisation. However, Goebel et al. (2010) verified that 56°C for 60 min with a heat penetration to a depth of 2.5 cm was not a sufficient treatment to control *A. planipennis* and recommended higher treatment temperatures and longer treatment durations would be needed for phytosanitary efficacy.

Gan et al. (2005) developed two dry heat treatments to control oriental wood borer, *Heterobostrichus aequalis* (Waterhouse) (Coleoptera: Bostrichidae), hairy powderpost beetle, *Minthea rugicollis* (Walker) (Coleoptera: Lyctidae), rubber termite, *Coptotermes curvignathus* (Holmgren) (Isoptera: Rhinotermitidae), and *R. dominica* (the latter does not infest wood but was used as a surrogate species). The treatments consisted of using kiln temperatures of 52°C or 60°C to raise the core temperatures of rubberwood (plantation hardwood), *Hevea brasiliensis* Müller Argoviensis (Malpighiales: Euphorbiaceae), from ambient to 48°C or 56°C for 30 min and the treatments achieved 100% mortality for all test insects (Gan et al. 2005). Similarly, Costanzo (2012) found that a dry heat treatment consisting of heating the core temperature of black walnut, *Juglans nigra* (L.) (Fagales: Juglandaceae), blocks from ambient to 50.1°C for 30 min killed all walnut twig beetle, *Pityophthorus juglandis* Blackman (Coleoptera: Curculionidae), but that heating the blocks to 48°C for 30 min resulted in survival.

Genera Limited, Mt Maunganui, New Zealand is the licensed operator for the BioVapor (Biovapor (NZ) Ltd., Hastings) heat treatment system (Genera 2014). According to the Genera and BioVapor literature (and personal site visits by the authors) the BioVapor system produces high volumes of turbulent and humidity-controlled heated air at specific temperatures for the application of quarantine phytosanitary heat treatments (BioVapor 2014a, b). The BioVapor heat treatment system, including the treatment facilities and the dry heat generators that can be fixed or mobile, is used as a methyl bromide alternative for treating vehicles, trucks, boats, caravans, machinery, 20- or 40-ft shipping containers, scrap steel, and non-compliant timber entering New Zealand, ISPM 15 heat treatments for wood packing materials and timber, and heat treatments of containerised goods, and mattresses (to kill bedbugs) (Genera 2014). The treatments (approved and certified by Ministry for Primary Industries Biosecurity) consist of heating air within the treatment facility to 60°C and holding at that temperature until the approved treatment duration is completed (generally treatments are completed within an hour (Genera 2014a, b). BioVapor used their treatment system to study the parameters for heating stacks of logs, but the information is not readily available (R. Newson, personal communication). Recently, BioVapor presented information showing a stack of logs being heat treated, but no data were given and the presentation slide states: “Requires new heat standard and change of export regulations” (Dear 2014).

Newbill and Morrel (1991) identified the general temperatures required to control Basidiomycetes generally found in wood, thereby demonstrating that heat treatment is a viable method for disinfesting fungal pathogen from timber and wood products. For example, Gan et al. (2005) stated that fungus in wood can be eliminated by sterilisation in an oven, but that fungi are so prevalent in the air that sterilised wood can be re-infested after a brief exposure to air when conditions for its grow are present. According to Gan et al. (2005), fungus control can be achieved by controlling the environmental conditions necessary for the fungus to survive, and there are four essential requirements for fungi to thrive on timber/wood:

1. The temperature must be between 10.0°C and 54.5°C. The optimal temperature for fungal growth occurs between 21°C and 32°C. Below 10°C, fungi are dormant and above 54.5°C they are killed.
2. There must sufficient oxygen present.
3. There must be sufficient moisture available. Generally, there is sufficient moisture when the moisture content in wood is > 22%.
4. Food, in the form of sugar, must be available. There is inadequate food supply in the heartwood, so fungi are found predominantly on sapwood.

In order to control the fungus, at least one of these four requirements for growth must be eliminated. Heat treatments become an obvious method of disinfestation. For example, mountain pine beetle, *Dendroctonus ponderosae* Hopkins (Coleoptera: Curculionidae), which attacks a number of *Pinus* spp. in the US and Canada, kills trees by boring and feeding and by introducing a number of plant pathogens, including the blue stain fungus, *Grosmannia clavigera* (Robinson-Jeffrey and Davidson) (Ophiostomatales: Ophiostomataceae), that is associated with pine sap- and heart-rot (Kim et al. 2005, Uzunovic & Khadempour 2007, Uzunovic et al. 2008). Phytosanitary treatments were needed to ensure that the pathogen was not transmitted on exported timber. Uzunovic and Khadempour (2007) and Uzunovic et al. (2008) tested dry heat treatments against nine isolates of *G. clavigera* and found that three fungal isolates survived a heat treatment at 56°C for 30 min, but that all of the isolates were killed by a heat treatment at 61°C for 30 min. Their results indicated that some fungi may increase their heat tolerance slightly if they have been slowly dried and desiccated before receiving a heat treatment (Uzunovic & Khadempour 2007, Uzunovic et al. 2008).

B. xylophilus is a major quarantine pest for the US and Canada that requires either fumigation or heat treatment to eliminate the nematode from wood chips and timber before export (Dwinell 1990). Numerous authors, including Dwinell (1990), Dwinell et al. (1994), Gan et al. (1998), and Panesar et al. (1994) developed heat treatments, generally using kiln-drying, to achieve wood temperatures of 60°C to kill the nematodes found in pine timber and chips. Gan et al. (2010) developed an automatic heat control system for the application of heat treatments against *B. xylophilus*.

The use of heat to eliminate insects represents one of the most certain approaches to minimising the risk of pest introductions with log imports (USEPA 1996a). Current regulations permit the treatment for export of kiln-dried lumber, and there is a wealth of data to support the ability of kiln-drying to eliminate fungi, insects, and nematodes from wood (Morrell 1995). Examples include:

- Wang et al. (2003c) studied a number of heat treatment times and temperatures with the result that a treatment using 55°C for only 25 min killed all life stages of *A. nobilis*, *C. cossus orientalis*, and *Sphecia siningensis* in infested wood.
- Mushrow et al. (2004) found that the approved 56°C for 30 min heat treatment for Canadian exported timber was more than adequate to ensure quarantine security against all life stages of brown spruce longhorn beetle, *Tetropium fuscum* (F.) (Coleoptera: Cerambycidae).
- Wang et al. (2009b) developed mathematical models to predict average heating times to a core temperature of both 82.2°C and 65.6°C for green ash firewood to control *A. glabripennis* under various heating conditions, including heating timetables for a series of heating temperatures for wood at different initial temperatures.
- To control *A. planipennis* overwintering larvae in firewood before movement through marketing chains, Myers et al. (2009) developed thermotolerance data and did follow-up confirmatory tests that demonstrated complete control using a heat treatment of 60°C for 60 min. The approved ISPM heat treatment of 56°C for 30 min was questioned by Sobek et al. (2011), who found that late instars of *A. planipennis* had a significant degree of thermal tolerance and thermal plasticity. Sobek et al. (2011) had some survival occur at 53°C after 30 min and suggested that the survival indicated that the ISPM heat treatment was not severe enough and could result in survival. However, Myers and Bailey (2011) tested the 56°C 30-min heat treatment against *A. planipennis* overwintering larvae and had no survival, which they felt vindicated the ISPM heat treatment.

7.3.2.2. Vapour heat and steam

Vapour heat is one of the oldest of the heat treatment methods. The original vapour heat treatment was developed during a *C. capitata* outbreak in Florida in the mid to late 1920s (Baker 1952). Shortly thereafter, the original vapour heat treatment was modified for use against *A. ludens* as a postharvest quarantine treatment before shipping citrus fruits from the Rio Grande Valley of Texas to US markets elsewhere (Hawkins 1932).

Vapour heat consists of heating the host fruit by moving hot air saturated with water vapour over the fruit surface. Heat is transferred from the air to the commodity by condensation of the water vapour (heat of condensation) on the relatively cooler surfaces of the fruit being treated. Fruit may be gradually heated over time (approach time) to a target temperature – which may be at the end of the treatment (i.e., all insects have been killed) or held for a specific time (holding time) required to kill all insects (Armstrong & Mangan 2007).

Chittenden (1897) recommended using steam on the flour mill machinery to control contamination by the Mediterranean flour moth, *Anagasta kuehniella* (Zeller) (Lepidoptera: Pyralidae), and reported using 52-60°C for a few hours to kill other grain insects. Howard and Marlatt (1902) suggested using steam to control carpet beetle, *Anthrenus scrophulariae* (L.) (Coleoptera: Dermestidae), that were found on woollen products. Brodie et al. (2002) developed a 1-h steam treatment against the golden nematode, *Globodera rostochiensis* Wollenweber (Tylenchida: Heteroderidae). Chen and White (2008) recently described a vacuum/steam treatment to control five species of mould on cotton.

However, vapour heat treatments are carried out in costly chambers that produce steam at regulated temperatures for the treatment duration. Similar to the forced hot air treatment described below in 7.3.2.4, the authors do not consider vapour heat to be an option for treating logs.

Snyder and St George (1924) determined the temperatures required to kill *L. planicollis* in ash (*Fraxinus* sp.) and oak (*Quercus* sp.) lumber in a steam-generating kiln. Mack and Chen (2011), according to a literature search, evaluated the use of vacuum steam equipment to treat whole logs for export. However, the proceedings document could not be obtained (*authors' note: a document request was sent to the Mack and Chen and any information that is forthcoming will be added to this section*).

Wood logs are heated in the veneer industry to heat the logs to soften or “plasticise” them so that they can be more easily peeled into high-quality veneer (Gates et al. 1973). According to Gates et al. (1973) the proper degree of heating and saturation of the wood softens the fibres, particularly the hard knots and rings of summer wood. Care is necessary in the heating and saturating of the logs because insufficient heat will not soften the blocks adequately and excessive heat tends to destroy the wood fibres. Gates et al. (1973) patented an industrial machine to carry out the proper softening of logs using steam tunnels and log-moving conveyors whereby logs entered the system and were steam-treated for a duration needed to soften the wood in preparation for veneer cutting. Their system consisted of four tunnels in tandem with each tunnel providing sufficient heat and moisture to prepare the log for the next tunnel and, ultimately, veneer cutting. However, the process for each log required about 2 h to complete (Gates et al. 1973). This process is discussed here to provide an idea of the capacity and time required to prepare the log for veneer cutting. If, hypothetically, this system could be used to treat logs to surface temperatures below the bark that would kill insects effectively, the temperatures and duration of treatment required to provide quarantine security would have to be evaluated. Steam generation may be too costly to use in this manner. Moreover, the size and number of treatment systems needed at the ports, duration and temperatures to achieve quarantine security, and the handling cost may be prohibitive. Another issue could be water run-off at the ports from the steam heating process. For these reasons, the authors do not consider a heat treatment based on steam to be a viable option for treating export logs.

7.3.2.3 Hot water immersion

Hot (>40°C) water baths and dips are the simplest of the heat treatments. They are anaerobic and have high energy transfer because of the aqueous medium. One of the earliest attempts at postharvest treatment of a horticultural commodity was in 1909 by immersion in hot water to control tarsonemid mites (Cohen 1967). Hot water treatment generally involves immersing a batch of fruit for a specified time at a specified temperature. Short but high-temperature hot water treatments are effective at controlling fungal pathogens and insects on the surface (Jamieson et al. 2009). Longer treatments are required for internal pests such as fruit fly to heat the whole fruit (Lurie et al. 1998), but such longer duration treatments are likely to damage many crops. Generally hot water treatments are more effective at the same temperature than hot air treatments, because of faster heat transfer in water and the more uniform heating of the fruit by use of high water flow, and therefore hot water generally costs less to apply (Waddell et al. 1993). Hot water treatments also have the added advantage of reducing residues, pathogens and may remove other contaminants as well as washing off dead insects (Jamieson et al.

2009). An historical overview of hot water treatments used commercially for a wide range of horticultural crops is provided by Hansen et al. (2011). However, because hot water immersion is a batch treatment and the cost of handling and heating water to treatment logs would be prohibitive, the authors do not consider hot water immersion to be a viable treatment for logs.

7.3.2.4 Forced hot air (high-temperature forced-air)

Forced hot air was patented in 1990 (Armstrong et al. 1990) and is similar to vapour heat, but does not have the moisture component and is a more recent development (Armstrong et al. 1989, 1995). Forced hot air has advanced as a technique because of improvements in temperature and moisture monitoring and in air delivery (Hallman & Armstrong 1994) and numerous forced hot-air quarantine treatments have been approved internationally (Armstrong & Mangan 2007). Hansen et al. (1997) obtained complete control of the banana moth, *Opogona sacchari* (Böjer) (Lepidoptera: Tineidae), infesting the ornamental 'cornstalk Dracaena,' *Dracaena fragans* Ker-Gawler, using treatment parameters of 44°C for 30 min without damage to the foliage or the ability of the plant to propagate. Treatments are being refined for commodities subjected to vapour heat and applied to new commodities. Its disadvantages are the long treatment durations and the sophisticated equipment needed for operation. Not all horticultural commodities are suitable, for example, avocado (Kerbel et al. 1987). Follett and Sanxter (2000), in examining forced hot air as a treatment against fruit flies in rambutan, also reported unacceptable commodity damage. Forced hot air is a "batch" treatment best suited for high-value fresh produce such as papaya, capsicum, eggplant, mango, and breadfruit treated before export to eliminate quarantine pests (primarily Tephritid fruit fly species).

Forced hot air treatment profiles, almost identical to vapour heat treatment profiles, have a ramp time of 4-6 h to equilibrate fruit centre temperatures to the required approved temperature (e.g., 47.2°C for papaya in Hawaii (Armstrong et al. 1989, 1990, 1995)).

The technology is not suited for chambers larger than 114 m^3 and a single forced hot air chamber to treat papaya and other fruits costs about US$100,000 - 125,000 (M. Williamson, personal communication). Therefore, no further consideration is given here to forced hot air as a potential methyl bromide alternative for New Zealand export logs.

7.3.2.5 Solar

Solar energy has been investigated as a thermal treatment and this is a relatively recent procedure compared with the other heat treatment methods (Hansen et al. 2011). Grooshevoy et al. (1941) anticipated that solar energy could provide sufficient heat to destroy pathogens in tobacco seed beds. However, Yeomans (1952), who examined different forms of radiant energy including radio frequency, did not mention solar energy and concluded that infrared radiation was impractical because of high cost and poor penetration. Grinstein et al. (1979) used polyethylene sheets to raise soil temperatures by solar heating, which is the procedure now frequently used. Very little has been done using solar energy to control insects. Although the approach is simple and has potential for long-term storage in rural areas and in developing countries, there are problems with temperature control and maintaining consistency (Hansen et al. 2011).

7.3.3 Pressure

Although the use of pressure was studied by Nzokou et al. (2006) for controlling *A. planipennis* in ash wood from infested trees, and by Yuejin et al. (2004) for controlling *B. xylophilus* in wood packaging materials, there is no research in the literature or on the internet that demonstrates the use of pressure could be a viable treatment, especially considering the high pressures needed to obtain kill and the specialised equipment required to carry out pressure treatments effectively even on a small basis. Hence, the authors do not consider that the use of high pressure is a viable treatment technology to replace methyl bromide.

7.3.4 Vacuum

A vacuum is a space entirely devoid of matter (or, absolute vacuum). In practice, a vacuum is when the air pressure in a closed system (e.g., a fumigation chamber) is below the normal atmospheric pressure (FESTO 2014). Low pressure, achieved by applying vacuum to a system, reduces atmospheric gases and imposes a controlled atmosphere. Atmospheres at 5% of ambient are sufficiently low in oxygen to kill insects in a matter of hours to days. Vacuum usually cannot be applied effectively in structures other than specialised pressure chambers, but flexible storage structures provide the potential to apply vacuum to a commodity for insect disinfestation without chemical pesticides (Phillips et al. 2000).

The possibility of using low pressures in postharvest storage was explored first by Back and Cotton (1925) and later by Bare (1948), and Calderon et al. (1966). The preponderance of research reported in the literature was specific to controlling stored-product insects. For example, Calderon et al. (1966) studied the effect of 10-15 mbar to 2.1-2.7 mbar on larvae and adults of six stored-products insects at 18°C and 25°C. They reported that *E*. *cautella* adults were the most susceptible stage, followed by sawtoothed grain beetle, *Oryzaephilus surinamensis* (L.) (Coleoptera: Silvanidae), adults; *T*. *castaneum* adults; cowpea seed weevil, *Callosobruchus maculatus* (F.) (Coleoptera: Chrysomelidae), adults; *T*. *castaneum* larvae, *T*. *granarium* larvae; *S*. *oryzae* adults; *C*. *maculatus* larvae; and *S*. *oryzae* larvae, and that 100% mortality was obtained after 120 h except for *C*. *maculatus* and *S*. *oryzae* larvae (Calderon et al. 1966). A noteworthy issue with the report by Calderon et al. (1966) is that eggs were not tested. To achieve the extremely low pressures for complete mortality of tolerant species (e.g., *C*. *maculatus* and *S*. *oryzae* larvae) a prohibitively expensive investment in massive vacuum chambers may be required (Finkelman et al. 2003).

There was significantly less research into the use of vacuum to control insect pests of fresh produce than of stored-product insects. In the most recent example, Phillips et al. (2000) achieved 99% mortality in eggs of *R. pomonella* infesting apples in 58 h at both 30°C or in 104 h at 25°C under vacuum of 6.7 mbar. Market-quality apples of ‘Red Delicious’ and ‘Golden Delicious’ were subjected to a 6.7mbar treatment for 5 d at 25°C with no significant loss of market quality, as determined by a human assessment panel.

Similar to the paucity of research reported on the use of vacuum treatments for fresh produce, there is very little research on the use of vacuum to control insects in wood products, and no research on the use of vacuum was reported for logs or timber. A notable example of the use of vacuum for wood products is the report by Chen et al. (2006, 2008) on the use of vacuum to control wood-boring insects in wood packaging materials. They achieved complete control using a vacuum of 3.0 mbar at 20°C for 96 h. More important, Chen et al. (2006, 2008) tested wood at 7, 12 or 23% moisture content and reported that their studies showed that lethal vacuum times were directly related to the moisture content of the wood and larval weight with lower moisture content and smaller larvae resulting in the more rapid control.

Although vacuum is known to kill insects (Phillips et al. 2000), the small number of research articles reported and the lack of reported commercial vacuum treatments or equipment for stored-product insects (the insect group receiving the most study) strongly indicates that vacuum is not a viable for either insect control or phytosanitary purposes. Some possible reasons that vacuum treatments were never developed as a treatment technology to control insects may include:

- Large vacuum chambers must be made of steel (mainly stainless steel) and constructed to withstand potential damage caused by the continual pulling and releasing a vacuum and collapse caused by external atmospheric pressure. The strength issue is dealt with by making the walls thick enough or by adding additional bracing or supports either internally or externally, but the main problem is found in assessing the possible gas loads (Danielson 2003).
- Developing extremely low pressures for complete mortality of tolerant species may be a prohibitively expensive investment in massive vacuum chambers (Finkelman et al. 2003). Furthermore, the number of chambers that would be needed at the ports to treat export logs would not be commercially viable on an economic scale and because of the amount of space required.
- Calderon et al. (1996) could not achieve complete control of their test insects under 2.1-2.7 mbar vacuum after 120 h at 18°C or 25°C. The handling costs for moving logs into and out of vacuum chambers and the time required to achieve 100% mortality probably would not be economically viable.
- Vacuum pump systems are expensive and the costs increase with the need for increased vacuum and increased speed in pulling the vacuum (Van Atta and Hablanian 2005).

For these reasons alone, vacuum is not considered a potential methyl bromide alternative for New Zealand export logs.

7.4 Recommendation for further research with physical or energy treatment

Based on the work of Dentener et al. (1997) that showed significant efficacy against *P.reticularis* in laboratory studies using carbon dioxide or nitrogen and 40°C in under 7 h, the use of combined heat and modified atmosphere is recommended for further study as a potential non-toxic treatment for New Zealand export logs (refer to 7.1.1, page 85). Laboratory studies on selected forest insects could rapidly establish whether a combined heat and modified atmosphere treatment had any potential under commercial conditions. However, research with ethanedinitrile (refer to 4.5.3, page 39) must take precedent.

8 Alternatives to chemical, physical or energy treatments

8.1 Debarking

Another treatment option is debarking, which is an approved treatment option for a number of countries including China. Debarking is typically carried out in the supply chain using fixed debarking equipment. The option of debarking in forest at time of harvest is being investigated. However there are a number of issues regarding debarking technology, particularly if its use is increased widely. These issues include additional handling costs and bark disposal (which is not a problem if debarking occurs in-forest at point of harvest), coupled with possible impacts on the value of higher quality logs used for veneer and lumber manufacture. Noise emissions and discharges of waste materials to air and to water will need to be identified and acceptable mitigation measures developed. Possible uses for large volumes of bark are speculative, would come at a cost and require research.

According to a report by Interpine Forestry Ltd. (2012), debarking may provide a possible phytosanitary treatment for export logs. To determine the economic feasibility of debarking, Interpine Forestry Ltd. (2012) investigated the actual cost of debarking in various scenarios benchmarked against the current cost of chemical fumigation and developed a high level national supply chain model which can be used to analyse various debarking scenarios. The study (Interpine Forestry Ltd. (2012) found that debarking costs are more expensive than chemical fumigation in spite of benefits gained through transport load improvements and possible bark sales offset. Additional to the debarking cost, debarking at intermediate nodes (off site log yards) in most parts of New Zealand has an additional cost for double handling and additional cartage from off port. The report (Interpine Forestry Ltd. (2012) also found that, although debarking at stump is the most economical option in most areas of New Zealand, logistical issues and phytosanitary effectiveness of the debarking process were unknown.

Obviously, further study will be needed to determine the capability to meet phytosanitary requirements, impact on wood quality and economic viability of debarking in forest, at point of harvest, if either phosphine or methyl bromide fumigation were lost as phytosanitary treatments, or the costs of fumigation increased sufficiently to make debarking options more economically viable. Because debarking is already approved for use on logs exported from New Zealand, no further consideration is given to the debarking process here.

8.2 Pest management systems (systems approach using multiple mitigations)

Holt (1985) wrote that “there is little doubt that computers will soon be integral components in production agriculture, automating data collection and analysis, simulating economic trends in the marketplace and biological trends in the field, and perhaps automating the control of irrigation and the scheduling of insect control”. Similarly, in entomology computers were becoming ever more popular as information managers, teaching aids, and communications devices in addition to their traditional scientific role in statistical analysis (Stone et al. 1986). The use of computers in the 1970s gave rise to the concept of “expert systems” and, although little had been attempted in agriculture or entomology due to the lack of exposure at that time to computer technologies, improved technology, software, and market competition were seen to both increase exposure and reduce the costs of using expert systems (Stone et al. 1986). Expert systems were first identified by Stone et al. (1986) to be ideal for agricultural or entomological problems that were well defined in scope but which required scarce human expertise to solve; problems that involved incomplete data and required judgment, approximation, or opinion in their solution for which expert “systems approaches” could be applied. Hence, systems approaches became viable with the widespread use of computers in the agricultural sciences.

The application of systems approaches for mitigating pest risk is not a new concept but has gained popularity over the last 20-30 years as the need for biologically based decision making for determine pest risk has increased and the need for alternatives to single treatments based on such analysis increased. Accordingly, quarantine authorities have prescribed various combinations of pest risk mitigation methods or treatments as a condition for certification and movement. These combinations have been created by selecting risk mitigation methods from available options including requirements for: pest-free planting stock, growing media, cultural practices, area-wide pest management, pest monitoring as a trigger for a specified chemical treatment, fruit maturity or harvest period standards, harvest methods, sorting, packaging and handling facilities, and postharvest treatment (USDA 2002).

Although single treatments are still important, the removal of effective fumigants, such as ethylene dibromide and methyl bromide (except for phytosanitary uses), postharvest damage and/or quality issues and the costs of such treatments have increased interest in other mitigation procedures (Jang et al. 2006). Systems approaches can be defined as “the integration of those pre- and postharvest practices used in production, harvest, packing, and distribution of a commodity which cumulatively meet the requirements of quarantine security” (Jang & Moffitt, 1994). More recently, the IPPC defined systems approaches in ISPM Pub. No. 14 (IPPC 2005, 2013b) as: “the integration of different pest management measures, at least two of which act independently, and which cumulatively achieve the appropriate level of phytosanitary protection”.

Systems approaches differ from single quarantine treatments in that multiple actions are utilised that cumulatively reduce the risk of pest establishment. Systems approaches integrate biological, physical and operational factors that affect the pest’s biology in such a way that the likelihood of establishment can meet the requirements of the importing country (Jang et al. 2006). Systems approaches have been codified as ISPM Pub. No. 14: The use of integrated measures in a systems approach for pest risk management (IPPC 2005, Quinlan, 2004)

Components of a systems approach can vary widely but in general start with identification of the pest(s) of concern, knowledge of the basic biology of the pest including the pest/host relationship, dispersal, alternate hosts, habitat and population dynamics. Often a method for detection and surveillance of the pest can be useful in identifying the pest population as well as determining “pest incidence thresholds” (Jang et al. 2006). Other components of a system can include postharvest practices, packing and marketing of products and regulatory aspects, such as phytosanitary certifications by importing and exporting countries under specific compliance agreements (Fig. 1, Jang et al. 2006). Although systems approaches are generally more difficult to manage than single postharvest treatments (Liquido et al 1997), they have been implemented widely in recent years in the US and the use of systems approach is rapidly gaining widespread acceptance internationally (Jang et al. 2006).

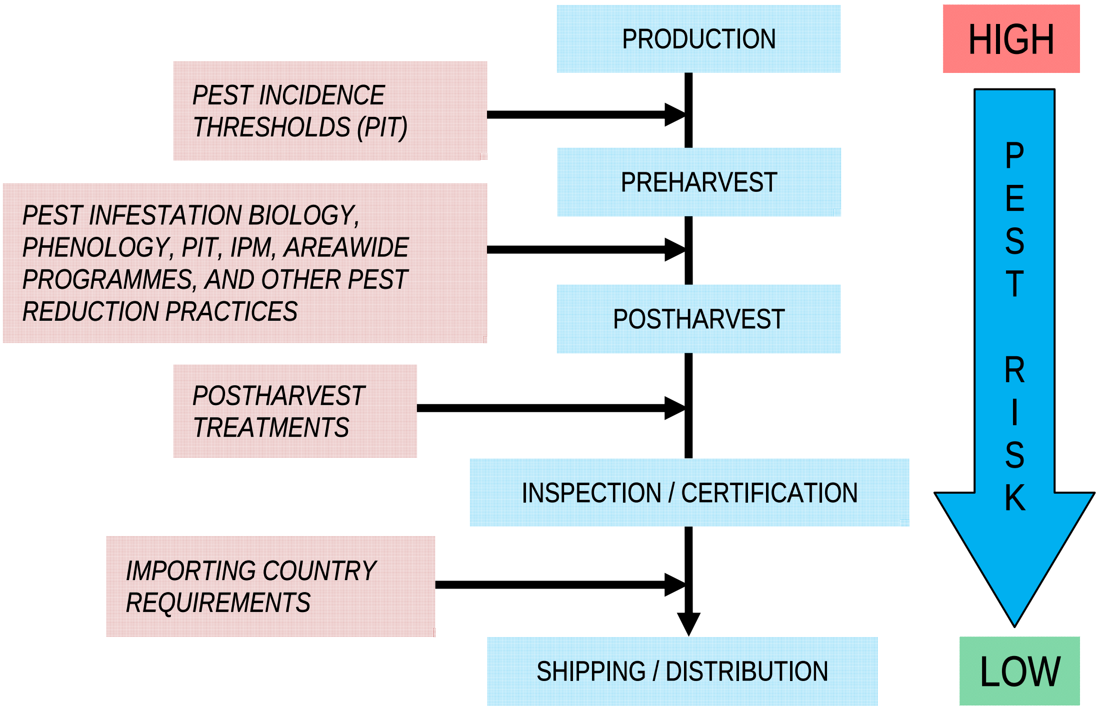

Fig. 1. Components of agricultural export systems approach using multiple mitigation measures (Jang et al. 2006).

Examples of applied systems approaches include the export systems approach to export apples and cherries from the US Pacific Northwest to ensure the fruits are not infested with codling moth (Jang & Moffitt 1994), to the integrated management of a complex of olive pests (Shoemaker et al. 1979), and mangoes from South Africa (De Graaf 2010). From these and other examples in the literature we found that most of the current systems approaches for quarantine purposes were for tropical, subtropical and temperate fruits (e.g., IPPC 2013b, Jang et al. 2006, Liquido et al. 1997). Although management of forest pests has advanced rapidly over the past decade in many countries where intensive forestry is practised, the development of monitoring systems (or, more broadly, the information base) required to support newly emerging programmes is generally lagging (Waters 1986). A more comprehensive approach to monitoring, which includes improved accounting of pest occurrence and damage through forest inventories and reliable indices of pest-related hazard and risk, is needed to augment customary procedures of surveillance and evaluation. Also, optimisation of pest management strategies requires a better accounting of the interactive effects of destructive insects and diseases and, thus, monitoring of pest complexes as they occur rather than uncoordinated monitoring of individual pests. Full realisation of the potential benefits of forest pest management depends on replacing the present-day fragmented approach to monitoring with a broader-based information system directed to the prime decision-maker, the forest resource manager (Waters 1986).

However, sustainable improvements have been made over the past several decades in forest management practices and foresters today often apply many practices to reduce pest problems throughout the entire production process, from planting and managing forests to harvesting operations (FAO 2011). These practices, often called integrated pest management (IPM), can help form the basis of a systems approach. Currently, an MBIE-funded, ecologically based, systems management approach (systems approach) is currently a long-term (2012-2016) Scion research programme[6] with the goal to reverse New Zealand's dependence on mandatory fumigation as a phytosanitary treatment for logs. This systems approach utilises biological knowledge and complex ecological modelling techniques to predict the infestation probability so that informed decisions can be made on potential infestation of logs at the point of export. If the system provides information that shows the logs are not infested, no quarantine treatment (e.g., methyl bromide fumigation) would be required. Defining winter periods where phytosanitary treatments are not required requires detailed knowledge of the biology and ecology of pest species (Pawson 2012). For example, New Zealand currently has a treatment-free period for sawn timber exports to China that occurs when adult *A. ferus* are not active (MPI 2014b). The Scion research programme is currently attempting to extend the treatment-free period to other regulated pests for export logs.

Adult beetles are the principal life-stage that represents a quarantine risk as they infest and lay eggs on export logs (Hosking & Bain 1977). Adult emergence and activity is known to be strongly linked to temperature which is in turn a function of factors such as, elevation, aspect, and host quality (Hosking & Bain 1977). The risk of infestation can be documented using a trapping network to determine the activity of adult insects as a proxy for pest pressure, however this provides information 'after the fact' – logs harvested during one particular trapping period may have already left port by the time the data are collected. The current programme of research incorporates a temporally and spatially explicit ecological risk framework that incorporates developmental growth models with spatial models that predict pest pressure as a function of landscape context for any point along the wood export supply chain.

The primary modelling methods used will be a Bayesian network which is a graphical model that depicts major cause-effect links in the system under consideration (Korb & Nicholson 2010). Both the relationships between variables and the model predictions are expressed probabilistically, so uncertainty is embedded and explicit. Bayesian networks have been widely used in environmental and ecological modelling (Aguilera et al. 2011). Relationships between the incidence of pests in spatially defined cells within the region will be defined by specific experiments that assess: (1) site factors (proportion of, and proximity to, plantation forest stands and stand age), (2) effects of land use type, (3) host quality (quantified using inter-annual emergence trapping of stumps and logging debris in clearfells[7] (Brin et al. 2011), (4) distance to the nearest possible source population, and (5) climatic factors to validate developmental growth models. An advantage of Bayesian networks is that they can be constructed using all information available from a range of sources, including empirical data, the research literature, opinion of experts, and output from other models – all relevant for this project (Korb & Nicholson 2010). The Bayesian approach provides information on uncertainty in parameter estimates and resulting model predictions (Berger 1985, Bernardo & Smith 1994) so the Bayesian network will provide distributions over the risk of contamination, which is more useful and realistic than point estimates provided by classical modelling methods. This modelling should allow determination of the probability of the lowest permissible level of infestation by the full suite of quarantine species (Pawson et al. 2012) being detected prior to export.

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[6] Information on the Scion systems approach research programme was provided by S. Pawson, personal communication.
[7] Clearfell logging is a logging method that involves the removal of almost all vegetation from an area of forest, and clearfells are the areas that remain after clearfell logging is completed.

Because a systems approach for the quarantine pests of New Zealand export logs is currently being investigated by the MBIE-funded Scion research programme, the subject is not given further consideration here.

9 Quarantine security statistics

Statistical analyses are used to estimate the probability that a treatment will successfully prevent the target quarantine pest from becoming established in the area into which the commodity is imported. Laboratory bioassays can evaluate the probable success of different treatments. A large-scale confirmatory test follows treatment selection. This sequence of testing resembles the protocol generally used to evaluate the probable success of a treatment to control any pest species on any crop, but is more complex because control must also prevent establishment (Robertson et al., 1994b). Providing trading partners and their respective regulatory agencies with the appropriate statistical criteria that will ensure quarantine security is difficult when few statistical standards are available, and even these are subject to debate. For many decades, the USA required that fruit fly disinfestation treatments meet the Probit-9 concept developed by Baker (1939), which assumes insect control at a mortality rate of 99.9968%. This corresponds to no more than three individuals from a treated population of 100,000 surviving a selected quarantine treatment. Using 95% confidence limits, probit-9 could have 29-136 survivors per million, with an average of 32 (Couey & Chew, 1986). Japan often uses a variation of the Probit-9 concept that requires no survivors from a treated population of 30,000 target pests that consists of three treatments with 10,000 target pests per treatment (Armstrong 1992).

Zero tolerance is impossible to demonstrate by treatment efficacy because this predicts that no survivor will ever be found. Additionally, Probit-9 should not be used to predict treatment time due to the high degrees of confidence in dose-response required and in many cases mortality is curvilinear, not logarithmic. Risks are clearly different for different commodities based on infestation rates. A commodity that averages one pest per unit provides a lesser degree of risk than a commodity that averages 30-40 pests per unit (Paull & Armstrong, 1994).

The Probit-9 concept came under scrutiny for the first time by Landolt et al. (1984), who pointed out that it does not consider several factors that directly impact quarantine situations, such as the actual infestation per volume of treated commodity, the potential for culling infested units of a commodity during processing, the infestation variability between good and poor hosts, or the probability of a potential normal mating pair occurring at the same time at the market destination. Hence, extrapolating Probit-9 for use on insect species other than fruit flies was both unrealistic and often unworkable when insect populations on the host commodity were low (Landolt et al. 1984, Robertson et al. 1994b).

Alternative quarantine statistics that challenge the Probit-9 concept have appeared in the literature (Landolt et al. 1984, Couey & Chew 1986, Robertson et al. 1994a, b). New Zealand developed a maximum pest limit concept for imported produce (Baker et al. 1990; Cowley et al. 1993) that includes a sampling model for the accurate assessment of infestation levels in the host commodity, and a limit on the number of immature pests that may be present in consignments imported during a specified time to a specified location (Baker et al.1990).

This assumes that the emerging adults will not be able to find a mate because the commercial distribution would scatter the arriving commodity over a large area. The difficulty with this system is the lack of available good biological data on infestation indices and the limitation of sampling methods for accurate assessment (Paull & Armstrong, 1994). Application of a treatment of known efficiency ensures that the limit is not exceeded if the infestation, determined by the sampling model, is below a predetermined value (Baker et al., 1990).

Mangan et al. (1997) performed an analysis of maximum expected surviving *A. ludens* in loads of citrus and mangoes imported into the USA from Mexico. In that analysis, which used actual load numbers of fruit and infestation rates (from field samples), they determined that a maximum pest level of two survivors per load was frequently exceeded even with a Probit-9 level postharvest treatment, and the numbers of fruit currently inspected at port inspection stations (usually < 50 fruit per truckload) are far below that necessary (usually several hundred) to detect infestation rates above this maximum pest limit. Additional discussions of quarantine security and Probit-9 can be found in Vail et al. (1993) and Follett and McQuate (2001). A biological statistics package for pest risk assessment in commodity quarantine treatments developed by Liquido et al. (1996) is available from US Department of Agriculture's Agricultural Research Service website at http://www.pbarr@pbarc.ars.usda.gov.

Following extensive use by the USDA, Probit-9 mortality is widely recognised as an efficacy standard for the quarantine treatment of insects, especially fruit flies. The extension of this standard to new quarantine treatments for timber and timber products, however, raises a number of problems. It is arbitrary to set Probit-9, or 99.9968% mortality as an efficacy standard, and Probit-9 mortality may be too conservative for rare pests, or too liberal for highly abundant pests. Verification trials are often impossible where insufficient individuals can be found or reared for testing. Extrapolation from modelling dose-response relationships suffers from increasing uncertainties the further the extrapolated values are from observed data. Efficacy testing needs to account for diverse conditions of the host material. Although the Probit-9 concept has been widely used for insect pests, its use for other organisms, such as nematodes or fungi, may be inappropriate. Alternatives to a Probit-9 efficacy standard must address the expected prevalence of a pest on the material in question, and a maximum pest limit that can be tolerated. Where treatment verification to appropriate numbers may not be possible, the analysis of carefully designed dose-response experiments may be used to define appropriate treatment dosages. The development of new timber treatments for use in international standards needs to consider these alternatives (Schortemeyer et al. 2011).

The large diversity of timber pests makes it impossible to verify quarantine treatments for most pests. The use of representative (model) species for some groups of pests has been suggested in the Draft appendix to ISPM 15:2009 (IPPC 2010). A representative species for quarantine purposes would have to be among the species of a pest group that are more tolerant to the treatment in question and abundant in large enough numbers to allow the experimental testing of treatments. A rationale would have to be provided why a particular species is representative of others. The Draft appendix to ISPM 15:2009 (IPPC 2010) requires that the organisms most resistant to treatment are identified and used to evaluate treatment efficacy. This is impractical with groups such as Scolytinae with ≈6,000 described species or Cerambycidae with ≈20,000 species (Schortemeyer et al. 2011).

Many different attempts to develop alternatives to Probit-9 can be found in the literature but most remain theoretical. Development of quarantine security statistics for insects other than fruit flies, for insects that are found in relatively few numbers in their host substrate or for insects that simply do not fit the quarantine security statistical models in effect for a variety of insects demonstrate the possibility that quarantine security statistics may be required on a species-by-species basis. Schortemeyer et al. (2011) asked the following questions:

- If a verified Probit-9 efficacy standard is not suitable for setting international standards for timber pests, such as ISPM No. 15, are there alternatives?
- Are there potential universal treatments such as the currently accepted heat treatments and methyl bromide fumigations that may be considered effective against all pests of concern?
- Do diverse pest profiles require a combination of treatments, and how can the efficacy of such treatments be verified?

The future development of alternatives to methyl bromide will rely heavily on whether these questions are answered if we are to develop new alternatives in a timely manner based on sound science and statistically viable data.

10 Recommendations

10.1 Ethanedinitrile

The authors recommend further research with ethanedinitrile as a potential methyl bromide alternative for New Zealand export logs (refer to 4.5.3, page 39) based on the recent findings of Pranamornkith et al. (2014a, b). However, because the literature (Brash et al. 2013) and the results of Pranamornkith et al. (2014a) clearly show that the sorptive properties of ethanedinitrile are significant, we further recommend that a technological and economic study on the use of ethanedinitrile be completed before further research on efficacy or penetration into logs is initiated.

10.2 Sulphuryl fluoride

Sulphuryl fluoride is recommended as a distant second choice for further study as a potential methyl bromide alternative because it is a common timber and structural fumigant (refer to 4.15.9, page 72). Environmental issues and the lack of efficacy against insect eggs cannot be overlooked. Therefore, sulphuryl fluoride should be considered for further research only if the authors' first choice, ethanedinitrile (refer to 4.5.3, page 39), is rejected as an option based on the recommended technological and economic study. In the event that ethanedinitrile is rejected, sulphuryl fluoride has enough positive characteristics that leave it as the only additional fumigant alternative to methyl bromide that can be recommended for further study.

10.3 Combined heat and modified atmosphere treatment

Based on the work of Dentener et al. (1997) that showed significant efficacy against *P. reticularis* in laboratory studies using carbon dioxide or nitrogen and 40°C in under 7 h, the use of combined heat and modified atmosphere is recommended for further study as a potential non-toxic treatment for New Zealand export logs. Laboratory studies on selected forest insects could rapidly establish whether a combined heat and modified atmosphere treatment had any potential under commercial conditions. However, research with ethanedinitrile (10.1 above) must take precedent.

10.4 Debarking

Further study is needed to determine if in-forest debarking, at point of harvest, can achieve phytosanitary requirements. This work is needed to establish a techno-economic baseline with which to compare the costs of alternative treatments (refer to 8.1, page 108)

Other than ethanedinitrile and sulphuryl fluoride, no other fumigant had any possibility of being considered for further research as a methyl bromide alternative for New Zealand export logs. Also, no energy or physical treatment, other than a combined heat and modified atmosphere treatment, showed any potential for use on export logs.

11 Acknowledgements

The authors thank Damian Clarke and Udo Froetschl, Ministry for Primary Industries, for providing phytosanitary treatment and species of logs exported from New Zealand, and Ian Gear, Stakeholders in Methyl Bromide Reduction, for providing the information given in Tables 5 and 6.

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