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TREATMENT EFFICACY REPORT

Use of Phosphine Fumigation on New Zealand *Pinus radiata* Logs

May 2004

Report Prepared for
New Zealand Ministry of Agriculture and Forestry
Biosecurity Authority

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Executive Summary

This report provides a summary of the scientific information supporting the use of phosphine for the in-transit fumigation of *Pinus radiata* logs being exported from New Zealand to Asian markets.

Research findings to date support the acceptance of phosphine as a phytosanitary treatment equivalent to methyl bromide on New Zealand grown *Pinus radiata* logs for export to Asian markets. Research has clearly demonstrated that a minimum of 200ppm phosphine for 10 continuous days is effective against risk pests presently treated by methyl-bromide fumigation of *Pinus radiata* logs exported from New Zealand.

At 200ppm for 10 days, phosphine has been demonstrated to achieve 100% mortality on all of the risk pests likely to be associated with New Zealand *Pinus radiata* logs. When applied in an operational environment, the application of 2g/m³ aluminium phosphide to each ship hold on departure from New Zealand and subsequently topped-up after 5 days with a further 1.5g/m³ per hold, maintains the atmospheric concentration of phosphine gas above 200ppm for greater than 10 days and in temperatures conducive to pest mortality. The New Zealand Ministry of Agriculture and Forestry recommends phosphine fumigation as a phytosanitary treatment equivalent in performance to methyl bromide when applied to New Zealand grown and exported *Pinus radiata* logs.

The New Zealand Ministry of Agriculture and Forestry would like to thank all those who have contributed to supporting the research programme and the development of this report. Specifically thanks given to the New Zealand Forest Owners Association, Frontline Biosecurity Ltd, Forest Research Ltd, New Zealand Forest Industries Council, and the New Zealand Institute for Crop and Food Research Ltd.

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1. Introduction

Phosphine has risen to favour as a fumigant as a result of international restrictions on the use of methyl bromide. New Zealand, together with 175 countries (including our significant trading partners), has signed the Montréal Protocol on substances that deplete the ozone layer. Except for exceptional quarantine purposes, under the Montréal protocol methyl bromide will be banned and/or severely restricted in developed countries by 2005 due to its role as an ozone depleter and greenhouse gas. New Zealand's current annual consumption of methyl bromide is 130 tonnes. Half of this is used for soil fumigation and a further 40% for pre-shipment treatment of forestry products to meet quarantine requirements.

Alternatives to methyl bromide need to be assessed against the properties of methyl bromide as a fumigant, and its place in the fumigation of durables and timber. The desirable attributes of methyl bromide as a fumigant are rapid speed of treatment, low infrastructure requirements, good penetrant ability, and rapid airing after exposure. Notwithstanding, methyl bromide is a highly toxic, odourless gas with substantial ozone-depleting potential and has adverse effects on produce with regard to loss of viability, quality, taint, and residues. Phosphine has been used successfully to eradicate pinewood nematode in southern pine woodchips exported from Georgia to Sweden and is a possible alternative to methyl bromide for the treatment of wood and timber products (Gooch, 1999). Phosphine fixes well, is cost-effective, has less taint and is registered with the US EPA (Environmental Protection Agency). Its major disadvantage is its slow action (3 to 10 days for fumigation), and its capacity to corrode copper, silver, and gold and damage pigments in paintings.

China, New Zealand's third and fastest growing market for forest produce, has agreed to the use of phosphine for in-transit fumigation of New Zealand *Pinus radiata* logs in sealed shipping holds, rather than fumigation with methyl bromide upon arrival in China. It is the intention of the New Zealand Ministry of Agriculture and Forestry to have phosphine recognized under the International Plant Protection Convention (1995) (IPPC) as an alternative to methyl bromide for wood product fumigation when used under specific conditions.

This report provides a summary of the scientific information supporting the use phosphine for the in-transit fumigation of *Pinus radiata* logs being exported from New Zealand to Asian markets.

2. Phosphine – Technical Specifications

The following section was taken from Worthing C.R. and Hance R.J. (1991) to provide a technical description of phosphine, available phosphine formulations, and human toxicity.

2.1 Properties of Phosphine

- Chemical name (PH_3), also known as phosphane, hydrogen phosphide or phosphorous hydride, is a grain fumigant, an industrial gas used in silicon chip manufacture, an air pollutant and a natural product of swamps and sewers.

- A gaseous state at ambient temperature with a boiling point at -87.4ºC and a freezing point at -134ºC.

- Sparingly soluble in water (0.26 vol at 20°C).

- Liberates hydrogen and forms phosphide when passed over heated metal.

- Reported to have the odour of decaying fish at concentrations of 0.3 ppm. However, Zaebest *et al.* (1988) reported workers noticed no odour when they worked in concentrations as great as 50ppm. This lack of apparent odour may be attributable to olfactory fatigue. Others have reported a garlic-like odour. This may be due to impurities which can form substituted phosphines, diphosphines, methane and arsine (AsH_3). Arsine is a highly toxic gas with a garlic-like odour.

2.2 Phosphine Formulations

a) **Aluminium phosphide (AIP):** Aluminium phosphide fumigants include Phostoxin and Fumitoxin. Both are used for product fumigation and rodent control. The equation for the release of phosphine is: $2AIP + 6H_2O = 2Al(OH)_3 + 2PH_3$. Some formulations also contain ammonium carbamate (approx. 40%), which releases ammonia gas and carbon dioxide. The carbon dioxide reduces the tendency of phosphine to oxidize spontaneously thus preventing explosions and fires. Aluminium phosphide forms dark grey or yellowish crystals and has a melting point >1002 ºC. Although stable when dry, it reacts with moist air, violently with acids, producing phosphine. When high concentrations are present it is spontaneously flammable in air and combines violently with oxygen and the halides.

b) **Magnesium phosphide (Mg_3P_2):** Products include Magnaphos and Magtoxin. Both are used for fumigation and rodent control.

c) **Zinc phosphide (Zn_3P_2):** More stable than aluminium phosphide and forms phosphine gas only when ingested. Zinc phosphide is therefore used for rodent control only and not for product fumigation.

2.3 Significant Chemical Reactions

- On contact with oxygen, phosphine tends to decompose to more stable forms of phosphorous and ultimately to phosphorous acid. This may occur explosively at oxygen concentrations above 1.8%.

- Phosphine gas also reacts violently with compounds containing fluorine, chlorine, bromine, and iodine. Phosphine gas can react with metals, including copper, brass, gold and silver.

2.4 Mammalian Toxicity

Phosphine is an acute mammalian poison, killing hamsters at 8ppm (inhalation). Feeding trials with fumigated foodstuffs have shown no chronic effect on rats.

Potential symptoms of overexposure in humans are:

a) Nausea, abdominal pain and diarrhoea, thirst, chest pressure, muscle pain, chills and stupor, skin irritation or burns (Jones *et al*. 1964);

b) Irritation of mucous membranes, especially those of the upper airways and deep lungs. Because phosphine gas releases highly acidic forms of phosphorus in the lungs (phosphoric acid) it tends to cause blistering and oedema (fluid in the lungs);

c) Mild headaches when exposed to intermittent, low concentrations of phosphine gas (0.08-0.3ppm).

The US National Institute for Occupational Safety and Health (NIOSH) recommends phosphine levels of 0.3ppm as an 8-hour weighted average and 1.0 ppm for 15-minutes should not be exceeded. NIOSH has established that 50ppm as immediately dangerous to life and health.

2.5 Product and Residue Analysis of Phosphine

Product and residue analysis is determined by analysing the phosphine liberated by acid treatment. Measurement is by gas liquid chromatography. Phosphine present during fumigation is determined using commercially available detector tubes. The presence of phosphine can also be detected using filter paper soaked with silver nitrate which changes colour from brown to black.

3. Phosphine for *Pinus radiata* Log Fumigation.

As well as having advantages over methyl bromide for log fumigation, phosphine also has a number of disadvantages. Some of these will have to be accommodated in the operational environment on an ongoing basis if it is to become a viable option to methyl bromide. A number of issues have been addressed to confirm the efficacy of phosphine against risk organisms in an operational environment, maintenance of a fumigation specification during in-transit fumigation, and the production of validation data for these activities.

It should be recognized that use of phosphine as an alternative to methyl bromide can not be viewed in isolation from the wider strategy to reduce methyl bromide use. Fumigation should be seen as a last resort after efforts have been made to reduce the risk of infestation of export produce. Highly infested export logs increase the risk of failure simply through the number of organisms present and the chance that unusual circumstances will continue to protect some from effective fumigation. New Zealand therefore strives to ensure that wood products are prepared for export in a manner that minimises the risk of unwanted pests establishing in the importing country from the exported product.

3.1 Efficacy of Phosphine Compared to Methyl Bromide

Research has clearly demonstrated that, at a minimum of 200 ppm for 10 days, phosphine is as effective as methyl bromide in treating pest risks of *Pinus radiata* logs exported from New Zealand. There is also considerable data indicating that no consistent relationship exists between concentration and reduced exposure time, and it may be possible that treatment will involve a minimum time period measured perhaps in days for log treatment.

3.2 Constraints on the Use of Phosphine as an Alternative to Methyl Bromide

As already mentioned it is likely that a minimum exposure time will be required for treatment with phosphine, irrespective of the concentration of phosphine used. While most methyl-bromide treatments take 24 hours to complete, phosphine fumigation requires up to 10 days to achieve an equivalent level of efficacy. Because of the voyage time between New Zealand and Asia (12 – 30 days), this is not a serious limitation to the New Zealand trade. However, maintaining the required fumigant concentration in ship holds, due to leakage and depletion (absorption by logs), needs particular attention.

4. Phosphine as a Phytosanitary Treatment – Literature Review

The following section provides a short summary of the published literature available on the effect and use of phosphine as a treatment.

4.1 Effect of Phosphine on Pests and Hosts

Phosphine is highly toxic to insects, has remarkable penetrative abilities, and dissolves well at the cellular level in water, oils and fats. Many studies on the sensitivities of insects to phosphine have shown that insects react differently to this gas than to other fumigants. Because the toxicity of phosphine is related to physiological activity, and hence the respiration rate, of the target organism, the egg and pupal stages are generally more tolerant than the larval and adult stages. Accordingly, it is essential that during fumigation, phosphine levels become sufficiently high to achieve 100% mortality to avoid the development of resistance.

Phosphine is considered the ideal seed fumigant since seed viability is not affected and residues are low, provided the seeds contain less than 20% moisture. Processed food in the US has a tolerance level of 0.01 ppm phosphine (Donahaye, 2000).

Once adsorbed into insect and mammalian tissues phosphine damages cell membranes and enzymes necessary for respiration and cell metabolism. Cell death and tissue necrosis leads to morbidity. In contrast, plant tissues and cells tolerate phosphine well. For example, phosphine failed to eradicate the oak wilt fungus (*Ceratocystis fagacearum*) from parenchyma cells in the sapwood of red oak because it failed to kill these tissues. Phosphine also causes little to no damage to cut flowers (Weller & Graver, 1998) and fruit (Williams *et al*, 2000).

4.2 Products Currently Fumigated with Phosphine

Phosphine is used extensively as a fumigant for stored produce, particularly if the produce is dry. No detectable toxic residues are left following ventilation. However, it has the disadvantage that longer fumigation times are required than for methyl bromide (Bond, 1984).

4.2.1 Fruit Products

Phosphine has been used to fumigate oranges in Australia to control larvae of Queensland fruit fly (Williams *et al.* 2000). The disinfestation of Californian walnuts in storage is carried out using phosphine from a cylinder (Banks, 2003). Other products disinfected using phosphine include dried fruit, nuts, cocoa, coffee, and bagged rice (Bell & Katan, 2000).

Phosphine failed to control the larval stage of the peach fruit moth in Japan (Soma & Misumi, 2000) due to a limited exposure period. In papayas, phosphine failed to control *Ceratitis capitata* following fumigation for 24 & 45h but was 100% effective after 48 & 72h (Filho & Piedade, 1987).

In China, aluminium phosphide has been used successfully to treat chestnuts without residual toxicity (Li *et al.*, 1989). Phosphine has also been used to control pest problems in potatoes, onions, cashew nuts, dates, cloves, lettuce, grapefruit, papaya, avocado, tomato, bell pepper, eggplant, and banana (Seo & Akamine, 1979).

A common theme from many of these papers is that the time of exposure to phosphine is more important for efficacy than the concentration of the gas.

4.2.2 Grain in Storage

Phosphine has garnered a bad reputation regarding its efficacy for the treatment of grain since its introduction as a pesticide in the early 1930s. For many years the convenient, cheap and safe application method (pellets) made phosphine the favoured treatment for bagged grain in the tropics. The slow release of gas gave the impression that a sufficiently high level of phosphine could be maintained, and a tightly sealed container was not necessary. This was incorrect and as a result of many poorly conducted treatments, populations of insects with high levels of phosphine resistance developed (Zettler, 1997).

Because of the resistance phenomenon, recommended fumigation times have progressively increased from 3 to 5 to 7 days and the importance of well sealed structures has been stressed to maintain high concentrations of gas. Recommended minimum concentrations were 150 ppm for 5 days (Friendship *et al.*, 1986) or 100 ppm for 7 days (van Graver & Annis, 1994).

Because there are limitations to the extent that phosphine will penetrate bulk grain, the practice of recirculating the gas through the grain has been developed and is termed “closed loop fumigation”. This technique has been applied in various forms to silos in the US (Donahaye, 2000).

In older poorly sealed silos in Australia, the concept of SIROFLO (Winks, 1993) has been adopted. In this pressurized system, a continuous low volume of phosphine is metered into an

air supply at the base of the silo. The dosage required is 35ppm for 14 days or 20ppm for 28 days. The method is currently being applied in other countries. A manifold system for silo complexes (SIROCIRC) has also been developed.

The fumigant methylphosphine has been shown to be more active against phosphine-resistant strains than susceptible strains (Chaudry *et al*., 1997). This raises the potential for alternating fumigants to reduce the phosphine resistance problem.

Western Australia exports around 80% of its annual grain harvest to markets that are becoming more discerning with regard to insect infestation and chemical residues. Western Australia is well placed to meet these markets through its extensive use of sealed storage with phosphine fumigation both on-farm and in the central handling system (Emery & Kostas, 2000).

4.2.3 Cut Flowers

Phosphine has been used to treat cut flowers with limited success due to the short exposure times available before flowers arrive at their markets. Weller & Graver (1998) reported that phosphine failed to control psocids, mites, whitefly, rice weevils, and ants in Proteas. They suggested that phosphine should be combined with other treatments to achieve a complete kill.

4.2.4 Seed

Because phosphine is generally non toxic to plant tissues, it has been used to kill seed-borne insects. Examples of seed treatment include pests of Chestnut (Li *et al*. 1989) and *Cryptomeria* (Xu *et al.* 1989).

4.2.5 Wood Products

i) Fungal Stained Wood: Fumigation of red oak with methyl bromide has been used successfully to eradicate the oak wilt fungus (*Ceratocystis fagacearum*) from exported veneer logs and the prevention of grey stain (Schmidt & Christopherson, 1997).

ii) Wood Chips: The pinewood nematode (*Bursaphelenchus xylophilus*) and its pine sawyer (*Monochamus*) vectors were intercepted in chips, green lumber, and logs exported from North America to the European Union. Phosphine applied in transit to a shipload of chips exported from Georgia to Sweden completely eradicated the pinewood nematode and is being considered as an alternative treatment to methyl bromide (Dwinell, 1997).

iii) Logs: Phosphine has been used successfully to kill all life stages of the Dermestidae beetles (Vincent & Lindgren, 1972; 1975). In China, transportation of logs harbouring pupae of *Hyphantria cunea* in cracks or holes in the bark was found to be important for spreading the pest. Tests showed that fumigation of logs wrapped in plastic with phosphine at 15-20 g/m³ for 3 days at 25-29 °C produced 100% pupal mortality (Shu & Yu, 1984). Soma and Oogita (1998) fumigated 10 species of forest insects with phosphine (1 and 2 g/m³ for 24 and 48 hours @ 15°C). Fumigation for 24 hours killed eggs of *Callidiellum rufipenne, Monochamous alternatus, Cryphalus fulvus, Ips cembrae*, and *Phloeosinus perlatus*, all stages of *Scolyoplatypus tycoon* and *Xyleborus validus*, while eggs of *Semanotus japonicus* and *Pissodes nitidus* and all stages of

X. pfeilli were not killed completely. However, mortality of *S. japonicus* and *P. nidulus* was 100% after 48 hours @ 15°C.

Oogita *et al.* (1997) concluded that phosphine fumigation alone is unlikely to be an effective quarantine treatment for forest insect pests when applied for short periods (48 hours). They fumigated the cerambycids (*Semanotus japonica, S. japonicus*), *Callidiellum rufipenne* and *Monochamus alternatus*, the scolytids (*Phloeosinus perlatus, Cryphalus fulvus* and *Xyleborus pfeili*) and the platypodids (*Platypus quercivorus* and *P. calamus*) with phosphine at concentrations of 1.0 and 2.0 g m³ for 24 and 48 hours at 15°C and 25°C. *S. japonica* and *P. perlatus* eggs were killed at 2.0 g m³ for 24 hours at 15°C, but larvae and pupae of all species were not killed at 2.0 g m³ for 48 hours at 15°C. At 2.0 g m³ for 48 hours at 25°C, all stages of *C. fulvus* and *X. pfeili*, except larvae of *C. fulvus*, were killed.

Zhang (2003) demonstrated that phosphine levels as low as 200ppm, maintained for 10 days, gave effective control of *Hylastes ater* and *Arhopalus ferus* (synonym *Arhopalus tristis*).

4.2.6 Buildings and Structures

Fumigation of milling facilities with phosphine has been difficult due to its corrosive effect on copper, brass, and other metals in computers and other equipment. This has been overcome by utilization of a new formulation called Eco2-Fume which is a combination of phosphine (2%) and CO2 (98%).

With a fumigation time of 24 hours, all life stages of the confused flour beetle (*Tribolium confusum*) were killed and the cost was comparable to that of methyl bromide (Mueller, 2001).

Phosphine was used in Norway to rid three 800 yr old churches of old house borer (*Hylotrupes bajulus*). The buildings were sealed with plastic and fumigated with 2.8 g/m³ phosphine for 5.5 days (Anon, 1985).

5. Report on Government-sponsored Phosphine Research Trials

While the review of existing literature on all aspects of phosphine fumigation indicates that, in many circumstances, phosphine can be considered equivalent to methyl bromide, it lacks any significant data pertaining to log fumigation. The application of phosphine on whole *Pinus radiata* logs is presently unique to New Zealand and its efficacy is largely based on extrapolation from fumigation of grain and informal observations during its use over the past year by New Zealand exporters. The New Zealand government and the forestry industry have sponsored research trials to formally validate the efficacy of phosphine fumigation of softwood logs originating from New Zealand.

The trials address the three key questions:

1. Is phosphine effective against the pests likely to be associated with New Zealand *Pinus radiata* logs and considered by export markets to be a quarantine risk?

2. Is phosphine fumigation at the recommended rate fully effective against these quarantine pests in naturally infested logs?

3. Will the required concentration of phosphine be met during log shipments in the operational environment of a ship's hold?

The first question was investigated by direct exposure of risk pests and their life stages in the laboratory environment. The second by the exposure of field collected logs in custom designed fumigation chambers, and the third by on-ship monitoring of hold concentrations in the course of a routine log shipment.

5.1 Proposed Phosphine Fumigation Treatment for New Zealand Logs

Based on indications of phosphine efficacy on wood pests provided in the literature, the target treatment for New Zealand exported *Pinus radiata* logs was set at a minimum phosphine concentration of 200 ppm for 10 days. This level of phosphine exposure can be achieved by adding 2g/m³ aluminium phosphide to each ship hold on departure from New Zealand and including a top-up after 5 days of a further 1.5g/m³ per hold.

It should be noted that the mortality threshold of the target pests is likely to be at a considerably lower phosphine concentration than 200 ppm. It is also possible that an initial treatment of 3g/m³ on departure from New Zealand may be all that is required to achieve the target atmospheric phosphine concentration for the required time. Further research on these two indices is currently being undertaken in New Zealand. Indications are however, that, even if phosphine concentrations where to drop below minimum target levels during the treatment period, the effect on the efficacy of the treatment would not be significant.

5.2 Pests Associated with New Zealand Export **Pinus radiata** *Logs*

Table 1 contains a complete list of pests considered likely to be associated with New Zealand exported *Pinus radiata* logs. For the Asian market, the only pests of concern are those not already widely established or under official control in those countries. Table 2 contains a list of pests recorded on *Pinus radiata* logs in New Zealand but are very unlikely to be associated with exported logs that are not left to lie exposed in the forest (logs would only become infested if left in the forest for more than 6 weeks).

Table 1: Pests considered likely to be associated with New Zealand exported *Pinus radiata* logs

Pest Name	Family	Distribution	Action
Arhopalus ferus (burnt pine longhorn)	Cerambycidae	Europe and New Zealand	**Yes**
Prionoplus reticularis (huhu beetle)[1]	Cerambycidae	New Zealand native	**Yes**
Hylastes ater (black pine bark beetle)	Scolytidae	Europe, Japan, Australia, Chile, South Africa, New Zealand	**Yes**
Hylurgus ligniperda (bark beetle)	Scolytidae	Europe, Japan, Australia, Chile, South Africa, New Zealand	**Yes**
Sirex noctilio (Sirex wasp)	Siricidae	**Eurasia**/N Africa (native), New Zealand, Australia, Brazil, Argentina	**None**

(from USDA (1992) and MAF data)

Note 1: Only *Prionoplus reticularis* eggs are likely to be associated with recently felled *Pinus radiata* logs.

Table 2: Pests considered very unlikely to be associated with New Zealand exported *Pinus radiata* logs

Pest Name	Family	Distribution	Action
Platypus apicalis (pinhole borer)	Platypodidae	New Zealand native	**None**
Platypus gracilis (pinhole borer)	Platypodidae	New Zealand native	**None**
Hexatricha pulverulenta (longhorn)	Cerambycidae	New Zealand native	**None**
Kalotermes brouni (dry wood termite)	Kalotermitidae	New Zealand native	**None**
Mitrastethus baridioides (Kauri weevil)	Curculionidae	New Zealand native	**None**
Psepholax spp. (pit weevils)	Curculionidae	New Zealand native	**None**
Stenopotes pallidus (pallid longhorn)	Cerambycidae	New Zealand native	**None**
Torostoma apicale	Curculionidae	New Zealand native	**None**
Pachycotes peregrinus	Scolytidae	New Zealand native	**None**

(from USDA (1992) and MAF data)

5.3 Laboratory Exposure Trials

The aim of the laboratory exposure trails was to measure the efficacy of phosphine on the target pests either directly or while in naturally infested material. All exposures were replicated at least three times and compared with untreated controls.

5.3.1 Direct Exposure Trials

The trials were completed in 92 litre stainless steel fumigation chambers with constant exposure of specified concentrations of phosphine for specified periods at 16ºC. The pests used in the exposure trials were collected from naturally infested logs in Tikitere and Kaingaroa Forests in the Central North Island of New Zealand. The *Arhopalus* eggs were collected from laboratory cultures derived from field collected adult insects.

The two species exposed (*Hylastes ater* and *Arhopalus ferus*) are the most common contaminants of export logs and represent the two groups of insects considered of most concern to trading partners, namely bark beetles and longhorn beetles. *Hylastes* bark beetles are representative of insects which complete their life history beneath the bark without entering the sapwood (Milligan, 1978). *Hylastes* is considered representative of the only other bark beetle risk in *Pinus radiata* logs (*Hylurgus ligniperda* (Bain, 1977)), an assumption supported by the results of log exposure trials (see section 5.3.2). *Arhopalus* is the primary risk longhorn beetle in export logs, larvae typically feeding beneath the bark during early development and entering the sapwood as late-instar larvae (Hosking, 1978; Brocherhoff and Hosking, 2002).

Trials were completed at a number of phosphine concentrations. However, results from tests using only the lowest concentrations (100 and 200 ppm) are reported here. *Hylastes ater* larvae and adults and *Arhopalus* eggs were exposed for 10 days while *Arhopalus* adults were exposed for 12 or 24 hours only. A minimum of 10 adults or larvae from either *Hylastes* or *Arhopalus* were exposed in each test, while the number of eggs exposed in each test exceeded 90. In each case 4 replicate trials where completed for each species, life stage and exposure concentration.

Table 3: Results from direct exposure trials on *Hylastes* and *Arhopalus* life stages

Pest species	Life stage	Phosphine conc.	Duration	Mortality (av)
Hylastes ater	Adults	0 (control)	10 days	20.5%
	Adults	200 ppm	10 days	100%
	Larvae	0 (control)	10 days	12.7%
	Larvae	200 ppm	10 days	100%
Arhopalus ferus	Adults	0 (control)	24 hours	27%
	Adults	100 ppm	12 hours	86%
	Adults	200 ppm	24 hours	100%
	Eggs	0 (control)	10 days	5%
	Eggs	100 ppm	10 days	100%
	Eggs	200 ppm	10 days	100%

Phosphine efficacy is related to the physiological activity, and hence the respiration rate, of the target organism. For this reason insect adults and larvae are killed at lower concentration rates and shorter exposure times than eggs and pupae, with eggs generally recognized as the most resistant stage (Fields and Jones, 1999). The results for *Arhopalus* egg exposure trials indicate that even resistant life stages will not survive a minimum concentration of 100ppm phosphine for 10 days.

5.3.2 Log Exposure Trials

The litmus test for phosphine efficacy was always going to be the successful treatment of naturally infested *Pinus radiata* logs similar to those encountered in shipments exported from New Zealand. Naturally infested logs were collected from appropriate aged logging sites in Kaingaroa and Tikitere Forests in the central North Island of New Zealand. The predominant insects detected were *Arhopalus tristis*, *Hylastes ater*, and *Hylurgus lidgniperda*, all of the key insects currently detected most frequently in *Pinus radiata* logs being prepared for export from New Zealand. All logs were cut to 1.3 m in length and ranged in diameter from 17 to 30 cm. No sampling of logs was carried out prior to exposure to ensure maximum infestation levels were retained but all logs were 100% autopsied following treatment.

The logs were confined in custom designed fumigation chambers of 3.4m³ (3400 litre) capacity, which allowed monitoring of fumigant concentration and addition of aluminium phosphide pellets. To simulate the operational environment, 2g/m³ aluminium phosphide was initially added to each chamber with a top-up after 5 days of a further 1.5g/m³ per chamber. All exposures were carried out at ambient temperature (24-26^{O}C). Logs were held for 24 hours after completion of treatment before autopsy. A total of 26 logs were used in the exposure trials.

Table 4: Results from log exposure trials

Pest species	Life Stage	Number found	Mortality
Hylastes/Hylurgus[1]	Larvae	417	100%
	Pupae	138	100%
Hylastes ater	Adults	19	100%
Hylurgus ligniperda	Adults	114	100%
Arhopalus ferus	Early Larvae	85	100%
	Mid Larvae	68	100%

	Late Larvae	42	100%
Prionoplus reticularis	Egg rafts	4	100%

Note 1: Hylastes ater and Hylurgus ligniperda larvae and pupae are difficult to distinguish and therefore have been grouped together.

The results from the log exposure trials clearly validate the current treatment specification of 200ppm of phosphine for 10 days and the operational strategy of topping up aluminium phosphide during the voyage.

5.4 Phosphine Depletion Trials

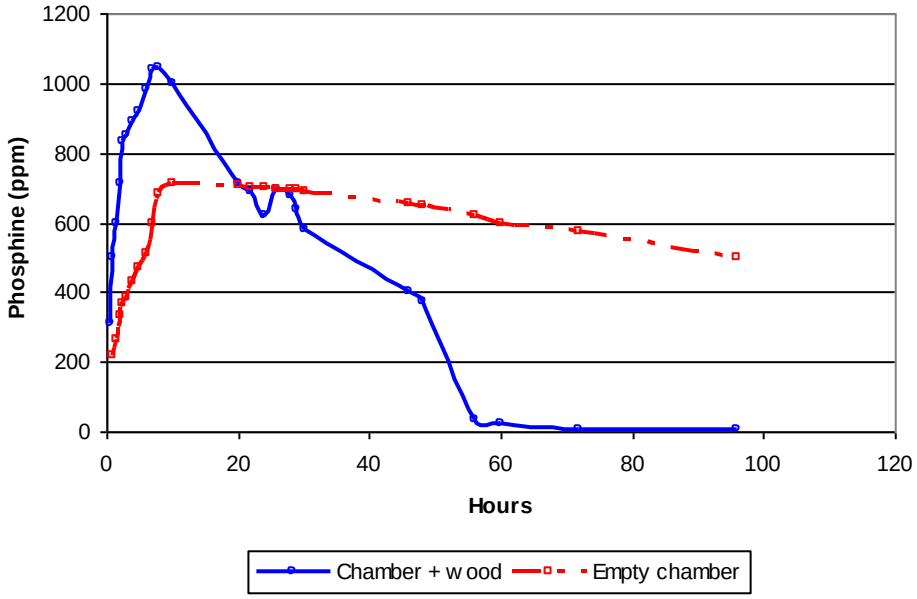
The issue of phosphine depletion during the course of fumigation of logs is a key operational issue for the use of the gas as a phytosanitary treatment. The fate of the depleted phosphine is unclear, but it appears it is absorbed or bound to wood products. Research was undertaken to determine the rate of depletion and the top-up necessary to maintain the required specification (minimum of 200ppm phosphine for 10 days).

5.4.1 Small Tank Trials

The performance of phosphine gas was studied in a 100 litre acrylic tank. The gas was generated from Quickphos aluminium phosphide tablets and phosphine levels were monitored with a Uniphos-250-Phosphine monitor. Results indicated that it took several hours to generate a constant and maximum level of phosphine gas in the tank (Figure 1). Covering the tank with a blanket to exclude light reduced the decay of phosphine. Notwithstanding, a ships hold would always be dark so decay of phosphine in light should not be a problem. Introduction of gas into the chamber from an externally generated source enabled easy regulation of gas levels. A fan in the chamber enabled the gas to reach equilibrium more quickly.

If the tank was empty, the phosphine concentration was stable for 30 hours and 66% of the gas was present after 96 hours. Inclusion of wood (18 kg pine, moisture content 63.2%) hastened the depletion of phosphine gas and it was fully depleted after 70 hours (Figure 1).

Figure 1: Phosphine depletion rate in an empty and wood filled acrylic tank

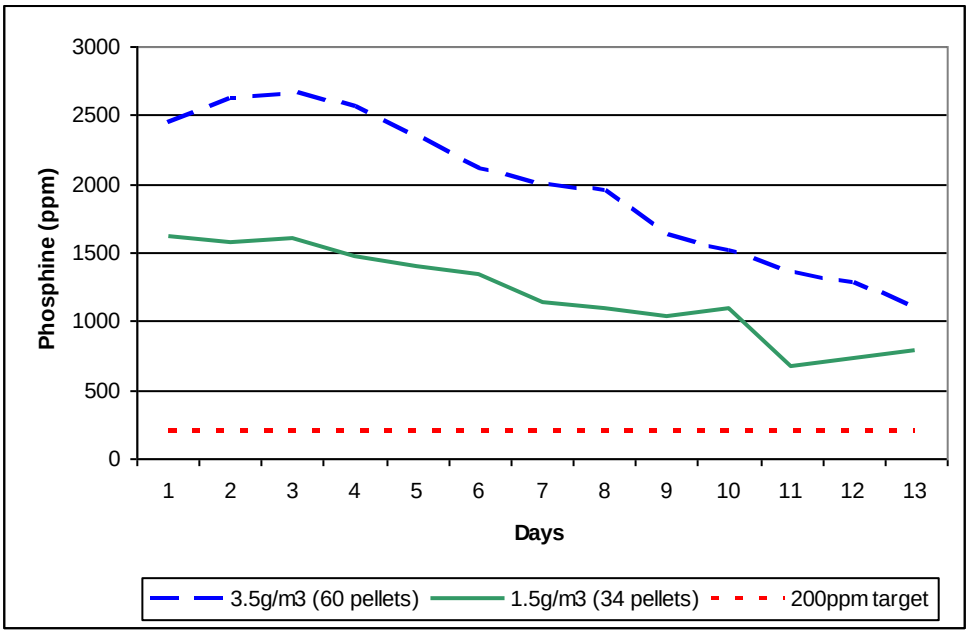


These results indicate that phosphine is absorbed by wood from the atmosphere relatively quickly. As a quick release formulation was used in the trial, atmospheric phosphine was not being replenished as it was being absorbed by the wood.

5.4.2 Chamber Trials

Phosphine levels were monitored in the 3.4m³ (3400 litre) chambers containing fresh *Pinus radiata* logs, over a 13 day period at two initial (day 1) phosphine concentrations, 3.5g/m³ and 1.5g/m³. Resulting concentrations remained well above the 200ppm target throughout the exposure period (Figure 2). These results are consistent with the small tank trial but not the in-hold monitoring discussed below. It should be noted that the fumigation chambers were approximately 60% air space, compared with perhaps 10% in a fully loaded ship's hold.

Figure 2: Chamber fumigation of logs at two initial phosphine concentrations



5.4.3 Ship Hold Dispersion and Depletion Trials

While the manufacturers of phosphine fumigants maintain that phosphine gas disperses exceedingly well, the unique application of phosphine for in-hold fumigation of logs requires validation of this characteristic. Information on variation between holds on the same vessel is also desirable as environments within individual holds will differ. On-vessel monitoring requires a suitable vessel with access to holds for sensors, placement of sensors during loading and their subsequent protection, and staff to make the minimum 4 week round trip to undertake the monitoring and recover the sensors.

Preliminary monitoring trials were commissioned by Whitham (2002) on the log vessel Ken Ryu in early February 2002. Gas samples were taken from the mid-hold position of 5 fully loaded holds throughout the 10 day voyage (Figure 3), and the bottom, mid, and top positions of one hold (hold number 4) (Figure 4).

Figure 3: Phosphine concentrations over 10 days at the middle position in five holds

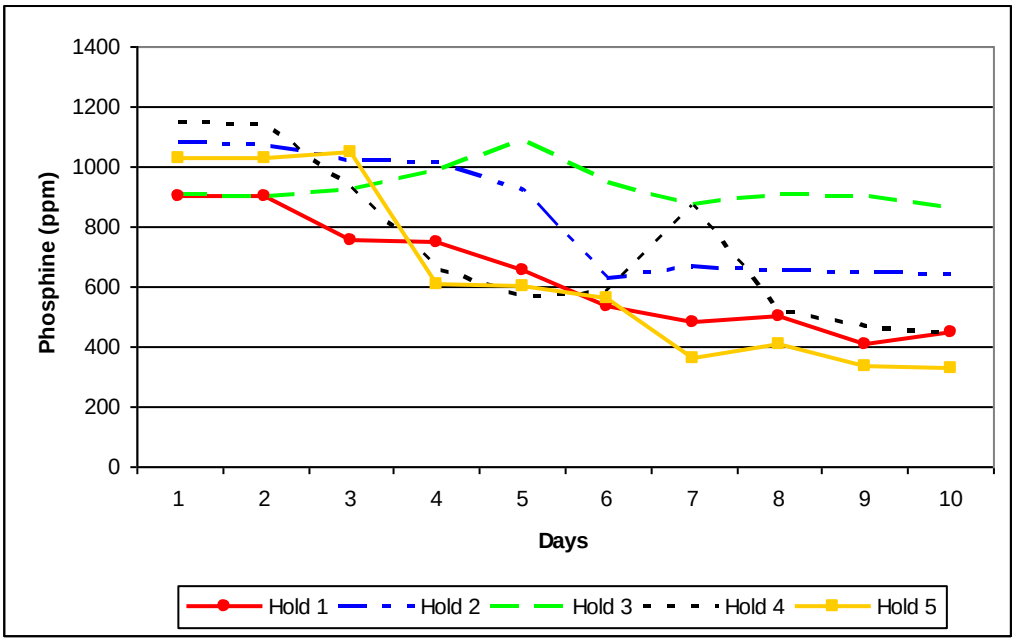
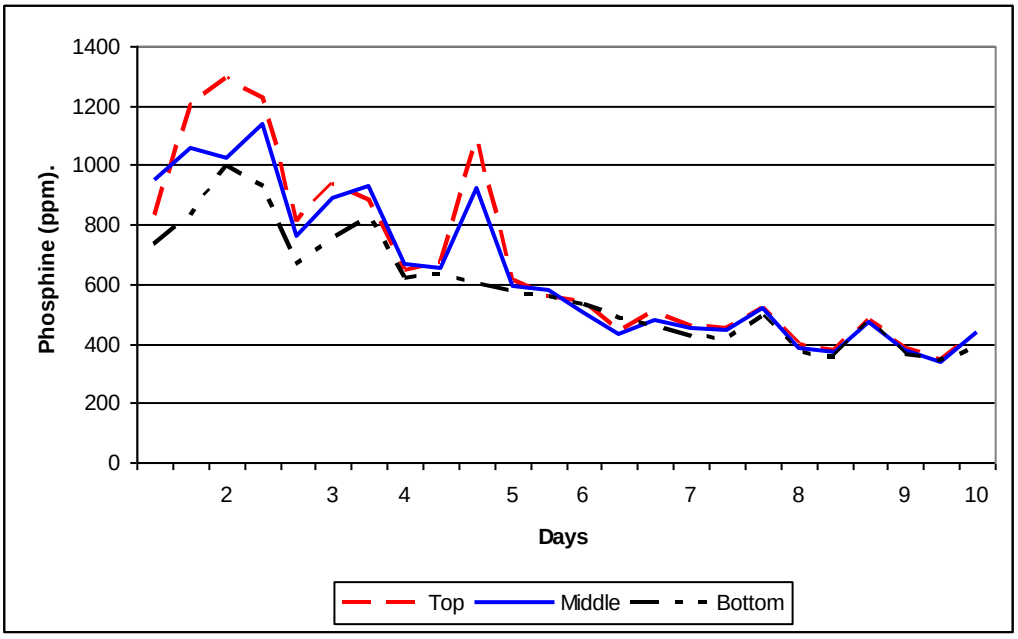
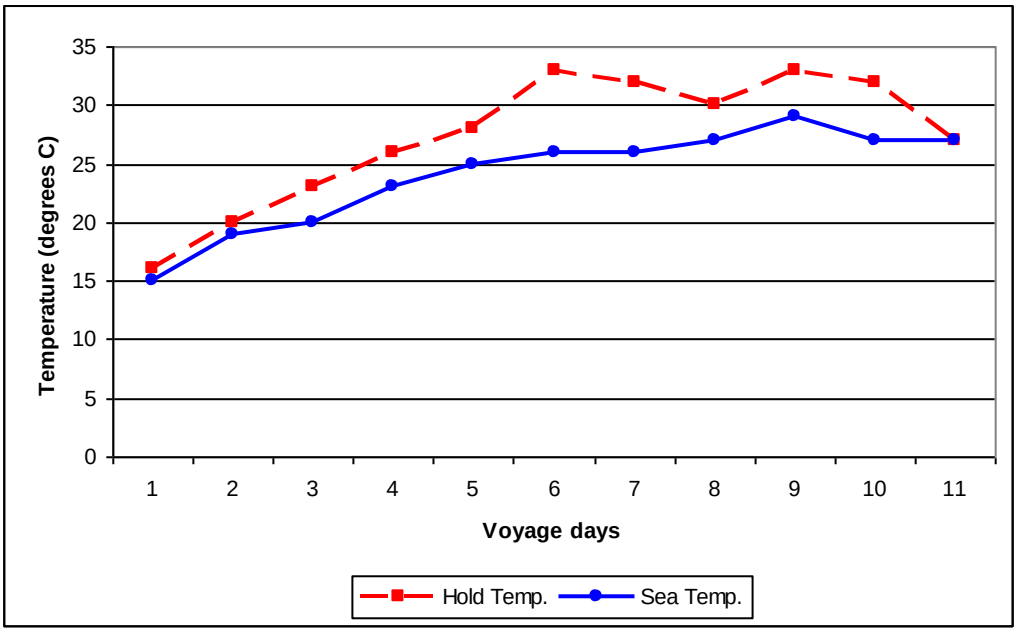


Figure 4: Phosphine concentrations over 10 days at three levels within hold number 4



The results (Figures 3 and 4) support the manufacturer's assertion that phosphine has high dispersion capability, and would penetrate rapidly throughout fully loaded holds (Figure 4). The expected decline in phosphine concentration occurred across all 5 holds (Figure 3) although there was considerable variation in both the rate and total decline between holds. The treatment rate of 3g/m3 was common to all 5 holds but both hold moisture and log moisture would influence the rate of phosphine release and its depletion over time. Temperature data showed hold temperature to be parallel to but slightly above that of the sea (Figure 5).

Figure 5: Comparison of sea and holding temperatures during voyage



6 Discussion

While further work is under way within New Zealand to validate the use of phosphine in a number of operational environments, the work completed to date and summarised above for the use of this fumigant on *Pinus radiata* export logs is comprehensive and provides a high level of confidence that phosphine can be accepted as a phytosanitary treatment with an efficacy equivalent to, or exceeding, that of methyl bromide.

At 200ppm for 10 days, phosphine has been demonstrated to effect 100% mortality on all of the risk pests likely to be associated with New Zealand *Pinus radiata* logs. When applied in an operational environment, the application of 2g/m³ aluminium phosphide to each ship hold on departure from New Zealand and subsequently topped-up after 5 days with a further 1.5g/m³ per hold, maintains the atmospheric concentration of phosphine gas above 200ppm for greater than 10 days and in temperatures conducive to pest mortality.

The New Zealand Ministry of Agriculture and Forestry therefore has no hesitation in recommending the acceptance of phosphine as a phytosanitary treatment equivalent to methyl bromide when applied to New Zealand grown and exported *Pinus radiata* logs.

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