PENETRATION OF METHYL BROMIDE INTO *PINUS RADIATA* WOOD AND ITS SIGNIFICANCE FOR EXPORT QUARANTINE

DAVID J. CROSS

New Zealand Forest Research Institute,
Private Bag 3020, Rotorua, New Zealand

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ABSTRACT

The data obtained from studies of penetration of methyl bromide gas into "green" and dry *Pinus radiata* D.Don sapwood were used to calculate the likely minimum "concentration : time" products at various depths into the wood. By largely graphical methods it was demonstrated that there is a curvilinear gradient into green timber and a linear one into dry wood. In the former, this gradient is such that it is not practical to achieve useful insecticidal doses much beyond a depth of 100 mm in green material using conventional tent fumigation techniques.

Keywords: methyl bromide; logs; radial penetration; *Pinus radiata*.

INTRODUCTION

Because of its geographical isolation, New Zealand has enjoyed freedom from a number of pests and diseases prevalent in the countries of its trading partners. Forestry is no exception but, as with the other land-based industries, this advantage has been bought at the cost of constant quarantine surveillance. This has been applied to exported produce as well as imports, since it has long been recognised that New Zealand's competitiveness depends on an acceptable standard of product presentation.

With forest products, one of the main tools for controlling pests, apart from vigilance, has been fumigation, almost exclusively with methyl bromide. In New Zealand, W.M.Barber was responsible in 1959 for carrying out the first practical trials with methyl bromide fumigation (New Zealand Forest Service unpubl. data), which set the official requirement at 5lb/1000 ft^3 (80 g/m^3) for 24 hours. This is still the regulation treatment in New Zealand.

Although this level of treatment was based on considerable over-kill conditions (single concentration experiments in which all insect infestation was satisfactorily exterminated), the interpretation of the requirements led to questionable results on many occasions. That interpretation consisted of loading the appropriate amount of gas for the volume involved,

and then leaving the stack unmonitored for the regulation 24-hour period. With tent fumigation being by far the commonest fumigation technique used, any fault in the sheeting or in the siting of the stack, along with unexpected deterioration in the weather, could result in severe under-dosing.

For this reason a system of fumigation monitoring, based on work by Heseltine & Royce (1960), was introduced in the early 1980s (Cross unpubl. data) where gas permeable plastic sachets, containing an absorbent for methyl bromide in one compartment and a reagent in another, were included within the target timber/log stack. The two-part contents of these sachets produce a distinctive colour upon mixing if the sachet has been exposed to a pre-selected minimum methyl bromide dosage, i.e., they give an immediate indication of the integrated product of concentration upon time, usually referred to as the "c : t product", for that fumigation (*see* Appendices 1 and 2). The effectiveness of the fumigation treatment against any specific insect or insect stage can therefore be judged from a knowledge of the c : t product known to kill that insect or insect stage.

In this study the same gas-absorption system, on a micro-scale, was used to determine the limits for effective methyl bromide penetration into green and dry timber of *P. radiata*.

METHODS

Determination of Methyl Bromide

The sachet method of methyl bromide determination is based on the absorption of that gas by an aqueous solution of ethanolamine (50:50 v/v), encapsulated in a packet made of permeable polyethylene film. After exposure, the contents are titrated against a silver nitrate (N/10) and ammonium thiocyanate aqueous solution acidified with nitric acid and including ferric ammonium sulphate as an indicator (Heseltine & Royce 1960).

The titration results (in terms of millilitres of silver nitrate) can be used to calculate the "accumulated" c : t product achieved after an elapsed time. Very small volumes of absorbent can be used if suitably thin plastic film is employed for the containment, making it possible to collect the methyl bromide molecules diffusing into very small void volumes of a size comparable to those immediately around insect larvae within wood. With suitable calibration a direct and accurate measure of c : t product can thus be made for such voids, without the sampling-induced errors from the use of instruments, such as chromatographs. However, it is inevitable that trapping gas as it arrives in such a small volume will still tend to scavenge the gas from the surrounding wood, giving rise, in some degree, to a concentration gradient. It was known from experience with the full-size sachet systems that only very small quantities of methyl bromide actually penetrate the plastic membrane to achieve the chemical reactions necessary for the titration.

The plastic film used for the micro-sachets was one-third the thickness of that for the larger form, and it was therefore assumed that this "scavenging factor" would be negligible, particularly through large thicknesses of timber where the long diffusion path would not be significantly influenced by such gas stripping. This was the location that held the greatest interest from the point of view of eradicating insects, being the "worst case" scenario for tent fumigation.

Test Blocks

A 6-mm-diameter disc of glass-fibre "paper" (Whatmans GF/B glass microfibre), impregnated with 20 µl of ethanolamine solution, was sealed into a 10 × 10-mm sachet formed of 10-µ-thick polyethylene film (domestic "Gladwrap").

The test blocks used for the trials were discs roughly 100 mm thick cut from *P.radiata* logs (for green tests) or posts (for dry tests), selected for freedom from knots and other defects, and of a diameter suited to the required block (Fig. 1). These were then cut longitudinally into quarters (or less) using a band saw, and the cut surfaces were smoothed off with a planer. Freshly felled trees were used for log material and the bark was left in place. These wedge-shaped pieces were then cut tangentially to give the required thickness from the original outer surface of the log, again smoothing the cut face.

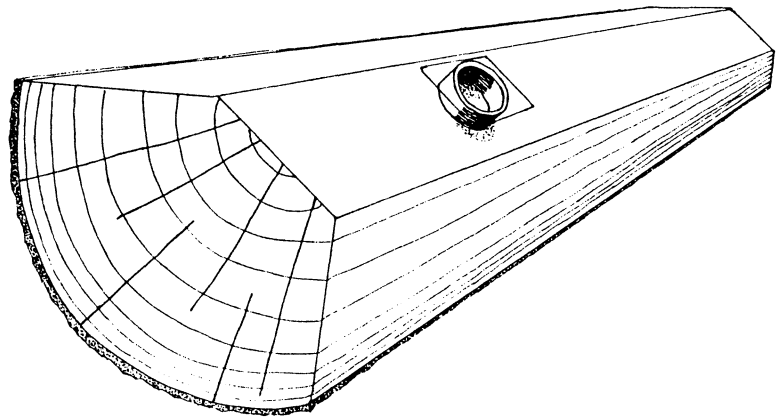

FIG. 1–Test block before sealing

For use in the fumigation trials, all the cut surfaces of the blocks were sealed by coating them first with builders' mastic compound ("Sealflex", butyl sealant compound), and then immediately covering them with aluminium foil to form a complete, impervious seal. Mastic had proved in preliminary studies to be the only readily available material that would adhere to green timber, and that had negligible adsorptive properties (D.J.Cross unpubl. data).

The tangential face was also sealed, but a 10-mm-diameter patch in its centre was left uncovered. Over this hole was glued a glass ring, 13 mm inner diameter by 3 mm deep, into which an absorptive sachet was placed; a microscope cover slip was glued (with mastic compound) on top of the glass ring to form a closed chamber (Fig. 1).

By using this form of block it was assumed that gas penetration would closely parallel natural conditions as they might be at the mid-point of a log, for the longitudinal component of gas penetration could be ignored because of the surface sealing.

Calibration Blocks

The calibration blocks were made up along similar lines—these were veneer blocks of 5 mm thickness, cut from the same material as the test blocks. The purpose of these blocks

was to relate the titration results from the test blocks to similar titrations carried out using wood containing a known gas concentration within its substance, thereby enabling computation of the actual void c : t products that had resulted from the various fumigations.

These thin blocks (sealed on one side but for an absorption chamber as above) were exposed to known controlled concentrations of methyl bromide for 12 hours. At the end of this period they were evenly diffused with the gas, whereupon the uncovered surface was quickly foil-sealed and a micro-sachet was placed within the absorption chamber. After 24 hours' exposure, titration with the silver nitrate solution was carried out.

Fumigation

Both test and calibration blocks were exposed (one or two at a time) in a 10-litre capacity fumigation chamber equipped with a circulating fan, with provision for introducing and dispersing measured amounts of the fumigant as a liquid. All fumigations and related calibrations were carried out at room temperature (c.20° to 25°C).

All the green blocks (20, 40, and 100 mm thick) were exposed to a gas concentration of 260 mg/*l* for either 12 or 24 hours, while the dry blocks (80 mm thick) were subjected to 160 mg/*l* for 6 hours.

Two sets of 20-mm and 40-mm and one set of 100-mm blocks were placed in the fumigation chamber in pairs, complete with absorption sachets, and the 20- and 40-mm blocks were removed together after 12 and 24 hours' exposure. The 100-mm blocks were given only 24 hours' exposure. Exposed blocks immediately had their sachets replaced with fresh ones, with careful resealing of the absorption chamber, a process repeated at intervals.

RESULTS

The results of titrations have been expressed as millilitres of silver nitrate, corrected to a standard time interval (24 hours) in order to make comparison with uptakes from the calibration blocks (Fig.2).

The data showed that:

(1) Amounts of methyl bromide reaching the absorbent per unit of time decreased rapidly with increasing penetration distance;

(2) The amount that did diffuse through was delayed in proportion to the thickness of wood;

(3) Fumigant continued to arrive even after the blocks were removed from the chamber (for more than a week in the 100-mm blocks);

(4) Timing of the peak concentration was approximately the same through 20 mm of green wood as it was for 80 mm of dry.

Of these findings, the third is the most significant (after confirmation that methyl bromide gas does penetrate green timber in the radial direction), as it showed that a considerable reservoir of the fumigant builds up in the outermost layers of the sap-filled (and dry) wood during the gas exposure period. These gas molecules are therefore available for continued penetration, though with decreasing effect due to losses by diffusion in the reverse direction, out of the timber.

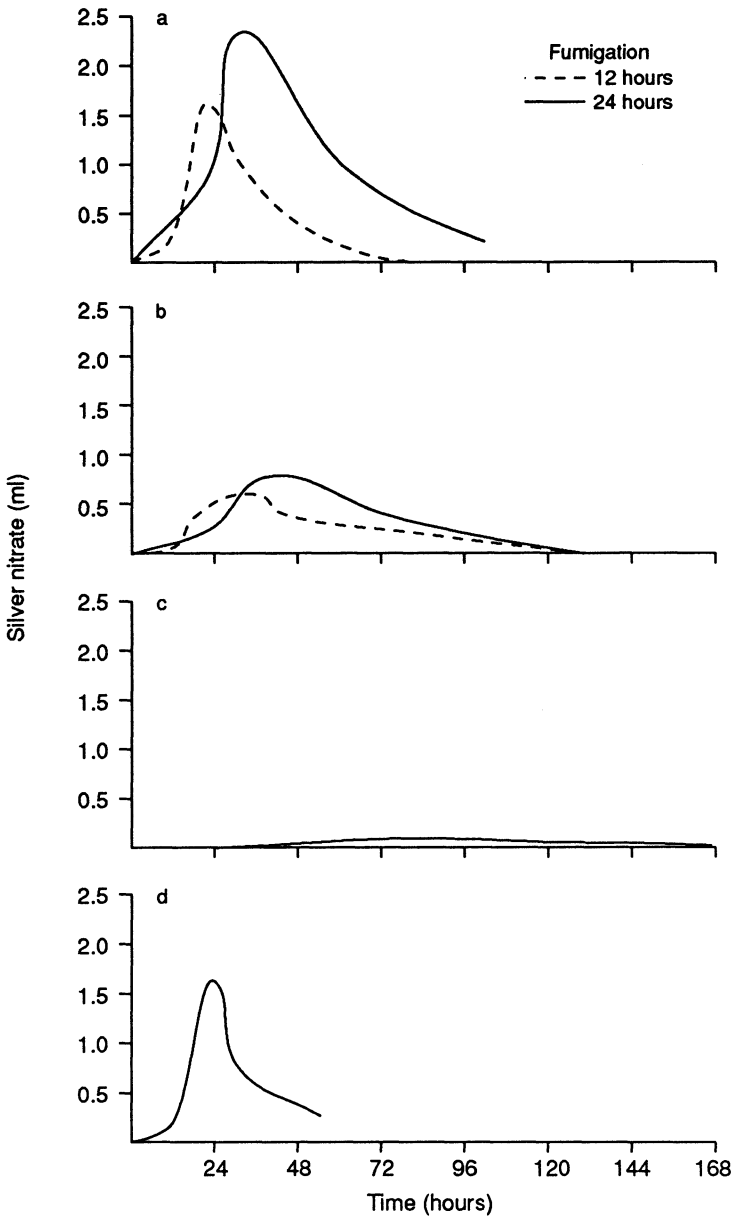

FIG. 2–Accumulated c : t products expressed as millilitres of N/10 silver nitrate for three thicknesses of green and one of dry wood.
a: 20-mm green; b: 40-mm green; c: 100-mm green; d: 80-mm dry.

In the 100-mm-thick green wood, the methyl bromide did not begin to arrive in the absorbent chamber in measurable quantities until nearly 48 hours had elapsed, with maximum rates achieved around 80 to 90 hours, falling away to trace amounts at the end of a week.

The results obtained from the calibration block series of experiments are given in Fig, 3, the uptake of methyl bromide again being represented by the volumes of N/10 silver nitrate needed to titrate the contents of the absorption sachets after 24 hours' exposure in the sealed blocks (hence the correction for time noted for Fig.2). This is plotted against the actual gas concentrations in the fumigation chamber for each test.

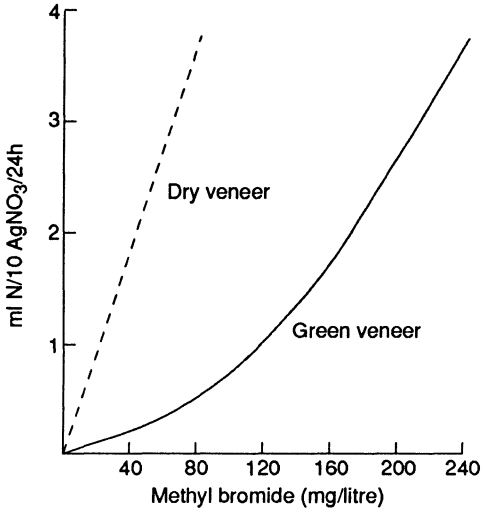

FIG. 3–Methyl bromide desorption from equilibrated veneers; —— green veneer (quadratic regression), - - - dry veneer (linear regression)

The dry and green series are very different, the dry wood releasing gas linearly and at much higher rates generally than the sap-containing material. In the latter, gas molecules were more strongly retained, particularly at the lower concentration levels, giving an exponential form to the graph (curves were fitted by linear and quadratic regression techniques).

ESTIMATION OF METHYL BROMIDE C : T PRODUCTS *IN SITU*

The data on penetration by methyl bromide as presented above do not directly equate to the c : t products actually achieved; that requires comparison with the results for equilibrium conditions, i.e., the calibration block observations. These permitted the penetration results to be converted to their equivalent concentrations approximately (in mg/*l*—*see* Fig. 4a) which, by integrating under the resultant curves, gave the c : t products (in mg/hours/*l*) equivalent for each sachet used in the trials.

The c : t products were plotted on a logarithmic scale against depth in Fig. 4b) where a line has been fitted by eye on the basis of known trends from Fig. 2. This line is necessarily approximate in the region zero to 200 mm but, since the chamber ambient c : t product was known to be 6224 mg/h/*l*, i.e., 260 mg/*l* × 24 hours, the curve as drawn (dotted portion) is a reasonable assumption.

The further assumption was made that, whatever the c : t product a volume of green wood was exposed to, the resultant cumulative dosages at depth within that wood would show the

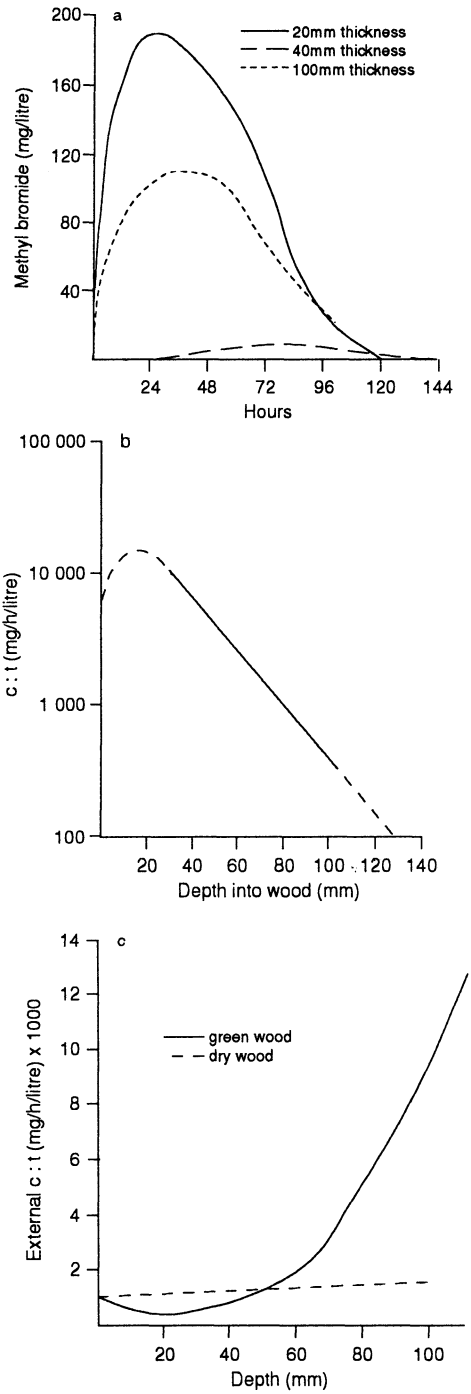

FIG. 4–a: Equivalent concentration curves for the three thicknesses of test block
b: Relationship of internal c : t to external c : t held at 6224 mg/h/*l*
c: C:t product to get 1000 mg/h/*l* at increasing depth in wood

same progression, though varying in magnitude in proportion to the initial exposure. Using this approach, the applied c : t products necessary to achieve "internal" c : t product of 1000 mg/h/*l* at any given depth in green *P. radiata* sapwood were plotted (Fig. 4c). This product (1000 mg/*l*) was chosen as it is regarded as significant in quarantine fumigation in New Zealand (*see* Appendix 2).

Though Fig. 4c is somewhat speculative, owing to the stepwise assumptions used in its derivation, point A in this Figure is exactly the same as point A in Fig. 4b, i.e., an external c : t product of 6224 mg/h/*l* (260 × 24) resulting in an internal c : t of 1000 mg/h/*l* through 87 mm of green wood. The fact that this is an interpolated point, and close to the measured value from the 100-mm test, makes it a reliable anchor for the curve.

For locations less than 80 mm into wood, the positioning of the line is constrained by the knowledge that it has to be a curve, since its origin at the surface **must** be at 1000 mg/h/*l*, while inspection of Fig. 4b shows that 20 mm into the wood the c : t product required to achieve 1000 mg/h/*l* must be less (because of gas retention increasing the exposure time).

Exactly where the curve lies, particularly at depths greater than 90 mm, is not very important, the real significance of Fig. 4c being that the c : t to depth relationship is exponential (beyond a few millimetres into the wood). This pattern is not unexpected for green wood, since it is typical of diffusive phenomena where a sorptive component is present, so-called non-Fickian diffusion (for a succinct discussion, *refer* Weisz 1981).

Where dry wood is concerned, the adsorption is greatly reduced; therefore, the dose against concentration trend is much nearer to linear (Fig. 4c). It is an important point that moisture contents intermediate between green and dry would also have intermediate forms of penetration curve. Even at the 10% to 11% m.c. of the test blocks the relationship, although a straight line, is distinctly sloped.

CONCLUSIONS

While the treatment of dry softwood timber poses few problems of adequate penetration, as also previously shown by Michelson (1964), it is evident from these studies that green, sappy timber is in a different category. The external dosage of gas is all-important, with the time element needing to be controlled as well as the concentration in order to get maximum penetration.

This degree of control has rarely been exercised with tent fumigations, but since the method has been used mainly for export log treatment the omission has had little practical importance. This has been due to the considerable overkill that the regulation dosage in fact gives, since any produce (particularly logs) with more than superficial insect damage is rejected for export anyway. This has eliminated any real need for deep penetration by a fumigant; only those insects on the surface, and in logs with the bark on, under the bark, need be targeted. None of these have a high tolerance to methyl bromide (*see* Appendix 1); if 150 mg/h/*l* is required to kill an organism, then 80 mg/*l* of methyl bromide is enough to ensure disinfestation within 2 hours on the surface (at constant concentration), and a little more (perhaps even less) for 20 mm into the wood.

However, of all the potential problems encountered in New Zealand export quarantine, the most difficult is the wood wasp *Sirex noctilio* F. (Zondag & Nuttall 1977), since at certain

stages it has a very high tolerance to methyl bromide, requiring 650 mg/h/*l* to ensure a kill (Harris 1963). The evidence presented from the penetration studies suggests that, if fumigation was sufficiently controlled, methyl bromide could be effectively employed against this species up to 80 mm into the wood, even assuming normal moisture content of healthy tissue. But a feature of *Sirex* attack is the drying out of the host tissue, which in practice would increase penetration effectiveness. Together with the tendency for smaller diameter trees to be attacked (or for attack to occur in the crown region), this means that fumigation should be effective against the immature stages of even this insect.

Where there is incipient attack (presence of eggs only, or very early instar larvae), the shallow location would ensure relatively easy eradication.

The critical factor is the effectiveness of the fumigation procedure, since to get 1000 mg/h/*l* (to give a reasonable safety margin) 60 mm into green *P. radiata* sapwood requires holding the regulation 80 mg/*l* level for the full 24 hours stipulated, i.e., nearly 2000 mg/h/*l*. To get deeper effective penetration requires either a longer exposure time or a higher concentration, requirements which begin to rise very steeply much beyond this depth, e.g., an external c : t of around 10 000 mg/h/*l* is necessary to get similarly effective levels at 100 mm.

With tent fumigations, such high c : t products can be obtained only by (i) topping-up the undersheet concentration periodically, on the basis of gas sampling, throughout a set exposure period, or (ii) putting in a much higher loading at the start and holding for a shorter period.

Either strategy has advantages and disadvantages, the choice ultimately depending on circumstances. No difficulty would arise with vault or container fumigations, of course, a comment that extends to treatments in a ship's hold.

Imported forest produce (including dunnage and pallets, etc.) presents the same general problem—if it is dry then penetration is relatively unimpeded, but green material requires high treatment c : t products. But to these problems can be added the fact that, of the many possible timber-related insects that could arrive, very few have known methyl bromide tolerances, and at least one *Coptocercus* sp. is known to require a c : t of around 1000 mg/h/*l*—other insects could well be higher. Neither is there any reason why they should not be deep inside a large pole or log that is still substantially green.

In such situations the only convenient course is to fumigate in a vault or ship's hold, since the external c : t products need to be high, requiring the maintenance of large concentrations for at least 24 hours.

REFERENCES

HARRIS, E.C. 1963: Methyl bromide fumigation and wood-boring insects. *Record of the Annual Convention British Wood Preservers' Association 1963*: 159–75.

HESELTINE, H.K.; ROYCE, A. 1960: A concentration : time product indicator for fumigations. *Pest Technology 2*: 88–92.

MICHELSON, A. 1964: Diffusion of methyl bromide into pine wood during fumigation against *Hylotrupes bajulus*. *Holzforschung und Holzverwertung 16*: 66–71.

WEISZ, P.B. 1981: The science of the possible: The non-Fickian dogs. *Chemtech. March 1981*.

ZONDAG, R.; NUTTALL, M.J. 1977: *Sirex noctilio* Fabricius. *New Zealand Forest Service, Forest Research Institute, Forest and Timber Insects in New Zealand, No. 20*.

APPENDIX 1

CONCENTRATION : TIME LIMITS FOR SOME NEW ZEALAND TIMBER INSECTS

Several insect species are routinely found during export quarantine inspections of *P. radiata* logs and sawn timber.

Various life stages of the commonest of these were exposed to a single concentration of methyl bromide in a fumigation chamber and, by varying the time of exposure, the toxic threshold c : t product for each was established (Cross unpubl. data).

These studies showed that the late egg/early larval stage of *Prionoplus reticularis* White (Coleoptera, Cerambycidae), a large New Zealand native insect, were most resistant and required a c : t product of between 100 and 150 mg/h/*l* for a reliable kill. All the other species and stages tested required less than 100 mg/h/*l*; these were larvae and adults of *Arhopalus tristis* (F.) (Coleoptera, Cerambycidae) and *Hylastes ater* Paykull (Coleoptera, Scolytidae), and worker castes of *Kalotermes brouni* Froggatt (Isoptera, Kalotermitidae).

Sirex noctilio F. (Hymenoptera, Siricidae) was not tested, as Harris (1963) had already published results for methyl bromide against this, and related, species. He showed that late larval and pupal stages of *S. noctilio* required c : t products of 650 mg/h/*l* for a reliable kill.

APPENDIX 2

USE OF FUMIGATION MONITORING SACHETS IN NEW ZEALAND

Since their introduction in the mid-1980s, the use of absorbent sachets for checking the effectiveness of methyl bromide fumigations of forest products has become virtually universal in New Zealand. On the basis of the information given in Appendix 1, two levels have been chosen for the standard sachet—150 mg/h/*l* for exported produce and 1000 mg/h/*l* for fumigations of imported material. Neither is really meant for deep penetration treatments of green timber.

The "150" sachet is intended to check that an adequate minimum dose is administered, one that will ensure eradication of superficial infestations (including eggs) provided that fumigation is carried out before shipping.

The "1000" sachet is also used to ensure a minimum standard is exceeded, giving good penetration dosages in dry wood (i.e., that below fibre-saturation point), the assumption being that this level is adequate for all possible insect introductions.

Where imported green timber of substantial dimension is involved it is handled on an individual basis, dependent upon the results of a careful quarantine inspection. "1000" sachets may be used in any fumigation decided upon, followed by checking for signs of life of the pest involved. Further periods of treatment, that include fresh sachets, are given should the results of the first prove unsatisfactory.

These sachets are currently produced by the Ministry of Forestry, Protection Service (Quarantine).