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Review of phosphine research for control of timber quarantine pests

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A report prepared for the

Chairman, STIMBR (Stakeholders in Methyl Bromide Reduction)

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Contents

1 Executive summary

A large number of both laboratory and operational trials have been undertaken over the past 7 years in New Zealand on the use of phosphine to control pests likely to be found in radiata pine logs and sawn timber.

There are six pests of quarantine importance for New Zealand log and timber exporters. They are (1) the bark-borne burnt pine longhorn (BPL) (*Arhopalus ferus (*Mulsant)), (2) black pinebark beetle (BPBB) *Hylastes ater* (Paykull) and the closely related (3) goldenhaired barkbeetle (GHBB) *Hylurgus ligniperda* (Fabricius) and the wood-borne (4) Sirex wasp *(Sirex noctilio* F.), (5) huhu (*Prionoplus reticularis* White) and (6) New Zealand drywood termite (*Kalotermes brouni* Froggatt). This review focuses mainly on bark-borne pests as wood-borne pests would not be expected to infest mature logs nor sawn timber from mature trees.

The research trials summarised in this report range from informal laboratory investigations to major operational trials as well as reviews of existing knowledge and literature. The report reviews phosphine studies between 2002 and 2008. Information is presented in the following sections:

1. Phosphine as a fumigant
2. Knowledge of phosphine fumigant performance for log and timber fumigation from scientific literature and New Zealand studies.
3. Research to confirm and improve 10-day x 200 ppm phosphine treatment protocol for logs
4. In-hold monitoring of phosphine for disinfestation of logs bound for China
5. Using phosphine for disinfestation of sawn timber.

For logs, research carried out to date and the results of ship-board monitoring supports the efficacy of the 10-day x 200 ppm protocol for controlling bark-borne quarantine pests. A top-up after 5 days is required to maintain phosphine concentrations during the 10-day period. There is insufficient evidence to support a treatment protocol shorter than 10 days although the experimental work strongly suggests durations as short as 5 days can be effective. It is very likely that a shorter treatment protocol will still rely on a top-up of phosphine.

For sawn timber, the trials show that a 16−24-hour phosphine protocol works well at high temperatures, e.g. at 20−30°C. The optimum treatment has yet to be ascertained, particularly at the lower temperatures that may be encountered at the start and end of the season.

Research trials require adequate numbers of fresh insects. Information on best methods to collect, store and transport various life stages of insects for trials is required. There has been no overseas work on the use of phosphine to control insects of quarantine importance to New Zealand.

Recommendations for future work on logs and sawn timber are:

1. **Carry out studies on infested logs.** Trials on infested logs provide 'real world' information for quarantine authorities and should enable data to be collected on all life stages of quarantine importance. The presence of logs will ensure the pattern of phosphine depletion matches industry experience and that laboratory information is directly applicable. There may still be a problem in determining phosphine efficacy for BPL as the incidence of this insect is low. In this situation, trial work should still include logs artificially infested with BPL.

2. **Ensure that fresh insects are available in sufficient numbers.** Another way to ensure accurate information is delivered to quarantine authorities is to ensure that trials are carried out with large numbers of freshly collected and properly stored and handled insects. Information on the best methods to collect, store and transport various life stages of insects for trials is required.

3. **Use shorter protocols.** To develop a shorter treatment protocol, infested logs should be used and treated at, say, 3 phosphine thresholds (including 200 ppm) over 3−10 days.

4. **Improve the safety of phosphine delivery.** The current manual method of top-up is hazardous for the MOB (man on board). Cost-effective and reliable alternatives to manual top-up are required and should not be difficult to devise.

5. **Review options for phosphine control of BPL beetle hitchhikers on sawn timber prior to shipment.** Phosphine treatments longer than 24 h should be tested for control of BPL beetles to enable an effective treatment to be developed for the range of temperatures experienced during the BPL flight periods.

6. **Define factors affecting phosphine depletion.** Research is required to better understand the effect of moisture content of the wood and bark, overall bark coverage on the logs and bark adsorption of phosphine on phosphine depletion.

7. **Decide on criteria for moribund insect evaluation.** It is important to take the uncertainty out of live/dead assessment. Periodic assessment of % live, moribund and dead after fumigation is required to determine the best method of assessing % mortality, e.g. assess BPL beetles 24 and 48 h after treatment.

2 Introduction

The search for alternatives to the environmentally harmful fumigant methyl bromide (MB), has led to the New Zealand forestry sector investing in the evaluation of phosphine as a pre-shipment and in-transit treatment for logs and sawn timber. The current acceptance of phosphine for the in-transit fumigation of radiata pine logs to China (MAF 2003) is a result of this investment. The industry is keen to expand the application of this fumigant both in other markets and on other products.

A large number of laboratory and operational trials have been undertaken over the past 7 years on the use of phosphine to control pests likely to be found in radiata pine logs and sawn timber. This report identifies, summarises, and evaluates data from all trials and provides references to the original trial reports. The review identifies gaps in our knowledge and makes recommendations for future study.

2.1 Phosphine research participants

Research into applications of phosphine within the New Zealand forestry sector has been led by the fumigant company Genera Ltd, which early on recognised that the continued use of large quantities of MB for log and timber fumigation was not a viable long-term strategy and that alternatives would have to be sought. Much of the early research presented in this report comes from initiatives undertaken or commissioned by Genera Ltd and its partner Frontline Biosecurity.

In recent years the impetus for research has come from STIMBR (Stakeholders in Methyl Bromide Reduction). Progress would not have been possible without the collaboration and support of the NZ Forest Owners Association, FIDA (Forest Industry Development Agenda), fumigant suppliers such as United Phosphorus, Chemcolour, Primaxa and Cytec, and research organisations Scion and Plant & Food Research (formerly Crop & Food Research).

2.2 Quarantine pests of export logs and sawn timber

There are six pests of quarantine importance for New Zealand log and timber exporters. They are the bark-borne burnt pine longhorn (BPL) (*Arhopalus ferus (*Mulsant)) (Coleoptera: Cerambycidae), black pinebark beetle (BPBB), *Hylastes ater* (Paykull) and the closely related goldenhaired barkbeetle (GHBB), *Hylurgus ligniperda* (Fabricius) (both Coleoptera: Scolytidae), and the wood-borne Sirex wasp *(Sirex noctilio* F. (Hymenoptera: Siricidae)), huhu (*Prionoplus reticularis* White (Coleoptera: Cerambycidae)) and New Zealand drywood termite (*Kalotermes brouni* Froggatt (Isoptera: Kalotermitidae)). This review focuses mainly on the bark-borne pests. The wood-borne pests would not be expected to infest well-managed mature logs nor sawn timber from mature trees. Sirex wasp only attacks young trees and huhu and dry wood termite only inhabit decaying wood.

2.3 Research reviewed in this report

The research trials that have led to the data summarised in this report range from informal laboratory investigations to major operational trials as well as reviews of existing knowledge and literature.

For ease of discussion information in this report is presented in the following sections:

1. Phosphine as a fumigant
2. Knowledge of phosphine fumigant performance for log and timber fumigation from scientific literature and New Zealand studies.
3. Research to confirm and improve 10-day x 200 ppm phosphine treatment protocol for logs.
4. In-hold monitoring of phosphine for disinfestation of logs bound for China.
5. Using phosphine to disinfest sawn timber.

It is quite clear that research on disinfestation of logs and sawn timber in New Zealand using phosphine has advanced considerably since it began in 2002. At that time there were very limited research facilities to handle phosphine fumigation and entomologists had little knowledge of how to handle timber pests for research purposes outside the forest. The original research may look inadequate now but it must be recognised that the work started from a small base of knowledge and with very limited facilities and funding. That early research led to New Zealand's log trade with China proceeding.

This report reviews phosphine studies between 2002 and 2008. The report concludes with recommendations for future research.

3 Phosphine as a fumigant

The key properties of phosphine are outlined below (from Chaudhry (1997) and Spiers (2003)).

3.1 Chemical and physical properties of phosphine

Phosphine is a colourless flammable gas that, in its pure form, is odourless. Its lowest explosion point is 1.79% in air. Phosphine is rapidly diffused in air because it has a similar density to air (relative densities 1.13:1). Phosphine is considered slightly soluble in water (0.26% (v/v) at 17°C). Phosphine can corrode several metals, including copper, when oxidised under high humidity conditions. Unlike MB, phosphine breaks down quickly in the atmosphere when exposed to sunlight.

3.2 Uses

Phosphine is highly toxic to insects and is known to penetrate treated material. Phosphine has replaced many MB applications for treatment of durable materials where its slower action on pests can be managed successfully. Phosphine is generally ineffective against fungi.

Grain vs Logs

For logs, the current in-transit dosage specification is based on Australian experience with stored grain pests and may be significantly higher than dosages required where no insect resistance is involved.

For grain, repeated phosphine treatment and poorly conducted fumigations in domestic silos have led to high levels of phosphine resistance in stored grain pests. Such resistance is not an issue for commodities such as forest produce being treated once during export.

3.3 Health and safety

Exposure to phosphine must not exceed the 8-h TWA (time-weighted average) of 0.3 ppm for applicators and workers during application. All people in the treated site and in adjacent indoor areas are covered by this exposure standard. Such exposures might occur because of leakage into enclosed areas from fumigation sites or during transfer of unaerated commodity. The short-term exposure limit (STEL) is 1.0 ppm phosphine for 15 min (Cytec 2009).

3.4 Generation of phosphine

Solid formulations are the usual source of phosphine worldwide. Phosphine is typically produced following the reaction of aluminium or magnesium phosphide pellets with water (Reaction 1). When phosphine (PH_3) is generated from pellets, maximum gas concentration may not be reached for some hours.

$$AlP + 3H_2O \rightarrow Al(OH)_3 + PH_3$$

$$Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2PH_3$$

(Reaction 1)

Phosphine can be generated directly as required from phosphine gas generators and cylinderised formulations. The gas generators allow rapid release of phosphine gas from solid formulations (e.g. magnesium phosphide). The cylinderised formulations allow for more rapid and controlled release of phosphine. This in turn allows shorter exposure times. The two formulations of phosphine available in cylinders (from Cytec Ltd) are VAPORPH_3OS (pure compressed gas) and ECO_2FUME (2% phosphine diluted with CO_2). The pure compressed gas formulation can be delivered safely (phosphine is explosive at concentrations over 1.8% in air) using the Horn Diluphos System (www.fosfoquim.cl/ingles/productos/hds.html). This formulation overcomes the problem of shipping heavy metal cylinders containing a small quantity of phosphine (2%, phosphine in ECO_2FUME).

3.5 Mode of action

Phosphine is a strong reducing agent. Biological redox systems, especially the components of the mitochondrial electron transport chain, are probably the site of its action in insects. The oxidation of phosphine could produce reactive phosphorylating species and interactions of phosphine with biological redox systems have been reported to generate highly reactive oxyradicals. This appears to be the basis of phosphine toxicity to insects, which differs from that of respiratory inhibitors such as hydrogen cyanide (Chaudhry 1997).

4 Use of phosphine to control wood pests

4.1 Overseas studies

Very little information is available in the scientific literature on the use of phosphine to control wood pests. There is no information from overseas on the control of the six pests of quarantine importance to New Zealand log and timber exporters, i.e. on BPL (*Arhopalus ferus*), BPBB (*Hylastes ater*), GHBB (*Hylurgus ligniperda*), Sirex wasp (*Sirex noctilio)*, huhu (*Prionoplus reticularis*) and drywood termite (*Kalotermes brouni*).

In China, transportation of logs with pupae of *Hyphantria cunea* in cracks or holes in the bark was found to be important for spreading the pest around the country. Tests showed that fumigation of logs wrapped in plastic with phosphine at 15−20 g/m^3 for 3 days at 25−29°C produced 100% pupal mortality (Shu & Yu 1984, cited by Spiers 2003).

Oogita et al. (1997) concluded that phosphine fumigation applied for short periods (48 h) would be unlikely to be an effective quarantine treatment for forest insect pests. They fumigated cerambycids (*Semanotus japonica, Callidiellium rufipenne* and *Monochamus alternatus)*, 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/m^3 for 24 and 48 h at 15 and 25°C. *S. japonica* and *P. perlatus* eggs were killed at 2.0 g/m^3 for 24 h at 15°C, but larvae and pupae of all species were not killed at 2.0 g/m^3 for 48 h at 15°C. At 2.0 g/m^3 for 48 h at 25°C all stages of *C. fulvus* and *X. pfeili*, except larvae of *C. fulvus*, were killed. The results show that treatment duration must be longer than 48 h to control all life stages of forest insect pests when using phosphine.

Wang et al. (2003) treated poplar timber infested with larvae and pupae of Asian longhorn beetle (*Anoplophora nobilis*) and larvae of two other pests with phosphine. Insects were 100% controlled at 15.5°C using a CT of 112 183 mg/h/L in a 120 h (5 day) treatment (i.e. a mean concentration of 935 ppm phosphine).

The US manual for ECO_2FUME (Cytec 2009) suggests a 10-day treatment is required for treating wood and wood products. It says ‘When fumigating wood or wood products, the fumigation rate may need to be adjusted depending upon the moisture content of the wood or wood product. For best results, fumigate with a dose of 750−1000 ppm phosphine for 10 days. Higher concentrations are recommended to counter the solubility of phosphine in water or moisture present in the wood or wood product.’

4.2 Fate of phosphine during log and timber fumigation

Rapid depletion of phosphine from the headspace was recognised early in the implementation of the phosphine protocol by New Zealand log exporters (Primaxa 2002). Earlier, Leesch et al. (1989) had shown a similar pattern when monitoring in-transit disinfestation of wood chips using used aluminium phosphide to control a pine wood nematode over a 24-day journey from Georgia (USA) to Sweden. Phosphine concentrations were generally 100−1500 ppm after 1 day but had dropped to 2.5−40 ppm after 7 days. The authors state that sorption of phosphine was rapid and that this was expected based on earlier unpublished laboratory studies. Wang et al. (2003) reported that by 96 h after phosphine application, fumigant concentration had dropped to below 3% of the initial headspace concentration at 21°C and that sorption was higher at higher wood moisture content.

A review by Zhang (2004a) addressed the issue of phosphine depletion with particular reference to declines in fumigant concentration during in-transit fumigation of logs within a ship's hold. He commented that methods needed to be devised to maintain the required 200 ppm phosphine requirement for in-hold treatment of logs. The rapid decline in fumigant concentration over the 10 days necessitated a fumigant top-up after 5 days.

Fumigant concentration can be depleted by:

1. leakage from the fumigation vessel,

2. reactions with other materials (such as metals),

3. dissolution in water.

   Phosphine is considered slightly soluble in water (0.26% (v/v) at 17°C). This means that 1 m^3 water can dissolve up to 368.4 g phosphine. Green logs have a high moisture content and can dissolve phosphine as well. When green logs are loaded into ship holds the air in the headspace quickly becomes very humid and saturated with moisture. When the humid headspace comes into contact with colder surfaces, such as the walls, condensation is produced and eventually accumulates at the bottom of the holds. The loss of moisture from the headspace air to condensation is replaced by further evaporation of water from the moist logs. A large amount of condensation could deposit in ship holds during a journey. The accumulated water from condensation may be capable of dissolving a significant amount of phosphine fumigant. The impact of this phenomenon is not known.

   As noted earlier, the fumigation rate may need to be adjusted depending upon the moisture content of the wood or wood product. Cytec (2009) recommend higher phosphine concentrations to counter the solubility of phosphine in water and in moisture present in the wood or wood product.

4. sorption

   Fumigant sorption can be caused by two processes − adsorption and absorption of the gas-phased fumigants by the treated commodity. Gas diffuses from higher concentrations (in the head-space) to lower ones, which is the driving force for both adsorption and absorption. However, most fumigant sorption is caused by adsorption, which can be reversed by aeration. Absorption cannot be reversed by aeration. Zhang (2004a) contended that forest products such as green logs (with or without bark on) and sawn/seasoned boards have enormous surface areas per unit weight so are likely to absorb and adsorb significant amounts of phosphine.

Annis & Dowsett (2001) studied the penetration of phosphine through *Pinus radiata* and hardwood (kwila) timber, using both seasoned (dry) and unseasoned (wet) blocks. They concluded that:

- a significant amount of gas was absorbed by the wood, both across and along the grain,
- phosphine penetrated along the wood grain of both seasoned and unseasoned hardwood and soft wood,
- gas did not penetrate across the grain of unseasoned *P. radiata* and penetration was negligible across the grain of seasoned hardwood and *P. radiata*.

This latter conclusion has implications for fumigation of wet logs harbouring wood-borne pests and needs to be further tested.

Zhang & Brash (2007) measured the effect of bark and soil contaminants on fresh logs on the rate of depletion of phosphine during a simulated in-transit fumigation trial. Phosphine was applied at 1.41 g/m^3 and after 48 h had declined to 500 ppm for the debarked logs and 250 ppm for both logs with clean bark and logs with soil-contaminated bark. The authors concluded that the presence of bark enhanced phosphine depletion. This could help explain variation in phosphine levels between shipments. Further study was recommended to define the effects of moisture content of the wood and bark, overall bark coverage on the logs and bark adsorption of phosphine on fumigant concentration profile during in-transit log fumigation.

5 Research to support phosphine protocol for logs to China

In 2002 Chinese quarantine authorities accepted the use of phosphine for in-transit fumigation of logs exported from New Zealand to China. The protocol requires maintenance of 200 ppm phosphine for 10 days during in transit fumigation. The challenge for the forestry sector from 2002 was to implement a suitable treatment regime to meet the protocol and verify its effectiveness through research and practical testing. The pioneering studies showed that the protocol could be achieved by applying 2 g/m^3 phosphine initially followed by a top-up of 1.5 g/m^3 phosphine after 5 days. For a number of reasons it has been difficult to gather the necessary information to verify the protocol quickly. Low numbers of quarantine pests on export logs, lack of funding, lack of knowledge of how to handle the forest pests outside the forest (for trials) and lack of fumigation research facilities have all hindered progress. The early experiments had some shortcomings but they have contributed to the knowledge, funding and facilities now available. This review acknowledges the pioneering progress made by all concerned.

In 2006 Crop & Food Research built a fumigation facility and purchased a gas chromatograph for phosphine measurement and calibration. Prior to this time it was difficult to control temperature and measure phosphine with confidence. Only in recent years has it been possible to collect and store large numbers of BPL and the bark beetles.

5.1 2002

Primaxa (2002) investigated the effect of moist wood (63.2% moisture content, from juvenile trees) on phosphine depletion. They compared phosphine concentration over time for an empty 100 L acrylic tank with one containing moist wood. An initial concentration of 800 ppm decreased to 500 ppm after 100 h in the empty tank while a starting concentration of 1000 ppm decreased to zero after 76 h when moist wood was included. The trial showed phosphine concentrations declined rapidly in the presence of wood. Phosphine concentrations were measured using a Uniphos 250 phosphine monitor. A range of arthropods (ants, beetles, slaters, etc.) were included in the experiment and all died. However, controls were inadequate for any indication of efficacy.

5.2 2003−04

A number of fumigation trials were carried out in this period to validate the phosphine protocol, ranging from direct exposure in the laboratory to fumigation of logs in experimental chambers.

Baker et al. (2003a,b) carried out two crude trials using infested billets of pine logs (200−300 mm diameter) in 230 L plastic barrels. In the first trial (Baker et al. 2003a) temperatures were not controlled and ranged from 8 to 53°C over the 10-day treatment period. Phosphine concentrations were measured daily using a Uniphos 250 phosphine monitor. Chambers were treated once, initially, with 0, 0.5, 1.0, 1.5, 2.0 g/m^3 phosphine as aluminium phosphide. There were 4 replicates of each treatment. BPL and GHBB comprised 95% of insects found following treatment. Estimates of mortality were 20% for controls and 80% for all treatments. In the second trial (Baker et al. 2003b) the methodology was the same as the earlier trial but with higher dose rates

(5, 5.5, 6, 7.5 g/m^3 of phosphine as aluminium phosphide) applied in 4 increments over 10 days. Temperatures fluctuated widely (17−41°C). The report provides daily phosphine levels. All insects in the controls were reported as alive and all treated insects were reported as dead. Control of fumigation conditions was very limited in these trials and there are serious questions as to their integrity, including phosphine measured in the control, phosphine concentrations poorly related to initial dose rate, and very poor log autopsy data. The results are considered unreliable.

Frontline Biosecurity carried out two trials in 2003 involving the exposure of naturally infested radiata pine logs within a custom designed fumigation chamber (Frontline Biosecurity 2003a). The cubic steel chamber had a volume of 3.4 m^3 with an inner frame that could hold up to 40 logs 1.2 m long and an average of 25 cm diameter. Fumigant concentration was monitored in the first trial without loss of fumigant using a Drager phosphine monitor.

The first trial involved exposing 13 naturally infested logs (170−295 mm diameter, 30−100% bark retention) for 10 days in a 200−300 ppm phosphine treatment regime maintained by periodic additions of aluminium phosphide. It took 9 h for the phosphine concentration to reach 200 ppm. Phosphine concentrations averaged 230 ppm over the exposure period (max. 389 ppm, min. 108 ppm). The trial involved a single treatment without a control (untreated) treatment. All logs were autopsied at the conclusion of the trial and no insects survived. There were 229 GHBB/BPBB larvae, 125 GHBB/BPBB pupae, 70 GHBB adults, 4 BPBB adults and 189 BPL larvae.

A second trial tested the recommended MAF protocol of 2 g/m^3 phosphine initially followed by a top-up of 1.5 g/m^3 phosphine after 5 days to achieve 200 ppm phosphine for 10 days. The data from the Drager monitor was considered suspect and not reported. All logs were autopsied at the conclusion of the trial and no insects survived. There were 188 GHBB/BPBB larvae, 14 GHBB/BPBB pupae, 44 GHBB adults, 15 BPBB adults and 6 BPL larvae. One BPL larvae was 60 mm deep in the wood. Four huhu egg rafts were found and all eggs were dead. The result showed the effectiveness of the MAF treatment protocol.

Direct insect exposure trials were carried out by Zhang (2003) using BPBB adults and larvae and BPL eggs. Two trials were carried out in sealed 92 L chambers and the temperature was described as ‘no less than 16°C’. Insect numbers were low. The report is unclear on method of phosphine delivery and measurement. It says that ‘specific concentrations of phosphine were fed into the containers using a pressurised applicator for specific periods of time’. This implies that a handgun was used to deliver cylinderised phosphine gas, most likely ECO_2FUME. Zhang (2003) reports that phosphine concentrations declined by no more than 10% during the treatment but the method and actual concentrations are not reported.

Results are shown in Table 1. Run 1 for BPBB larvae was not reported because all untreated control larvae died of dehydration or starvation. In the second run the larvae were placed in small pine chips and survived well.

Table 1: Mortality (%) of BPBB and BPL life stages after 10 days' exposure to phosphine. Mortality assessments were made 24 h after fumigation, except for egg hatch which was assessed for 2 weeks after fumigation.

Run	Species & life stage (number) BPBB	Nominal PH_3 concentration (ppm)	Replicates	Mean mortality (%)
One	Adults (10/rep)	0	3	13
		200	4	100
		700	4	100
		2000	4	100
Two	Adults (10/rep)	0	3	25
		200	4	100
		700	4	100
		2000	4	100
Two	Larvae (10/rep)	0	3	12
		200	4	100
		700	4	100
		2000	4	100
One	BPL Eggs (35)	0	3	74*
	(42)	200	4	100
	(37)	700	4	100
	(39)	2000	4	100

*That is, 26% hatch rate (9/35) and none hatched in the other treatments.

Zhang (2003) also reported that a 24-h exposure of BPL adults to 200 and 2000 ppm phosphine gave 100% control. The trial involved 10 adults per rep and 4 replicates and the control treatment had 27% mortality.

Zhang undertook a further study using greater numbers of BPL eggs and comparing lower phosphine concentrations (down to 100 ppm phosphine) and shorter exposure periods (Zhang 2004b). The study was carried out using 1 L glass jars at 15−18°C. As in the earlier report, there are few details on methods of phosphine delivery and monitoring. There was no indication that phosphine levels were monitored during the trial. Results are shown in Table 2 and indicate BPL eggs can be controlled in 5 days at 200 ppm phosphine and in 10 days at 100 and 200 ppm phosphine.

Table 2: Effect of phosphine concentration and exposure duration on BPL egg mortality (100% – hatch rate).

Nominal PH3 concentration (ppm)	Exposure time (days)	Replicates	Eggs per rep	Mean mortality (%)
0	5	4	96-104	35
100	5	4	96-108	72
200	5	4	96-100	100
0	10	4	96-107	4
100	10	4	96-100	100
200	10	4	94-102	100

Zhang et al. (2004) summarised the data in Zhang (2003) and Zhang (2004b) with the addition of some statistics (SEMs for control treatments).The paper also reports BPL adult data as a 10-day treatment when Zhang (2003) reports the same data as a 24-h treatment (see above). This adds concern to the quality of the data.

5.3 2005

Hosking & Goss (2005) simulated in-hold fumigation in two sealed 2 m^3 chambers. In a trial similar to an earlier study (Frontline Biosecurity 2003a) they compared two phosphine treatments − the current protocol of 2.0 g phosphine/m^3 as aluminium phosphide with a top up of 1.5 g phosphine/m^3 on day 5 and a single application of 4 g phosphine/m^3. There was no control treatment. The aim was to find out whether phosphine concentrations could be maintained over 200 ppm for 10 days in both treatments and to check efficacy on infested logs.

Both trials used an exposure period of 10 days with ventilation of the chambers on day 11. The chambers were not opened until day 18 to simulate what would occur with a shipment to China. Three insect-infested logs (2 x 1.2 m, and 1 x 600 mm) were included in each treatment. The balance of the 30 logs in each chamber were freshly harvested and typical of logs being shipped. Phosphine concentration was measured daily (although the name of the monitoring device is not recorded). There is no record of temperature during treatment. Infested logs were autopsied on day 19.

Neither treatment maintained phosphine concentrations over 200 ppm for 10 days. The chamber for the conventional top-up treatment may have had a leak as concentrations declined rapidly after the initial charge. The top up restored the concentration to 800 ppm, declining to about 200 ppm by day 10. The single charge treatment generated high initial phosphine concentration decreasing to about 200 ppm by day 4 and remained at 70 to 100 ppm through to day 10. The average phosphine concentration for the conventional top-up treatment over the 10 days was 208 ppm (max 815 ppm, min 58 ppm) and for the single charge treatment the average concentration was 235 ppm (max 1708 ppm min 34 ppm).

The insect-infested logs contained a good representation of risk insects, including adults, pupae and larvae of GHBB and BPBB and larvae of BPL. Huhu eggs were also found. No live individuals were found in either treatment.

Zhang & van Epenhuijsen (2005) carried out two trials. One examined a range of 10-day phosphine treatments to control two quarantine pests, huhu (eggs only) and New Zealand drywood termite (nymphs only), that had not been looked at in detail previously. The other trial examined the threshold phosphine concentration for control of BPL eggs over 10 days. Experiments were carried out using direct exposure of the insects in sealed 1 L jars. As in the earlier report, there are few details on methods of phosphine delivery and on the monitoring method. There was no indication that phosphine levels and temperature were monitored over the period of the trial. The termite treatments included a high concentration (1200 ppm) for 2 days followed by a lower concentration (200 ppm) for 8 days to more closely simulate actual conditions in a ship's hold fumigation where initial phosphine concentrations are high but rapidly taper off after 2 or 3 days. This treatment gave 100% mortality, as did exposure to 200 ppm phosphine fumigation for 10 days. BPL eggs exposed to phosphine concentrations below 200 ppm (50, 100 and 150 ppm) for 10 days continued to hatch. Results are shown in Table 3. The authors did not report huhu egg hatch in detail but did report no emergence from phosphine treatments and 30−40% emergence in control treatment.

Table 3: Drywood termite nymph and BPL egg mortality (%) after phosphine treatment. (Egg mortality is 100% - hatch%).

Species & life stage	Nominal PH_3 concentration (ppm)	Exposure time (days)	Replicates	Insects per rep	Mean mortality (%)
Termite nymphs	0	10	4	29-38	10.2
	50	10	4	15-47	76.8
	100	10	4	27-54	98.5
	200	10	4	25-41	100
	1200-200	2+8	4	23-33	100
BPL eggs	0	10	4	50-100*	40.8
	50	5	4	50-100*	39.1
	50	10	4	50-100*	53.8
	150	5	4	50-100*	88.7
	150	10	4	50-100*	96

* Actual number not given.

5.4 2006−07

In 2006 Crop & Food Research built a fumigation facility and purchased a gas chromatograph. Cytec Australia Ltd funded the only trials carried out in this period, with the main focus on developing a single application phosphine protocol (i.e. no top-up) that was suited to delivery from a cylinderised supply (ECO_2FUME or $VAPORPH_3OS$).

Zhang et al. (2006) used ECO_2FUME to test three 72-h phosphine regimes. The treatments were:

1. Control (no phosphine),
2. 2 g phosphine/m^3 applied initially,
3. 2 g phosphine/m^3 applied initially, followed by 1 g phosphine/m^3 after 24 h,
4. 3 g phosphine/m^3 applied initially.

The trial was conducted in 92 L stainless steel fumigation chambers that were placed in a temperature-controlled environment for fumigation (the actual temperatures were not given but are presumed to be 15−20°C). To simulate in-hold fumigation chambers had 50% loading with fresh logs (58% moisture content). The trial included BPL adults and eggs, BPBB larvae (although likely to be a GHBB/BPBB mix), huhu larvae and drywood termite nymphs and adults. Phosphine, oxygen and carbon dioxide concentrations were monitored during treatment. Changes in phosphine concentration are shown in Figure 1. The top-up treatment was the only one that maintained phosphine concentrations over 500 ppm for the 72 h. Carbon dioxide concentrations rose to 5−9% (aided by the CO_2 from ECO2FUME) and oxygen concentrations dropped from 20% to 13−16% over the treatment period.

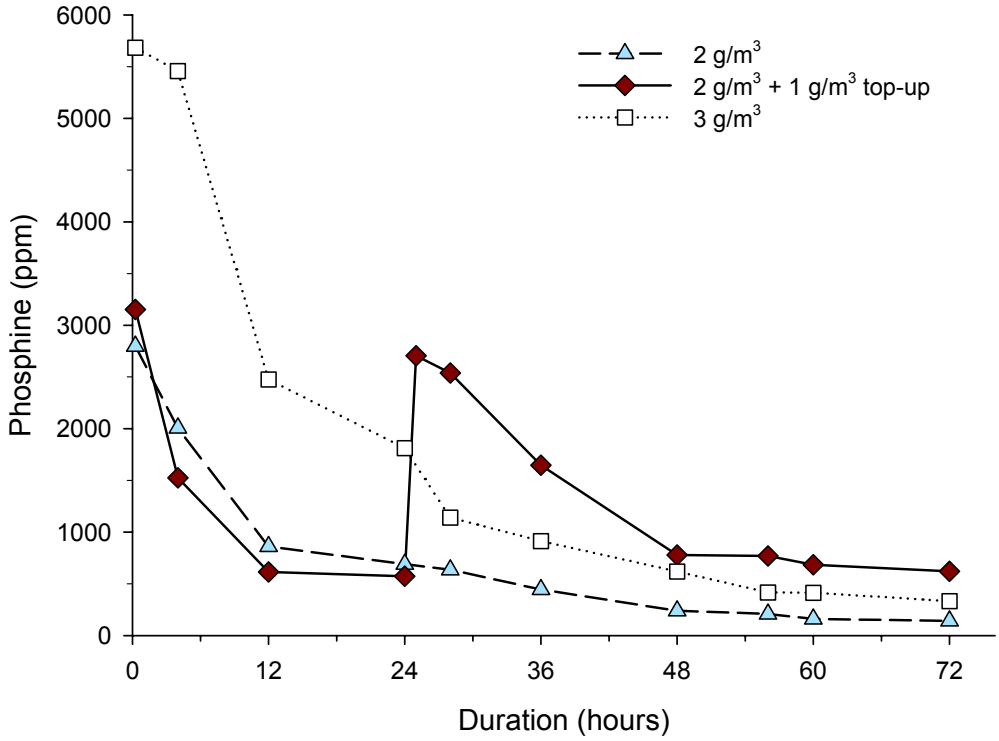

Figure 1: Phosphine concentration profiles for three fumigation treatments.

Table 4 shows that the three 72-h phosphine treatments controlled BPL adults and huhu larvae, but not BPL eggs nor BPBB larvae. Mortality in the control (untreated) treatments varied and was often too high, e.g. 70% for BPL adult. It is worth noting that the only insect with low mortality in the control treatment was BPBB larvae, which were collected locally and treated quickly after collection.

Table 4: Effect of three 72-h phosphine treatments on mortality of BPL adults and eggs, BPBB larvae and huhu larvae (means of three replicates).

Species & life stage	PH_3 treatment (g)	Insects per rep	Mortality (%)	95% confidence interval
BPL adults	0	20	70	(9,98)
	2	20	100	(94,100)
	2 + 1	20	100	(94,100)
	3	20	100	(94,100)
BPL eggs*	0	83-135	56	(32,78)
	2	134-175	85	(66,96)
	2 + 1	113-191	93	(71,98)
	3	132-179	94	(73,99)
BPBB larvae	0	17-18	15	(7,28)
	2	16-18	73	(40,92)
	2 + 1	13-18	63	(33,88)
	3	16-18	81	(66,95)
Huhu larvae	0	14	40	(18,68)
	2	14-15	100	(92,100)
	2 + 1	13-14	100	(91,100)
	3	7-14	100	(90,100)

*We measured larval emergence from eggs (Mortality% = 100 - Egg hatch%)

Zhang et al. (2007) followed up the earlier study by examining use of higher rates of phosphine (3−4 g/m^3) and longer durations (72−120 h). ECO2FUME was applied in three combinations: 3 g phosphine/m^3 for 120 h, 3.5 g phosphine/m^3 for 96 h and 4 g phosphine/m^3 for 72 h. GHBB/BPBB larvae and eggs and BPL eggs were treated. The trial was carried out in a similar way to Zhang et al. (2006). Temperature was maintained at 15°C. Logs were placed in the fumigation chamber and had higher moisture contents than in the previous year (84−158%). Phosphine concentrations are summarised in Figure 2.

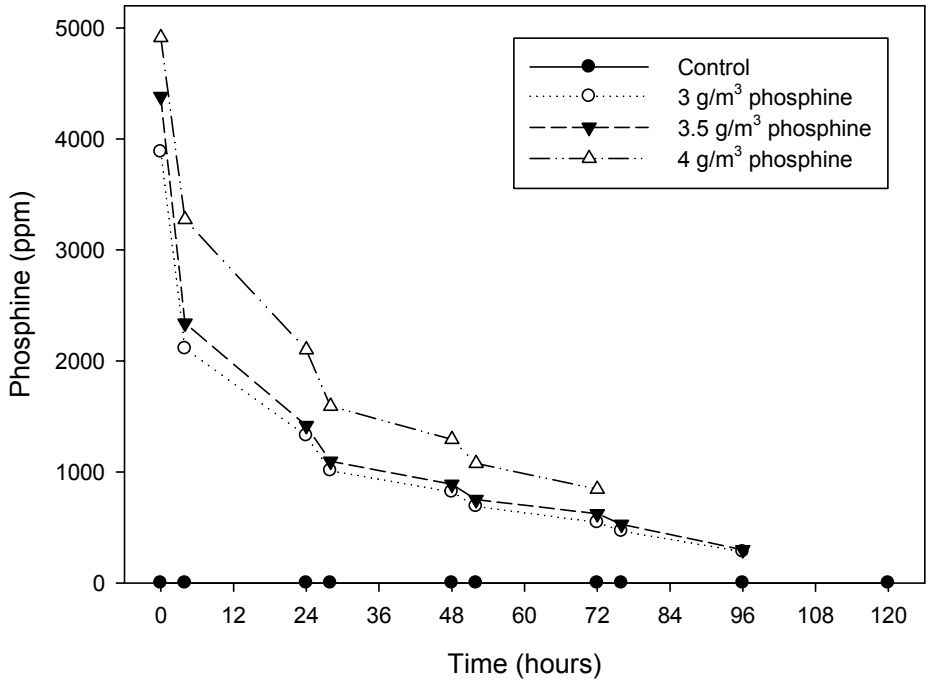

Figure 2: Phosphine concentration profiles for three fumigation treatments.

Results are shown in Table 5. There were no differences between fumigation treatments. There were some GHBB/BPBB larvae classified as moribund during assessment (greatest numbers occurred on the shortest treatment). All treatments gave 100% control of BPL eggs and GHBB/BPBB larvae if it is assumed that moribund larvae were going to die.

Table 5: Effect of three 3−5-day phosphine treatments on mortality of BPL eggs and GHBB/BPBB larvae (means of four replicates).

Species & life stage	PH_3 treatment (g)	Duration (days)	Insects per rep	Live (%)	Moribund (%)	Dead (%)	95% confidence interval for % dead
BPL eggs*	0	120	200-300	62		38	(38,52)
	3	120	200-300	0		100	(91,100)
	3.5	96	200-300	0		100	(90,100)
	4	72	200-300	0		100	(92,100)
GHBB/BPBB larvae	0	120	22-31	77	0	23	(14,35)
	3	120	22-31	0	11	89	(80,95)
	3.5	96	22-31	0	2	98	(99,>99)
	4	72	22-31	0	32	68	(57,78)

*Measured larval emergence from eggs (Live% = % emergence from eggs).

5.5 2008

In 2008 FIDA (Forest Industry Development Agenda) supported research aimed at better definition of phosphine requirement in direct exposure trials (i.e. no logs present) at 15°C. BPL eggs and GHBB/BPBB larvae were treated, although GHBB/BPBB larvae numbers were very low because of the dry season. There were 11 treatments (3−7 days duration and 0−3200 ppm phosphine) and four replications of each treatment. Treatments were carried out in 1 L sealed chambers.

Table 6 shows the mean phosphine concentrations for each treatment and summarises efficacy data. Phosphine concentrations were more variable than expected because of phosphine sorption from the bark/cambium mix used to hold GHBB/BPBB larvae in the small chambers. GHBB/BPBB larvae were difficult to find in the mix as well. Table 6 reports actual larvae found rather than the number introduced (which was 10/rep).

Table 6: Effect of phosphine treatment on BPL egg hatch and mortality of GHBB/BPBB larvae (means of four reps).

			BPL eggs			GHBB/BPBB larvae		
Treatment	Duration (days)	Phosphine (mean ppm)	No./rep	Hatch (%)	95% conf. interval	No./rep	Mortality (%)	95% conf. interval
1	3	0	113-225	86	(80,91)	4-8	63	(42,80)
2	3	670	110-210	<1	(0,4)	3-6	95	(71,99)
3	3	1800	98-232	<1	(0,7)	4-8	100	(85,100)
4	3	3180	98-223	0	(0,2)	4-10	100	(89,100)
5	5	0	107-227	74	(67,81)	7	57	(38,74)
6	5	260	102-224	0	(0,2)	5-10	100	(89,100)
7	5	580	98-217	<1	(0,10)	7-9	100	(85,100)
8	5	1820	95-222	0	(0,2)	5-6	100	(85,100)
9	7	0	99-214	53	(45,61)	5-9	76	(55,89)
10	7	260	100-253	0	(0,2)	4-8	96	(74,99)
11	7	540	97-207	0	(0,4)	5-8	100	(87,100)

BPL eggs exposed to a mean concentration of 3200 ppm for 3 days and a mean concentration of 1820ppm for 5 days gave 100% mortality. For GHBB/BPBB larvae this was achieved at 1800 ppm for 3 days and 260 ppm for 5 days (although these results are less reliable because of low numbers of larvae available).

5.6 Phosphine for log treatment

The research carried out to date supports the efficacy of the 10-day x 200 ppm protocol for bark-borne quarantine pests. A top-up after 5 days is required to maintain phosphine concentrations for the 10 days.

There is insufficient evidence to support a treatment protocol shorter than 10 days although the experimental work strongly suggests durations as short as 5 days are possible. It is likely that a shorter treatment protocol will still involve a top-up of phosphine.

Recommendations for future work are:

Carry out studies on infested logs. Trials on infested logs provide 'real world' information for quarantine authorities and should enable data to be collected on all life stages of quarantine importance. The presence of logs will ensure the pattern of phosphine depletion matches industry experience and that laboratory information is directly applicable. There may still be a problem in determining phosphine efficacy for BPL as the incidence of this insect is low. In this situation, trial work should still include logs artificially infested with BPL.

2. **Ensure that fresh insects are available in sufficient numbers.** Another way to ensure accurate information is delivered to quarantine authorities is to ensure that trials are carried out with large numbers of freshly collected and properly stored and handled insects. Information on the best methods to collect, store and transport various life stages of insects for trials is required.

3. **Use shorter protocols.** To develop a shorter treatment protocol, infested logs should be used and treated at, say, 3 phosphine thresholds (including 200 ppm) over 3−10 days.

4. **Improve the safety of phosphine delivery.** The current manual method of top-up is hazardous for the MOB (man on board). Cost-effective and reliable alternatives to manual top-up are required and should not be difficult to devise.

5. **Define factors affecting phosphine depletion.** Research is required to better understand the effect of moisture content of the wood and bark, overall bark coverage on the logs and bark adsorption of phosphine on phosphine depletion.

6. **Decide on criteria for moribund insect evaluation.** It is important to take the uncertainty out of live/dead assessment. Periodic assessment of % live, moribund and dead after fumigation is required to determine the best method of assessing % mortality, e.g. assess BPL beetles 24 and 48 h after treatment (see Wimalaratne et. al, 2009).

6 In-hold monitoring of phosphine fumigation on log ships

Maintaining phosphine concentration in ships' holds during in-transit fumigation is critical to meeting the required standard of 200 ppm for 10 days. Data is available for eight individual vessels − Pacific Logger, Ocean X, Cleo Pacific, Mt Travers, Ken Ryu, Misola Shiner, Northern Light and Kiwi Trader. Of these vessels, full reports are available on Mt Travers, Ken Ryu, Misola Shiner and Kiwi Trader.

6.1 Ken Ryu (2002)

This comprehensive trial (Genera 2002) used the standard fumigation treatment for in-hold fumigation of logs to China, although the actual amount used is not stated. One hold was monitored in three positions (top, middle and bottom). Phosphine levels never fell below 300 ppm at any monitoring point during the 10-day monitoring period. External temperatures were 20−31°C during the treatment period.

6.2 Mt Travers (2003)

The trial aimed to monitor phosphine depletion rates over 10 days using different application strategies in different holds (Frontline Biosecurity 2003b). Although hold access was difficult and the voyage rough, 3 holds were monitored at three levels (top, middle, bottom) for 10 days and sea and hold temperatures recorded.

Table 7: Effect of fumigation treatment on phosphine concentration in the holds on board Mt Travers.

Hold no.	Treatment (g/mg^3)	Phosphine concentration day 2 (ppm)	Phosphine concentration day 10 (ppm)
1	2	900	100
2	2 g + 1.5	900	350
3	1.5 g + 1.5	1150	250

Second applications were made on day 5. Phosphine concentrations were very similar at the top, middle and bottom of holds. Hold temperatures reached 33°C and were about 7ºC higher than sea temperatures for much of the voyage.

6.3 Misola Shiner (2005)

Monitoring was undertaken of two treatments – one hold was allocated the current practice for logs to China of 2 g/m^3 with a top up after 5 days of 1.5 g/m^3 and in another hold a single application of 2 g/m^3 was applied (Frontline Biosecurity 2005). The two holds were monitored at least daily for phosphine concentration and oxygen concentration. Temperatures were in the 12−28°C range for the 10 days. The hold receiving current practice fell to just over 200 ppm on day 6 and ended on 300 ppm on day 10, meeting the 200 ppm for 10 days requirement. The hold receiving a single application of aluminium phosphide declined to 200 ppm on day 7 and recorded 50 ppm on day 10. Oxygen concentrations in both holds declined steeply to reach near zero by day 7.

6.4 Kiwi Trader (2007)

Genera (2007) undertook a comprehensive monitoring of phosphine in two holds. Results from both holds showed the standard phosphine protocol maintained phosphine concentrations over 200 ppm for 10 days. Phosphine was applied as pellets and blankets of aluminium phosphide. In-hold temperature ranged from 15 to 37°C and oxygen concentrations were 1% after 7 days. Phosphine distributed evenly within a hold even when applied at one location.

6.5 In-hold phosphine fumigation

The ship monitoring shows that the 10-day protocol is being achieved in practice with the current treatment protocol. Single fumigant dose application did not meet the 10-day x 200 ppm phosphine protocol. It may be possible to explain some of the variation in phosphine concentration between holds and between shipments if more was known about the influences of moisture content of the wood and bark, overall bark coverage on the logs and bark adsorption of phosphine on phosphine depletion.

7 Fumigation of sawn timber

The introduction of the phosphine protocol for logs destined for China was the primary impetus for the evaluation of phosphine for control of quarantine pests on forestry exports. At the same time, forest exporters and fumigators soon realised that phosphine may also have a role in the control of 'hitchhiker' pests on packets of sawn timber destined for export, particularly to Australia where MB treatment is mandatory. The continued use of MB for treating sawn timber at Nelson port has been a major public health concern in recent years.

The sole focus for fumigation of sawn timber is on control of BPL adults, which are attracted to sawn timber packets at mills and ports. This section of the report summarises experimental studies aimed at control of BPL adults using phosphine.

7.1 2003−04

Zhang (2003) reported 100% mortality of BPL beetles after exposure to 200 and 2000 ppm phosphine for 24 h. The trial involved 10 adults per rep and 4 replicates and the control treatment had 27% mortality. For details on experimental methods see Section 5.2.

Zhang (2004b) tested 100 and 200 ppm for 12 h and 200 ppm for 24 h in two trials. He reported about 15% survivors from the 12-h treatments (18−23 BPL adults per rep, 4 reps). He also reported 98% BPL beetle mortality for the 200 ppm/24-h treatment (12−13 adults per rep, 4 reps). However, the assessment assumed moribund beetles were dead when they should be considered live. Mortality was 88% when moribund insects were considered as live. All treatments were conducted at 15−18°C.

7.2 2005−08

Results from the laboratory trials provided baseline data and encouraged two operational-scale trials in 2005, one in 2007 and one in 2008. Cytec Australia Ltd supported three of the trials.

Hosking (2005) twice tested a UPL phosphine generator on 54 packets of dried, dressed timber with each packet wrapped in plastic but open on the bottom. The whole stack (220 m^3) was covered with a tarpaulin and sealed using water snake seal on to a concrete floor. In this configuration the loading % is very high, which leads to high initial fumigant concentrations. BPL adults were held in gauze-covered holes drilled into 100 x50 mm timber placed amongst the stack. Some infested timber was kept alongside the fumigated stack as an untreated control. Phosphine concentrations were measured at four locations in the stack (monitoring device not recorded). Phosphine took 1 h to be delivered (reaching 330 ppm) and the treatment continued for a further 16 h (80 ppm at the end). Phosphine concentrations were consistent between sampling sites. Temperatures were a minimum of 15°C and maximum of 28°C. There were some survivors from the treatment (3/101) compared to 81% survival for the controls (34/42).

A second trial tested a 24-h treatment period. At the start of the treatment period phosphine concentrations were 352 ppm and declined in a similar way to the first trial (52 ppm after 24 h). Temperatures were not recorded but are likely to be as warm or warmer than the earlier trial (the trials were run one week apart in February). There were no BPL adult survivors (0/40) 24 h after phosphine treatment and high survival in the control treatment (18/20).

Tumambing (2005) used shipping containers and tarped timber stacks to test 16 h (three containers and two stacks) and 24-h (one container) phosphine treatments for control of BPL beetles. He applied ECO_2FUME (2% phosphine in CO_2) at a dose rate of 2 g phosphine/m^3. Phosphine concentrations started at 1600 ppm and declined to 100−200 ppm over 16 h for the shipping containers and from 2400 and 3400 ppm to 700 and 500 ppm, respectively, for the two tarped stacks. All treated insects died but insect numbers were very low (3−5 BPL beetles per run for treated and control containers). The experiment was carried out outside in December. The minimum temperature was 18−19°C but no maximum temperatures were recorded.

Tumambing (2007) carried out further testing of ECO_2FUME under cover in April 2007. Phosphine was applied at 0.28 g phosphine/m^3 to three sealed timber packets for 12 h. There was another timber packet as untreated control. Each timber packet had 24−25 BPL adults placed in gauze-covered holes in lengths of timber. Temperatures were 16−18°C during the treatment. Initial phosphine concentrations were 500−800 ppm (depending on void volume in each stack) and declined to about 300 ppm phosphine at the end of the 12-h treatment. Although high initial mortality was reported (100, 100 and 92% for the three stacks in assessments carried out after 3 h), mortality was 67−88% after 24 h and 79−96% after 48 h. Mortality in the untreated control timber packet was 0% after 3 h, rising to 48 and 76% after 24 and 48 h. BPL beetles had been collected 1 week before the experiment and stored in a refrigerator. The 12 h phosphine treatment tested was ineffective as most mortality could be attributed to natural mortality.

In January 2008 nine timber stacks were sealed under tarpaulin. Three were treated with ECO_2FUME for 16 h, three with $VAPORPH_3OS$ (99.3% phosphine) for 24 h and three were untreated controls (Hosking & Burridge 2008). Thirty BPL adults were placed in each timber stack. An initial phosphine dose of between 1.5 and 1.9 g/m^3 was applied. Phosphine concentrations were over 3500 ppm at the start of fumigation, dropping rapidly to 800 ppm within 4 h, then decreasing slowly to 350−550 ppm by the end of the treatment. The temperatures were between 20 and 30°C throughout the trial. Mortality of 100% of the treated retrieved beetles was achieved compared to 12% mortality in the controls (assessed 12 and 24 h after completion of treatment).

Although not part of this review, we know from very recent work (Wimalaratne et al. 2009) that 24-h treatments are not long enough to control BPL beetles at 10 and 15°C.

7.3 Phosphine for sawn timber

The trials show that a 16−24-h phosphine protocol works well at high temperatures, e.g. at 20−30°C (Hosking & Burridge 2008). The optimum treatment has yet to be ascertained, particularly at the lower temperatures that may be encountered at the start and end of the season.

We recommend assessment of % live, moribund and dead BPL beetles 24 and 48 h after treatment (see Wimalaratne et al. 2009).

Phosphine treatments longer than 24 h should be tested for control of BPL beetles to enable an effective treatment to be developed for the range of temperatures experienced during the BPL flight periods. We also recommend a thorough review of all control options. Wimalaratne et al. (2009) gives some options.

Two research recommendations from Section 5.6 are also applicable for sawn timber studies:

- the need for sufficient numbers of fresh insects for trials (Recommendation 2)
- knowledge of factors affecting phosphine depletion for sawn timber (Recommendation 5).

8 Conclusions

The research carried out to date and ship-board monitoring supports the efficacy of the 10-day x 200 ppm protocol for bark-borne quarantine pests. A top-up after 5 days is required to maintain phosphine concentrations for the 10 days.

There is insufficient evidence to support a treatment protocol shorter than 10 days, although the experimental work strongly suggests durations as short as 5 days are possible. It is likely that a shorter treatment protocol will still involve a top-up of phosphine.

For sawn timber, the trials show that a 16−24-h phosphine protocol works well at high temperatures, e.g. at 20−30°C. The optimum treatment has yet to be ascertained, particularly at the lower temperatures that may be encountered at the start and end of the season.

9 Recommendations

Recommendations for future work on logs and sawn timber are:

1. Carry out studies on infested logs. Trials on infested logs provide 'real world' information for quarantine authorities and should enable data to be collected on all life stages of quarantine importance. The presence of logs will ensure the pattern of phosphine depletion matches industry experience and that laboratory information is directly applicable. There may still be a problem in determining phosphine efficacy for BPL as the incidence of this insect is low. In this situation, trial work should still include logs artificially infested with BPL.

2. **Ensure that fresh insects are available in sufficient numbers.** Another way to ensure accurate information is delivered to quarantine authorities is to ensure that trials are carried out with large numbers of freshly collected and properly stored and handled insects. Information on the best methods to collect, store and transport various life stages of insects for trials is required.

3. **Use shorter protocols.** To develop a shorter treatment protocol, infested logs should be used and treated at, say, 3 phosphine thresholds (including 200 ppm) over 3−10 days.

4. **Improve the safety of phosphine delivery.** The current manual method of top-up is hazardous for the MOB (man on board). Cost-effective and reliable alternatives to manual top-up are required and should not be difficult to devise.

5. **Review options for phosphine control of BPL beetle hitchhikers on sawn timber prior to shipment.** Phosphine treatments longer than 24 h should be tested for control of BPL beetles to enable an effective treatment to be developed for the range of temperatures experienced during the BPL flight periods.

6. **Define factors affecting phosphine depletion.** Research is required to better understand the effect of moisture content of the wood and bark, overall bark coverage on the logs and bark adsorption of phosphine on phosphine depletion.

7. **Decide on criteria for moribund insect evaluation.** It is important to take the uncertainty out of live/dead assessment. Periodic assessment of % live, moribund and dead after fumigation is required to determine the best method of assessing % mortality, e.g. assess BPL beetles 24 and 48 h after treatment.

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