Influence of dose, bark cover and end-grain sealing on ethanedinitrile (C_2N_2) sorption by pine (*Pinus radiata* D. Don) logs

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Abstract High sorption by *Pinus radiata* (D. Don) logs may limit insecticidal efficacy of a fumigant by rapidly removing it from the treated headspace. The sorption characteristics of a new fumigant, ethanedinitrile (EDN), were quantified for recently harvested pine logs, and the robustness of a proposed EDN sorption model developed for sawn timber was tested. Over a 10-h period, average concentrations were 17.3% ± 0.7 of the initial dose for logs with sealed ends and 9.4% ± 0.4 for unsealed ends. This is a high rate of sorption compared with other fumigants, such as methyl bromide. A proportional drop in headspace concentration over time was consistent for the two doses (20 and 50 g/m^3) evaluated, confirming that EDN sorption is influenced by the dose applied. Bark cover did not significantly influence EDN sorption. A revised sorption model for EDN is proposed here.

Keywords alternative, EDN, fumigation, methyl bromide, quarantine treatments.

INTRODUCTION

Fumigant sorption refers to the removal of fumigant from the headspace by the substrate being treated. Sorption rates vary with the fumigant used, the substrate being treated and the load factor (Pranamornkith et al. 2014a). High rates of sorption are generally undesirable because less of the applied fumigant is available in the headspace to control the target insects (Lorraine 2014).

Ethanedinitrile (EDN) is being evaluated as an alternative fumigant to methyl bromide (MB; an ozone-depleting compound), and as a pre-shipment treatment for pine logs (*Pinus radiata* D. Don) exported from New Zealand. EDN is considered a highly sorptive fumigant, which may affect the initial dose needed to be efficacious against insects potentially infesting logs (Armstrong et al. 2014). Ren et al. (2011) compared EDN with MB and phosphine (PH_3) sorption rates in timber (*Pseudotsuga menziesii* (Mirb.) Franco) and found that EDN had a faster sorption rate than either MB or PH_3. When used to treat logs (*Pinus koraiensis* Sieb. et Zucc.), EDN sorption was 66 and 87% of the initial concentration after 6 and 24 h, respectively (Park et al. 2014). High EDN sorption of 61 and 20% of the applied dose remaining after 10 h has also been reported when treating pine sawn timber at 11 and 44% load factors (Pranamornkith et al. 2014a). In contrast, MB sorption by *Populus* spp. timber packing material of 50-55% of the applied dose over a 16-h period was reported at a 25% load factor (Barak et al. 2005). However, Pranamornkith et al. (2014b) and Najar-Rodriguez et al. (2015) have shown that EDN, at low doses, is highly toxic to naked insects from different life stages of the burnt pine longhorn beetle, *Arhopalus ferus* (Mulsant). Thus, although the concentration of EDN is depleted more quickly from the headspace than other fumigants such as MB, this fumigant nevertheless seems able to control forest pests at lower concentrations than MB (Najar-Rodriguez et al. 2015, and references therein).

Although EDN is water soluble and believed to breakdown into hydrogen cyanide (HCN) under high moisture conditions (CSIRO et al. 1996; Brash et al. 2013), Pranamornkith et al. (2014a) found that the moisture content of pine sawn timber does not significantly influence the EDN sorption pattern. In addition, Park et al. (2014) did not detect HCN during log fumigation, indicating that the predicted breakdown process of EDN to HCN may not be occurring. The combination of similar sorption when used to treat high and low moisture content material, along with high toxicity compared with MB, shows that EDN may have potential as a chemical alternative for pre-shipment treatment of recently harvested logs.

The objective of this work was to measure the effects of fumigant dose, bark cover and end-grain sealing on EDN sorption by recently harvested pine logs. This work builds on the EDN sorption model proposed by Pranamornkith et al. (2014a) and forms part of a broader evaluation of EDN as an alternative chemical treatment to MB.

MATERIALS AND METHODS

Source and physical characteristics of logs

Recently harvested pine logs were sourced from the Tararua Range near Tokomaru, New Zealand (latitude -40.51°, longitude 175.58°) on 11 April 2014. Selected logs were from a commercial stand of 20-year-old pruned trees. Timber sections were cut from the upper trunk of six trees so that they would fit into a fumigation chamber with internal dimensions of 305 mm × 305 mm × 305 mm. The diameter of upper trunk sections was 250 mm, allowing them to fit into a 28-litre fumigation chamber (Labconco® desiccators, Kansas City, Missouri, USA). Logs were then cut into 300-mm long sections so that a load factor of approximately 50% was achieved. Load factor is the proportion of the treated volume occupied by the product being treated and is typically close to 50% for logs treated under tarpaulin.

Sections of logs were used to determine their moisture content. This material was weighed before and after oven-drying using a Marford temperature-controlled cabinet (GEO Wilton & Co. Ltd, Wellington) set at 103°C ± 2 for 72 h. Moisture content (MC) was calculated on a percentage oven-dry basis adapted from standard test methods (ASTM Standard D4442, 2007) as follows:

$$MC\% = (A - B)/B \times 100 \qquad (1)$$

where A = original mass (g) and B = oven-dry mass (g).

Experimental design

A factorial design was used to quantify EDN sorption by recently harvested pine logs with a moisture content of 119% ± 1. The influence of three factors: dose (20 and 50 g/m^3), bark cover (0, 50 and 100%) and end-grain sealing (either sealed or unsealed), was compared at 15°C. Each treatment was replicated three times with an average load factor of 50% ±2. These factors were chosen as they either represent commercially important variables for fumigation or have been previously shown to significantly influence EDN sorption (Ren et al. 2011; Pranamornkith et al. 2014a).

Bark was removed from log sections using a hammer and wood chisel. For logs with 50% cover, the bark was removed from one side of the log. End-grain sealing of logs with paraffin was as described by Pranamornkith et al. (2014a).

EDN delivery and monitoring

Either 250 or 625 ml of pure EDN was delivered to chambers in order to dose 20 or 50 g/m^3, respectively. Pure EDN was transferred from a cylinder to each fumigation chamber using either a 0.5 or 1.0-litre gas-tight syringe connected to an EDN delivery system (BOC Australia, Sydney), as described by Roynon (2012). After the EDN was delivered to the chamber, a fan provided air circulation during each fumigation period to ensure thorough gas mixing. Fumigations were conducted in a temperature-controlled room at 15°C ± 2.

The EDN Fumigas® label for treatment of logs and timber in Australia is 50 g/m^3 for 10 h (BOC 2014). Sorption measurements of separate chambers containing logs were made following fumigation for up to 10 h, matching the label recommendation. Headspace measurements were taken at 0.25, 0.50, 0.75, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9 and 10 h after fumigation. The concentration at time zero was estimated taking the load factor into consideration. At each time point a 3-ml gas sample was collected from the chamber headspace and analysed on a gas chromatograph (GC) instrument.

The concentration of EDN was measured using an Agilent 7890A GC fitted with a flame ionisation detector (FID) and a GS-Q column (30 m length and 0.53 mm diameter, Agilent Technologies Inc., Auckland, NZ). The inlet and oven were maintained at 100°C and the detector at 300°C. A five-point calibration using dilutions of pure EDN in air was performed at the beginning of each measurement period.

Statistical analysis

Curve parameters were estimated by the method of least squares, using SAS PROC NLIN Version 9.2 of the SAS System for Windows (Copyright ©2008 SAS Institute Inc., Cary, NC, USA). The effects of dose, bark cover and end-grain sealing on the ratio of EDN concentration at any time to the applied dose were estimated by regression analysis using SAS PROC GLM.

For each replicate of each treatment, a smooth curve was fitted to the EDN sorption data, from which concentrations at any time could be estimated for statistical comparison:

$$C(t) = A\exp(-kt^{p}) \qquad (2)$$

where $C(t)$ is the concentration at time t in hours, and A, k and p are parameters to be estimated separately for each replicate.

RESULTS AND DISCUSSION

Influence of dose

The effect of fumigant dose, bark cover and end-grain sealing on EDN sorption by recently harvested pine logs was measured. The proportional drop in concentration over time was relatively consistent for the two doses evaluated, confirming that EDN sorption is influenced by the dose applied. Only at 0.5 h was a significant difference detected ($P=0.015$), with relatively more sorption in the first half hour in the 20 g/m^3 treatments (data not presented). Differences at later times were not significant. This response is similar to that reported by Pranamornkith et al. (2014a), illustrating that the sorption pattern across different doses is similar and that this response is proportional to the applied dose.

Sorption curves for respective doses were similar but their magnitudes were different. This means that EDN sorption can be estimated with a reasonable degree of certainty when used to treat logs, whatever the applied dose. Smooth curves using equation (2) fitted all replicates well. Parameter A represents the point where the extrapolated curve would cross $t=0$, while parameters k and p define the shape of the curve as the concentration drops over time. Note that in nearly all cases the fitted value of A was less than the initial concentration calculated from the dose and load factor, so there must have been an initial rapid drop in concentration before data collection began. If $p=1$, then equation (2) would be a simple exponential. However, for all replicates, the fitted value of p was always less than 1, and in all but one case the difference from 1 was significant ($P<0.05$). Thus, the new equation (2) proposed here is able to describe EDN sorption responses better than Pranamornkith et al. (2014a). Additional sampling points were added in this study to better define the two-phase sorption model proposed by Pranamornkith et al. (2014a). Other studies have also proposed a two-phase exponential function to describe fumigant losses for MB and PH_3 when used to treat grain (Banks 1985; Darby 2008). By collecting additional information at this transitional zone between phases 1 and 2, this response can now be described with a better exponential decay function.

Influence of bark cover

The ratio of headspace concentration to dose at any time was found to be independent of bark cover at all times, and independent of the dose applied at all fumigation times from 1 h onwards. Therefore, the amount of bark cover on pine logs did not significantly influence EDN sorption, indicating that sorption rates for wood and bark are similar. This is a positive characteristic for a fumigant, as commercially harvested logs will vary greatly in bark cover. This result also suggests that pine logs can be universally treated without wide-ranging effects on fumigant sorption caused by varied bark cover.

Influence of end-grain sealing

Sealing of log ends had a significant effect on the concentration at all times ($P<0.001$). For both the 20 and 50 g/m^3 doses, the drop in headspace concentration in the first 0.5 h of the treatment was 30% less when the ends were sealed. This is very close to what would be expected if end-grain and cross-grain sorption rates were the same, as sealing log ends reduced the total log surface area by 29%. This result for end-grain sealing is similar to that reported by Pranamornkith et al. (2014a) for pine sawn timber, but in contrast to the results of Ren et al. (2011), who showed that EDN sorption by the end grain of Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) was higher than that by the cross-grain surfaces. The present results and those of Pranamornkith et al. (2014a), show that EDN sorption along and across the grain are similar when used to treat both pine sawn timber and logs.

For logs with unsealed end-grains, headspace concentrations on average dropped to that of the applied dose after just 0.5 h, to one-half the applied dose after 2.6 h, and to one-quarter of the applied dose after 5.3 h (Figure 1). In comparison, for logs with sealed end grains, the times were considerably longer, at 1.4, 4.3 and 7.9 h, respectively. After 10 h, concentrations were only 17.3% ± 0.7 of the initial dose for logs with sealed ends, and 9.4% ± 0.4 for those with unsealed ends (Figure 1). This shows slightly more sorption than the 20% EDN remaining after 10 h reported by Pranamornkith et al. (2014a), when used to treat pine sawn timber at a load factor of 44%. Note that a direct comparison with the results of Pranamornkith et al. (2014a) is difficult, as the surface area of sawn timber was much higher than for logs of this study, as timber planks were separated during fumigation. For much longer logs used for export, where end-grains represent a smaller proportion of the total log surface area, it is likely that the importance of sorption along the grain versus across the grain is minimal.

Times taken for concentrations to drop to any amount can differ considerably from these average values. For instance, while the average curve for headspace concentrations for logs with sealed end-grains dropped to 1 (the applied dose) after 1.4 h, the lines for one standard deviation below or above the average crossed at approximately 1.0 and 1.8 h, respectively (Figure 1). Using a normal approximation, it would therefore be expected that the headspace concentration would drop to the applied dose in 1.0 to 1.8 h in about 68% of cases, but in 32% of cases the time would be either shorter or longer than this estimate. Therefore, the model described here is able to predict the vast majority of factors contributing to EDN sorption.

On average, log sections were ca 250 mm in diameter and 300 mm in length, from which it can be calculated that the two cut surfaces (exposing the end grain) make up approximately 29% of the surface area of the log sections. If EDN is initially absorbed at the same rate per unit area from the ends and sides of the logs, it might therefore be expected that the initial rate of loss of EDN from the headspace would be 29% lower if the ends were sealed. Using the average loading of 50% ± 2 in this experiment, it was found that: (1) For a dose of 50 g/m^3, the initial headspace concentration was 102 g/m^3, and after 0.5 h the average concentrations were 68 and 53 g/m^3 for treatments with sealed or unsealed end-grains, respectively. From this it was calculated that the drop in concentration in the first 0.5 h with sealed ends was 70% of the drop with unsealed ends. (2) For a dose of 20 g/m^3, the initial headspace concentration was 41 g/m^3, and after 0.5 h, the average concentrations were 26 and 20 g/m^3 for treatments with sealed or unsealed end-grains, respectively. From this it was calculated that the drop in concentration in the first 0.5 h with sealed ends was again 70%

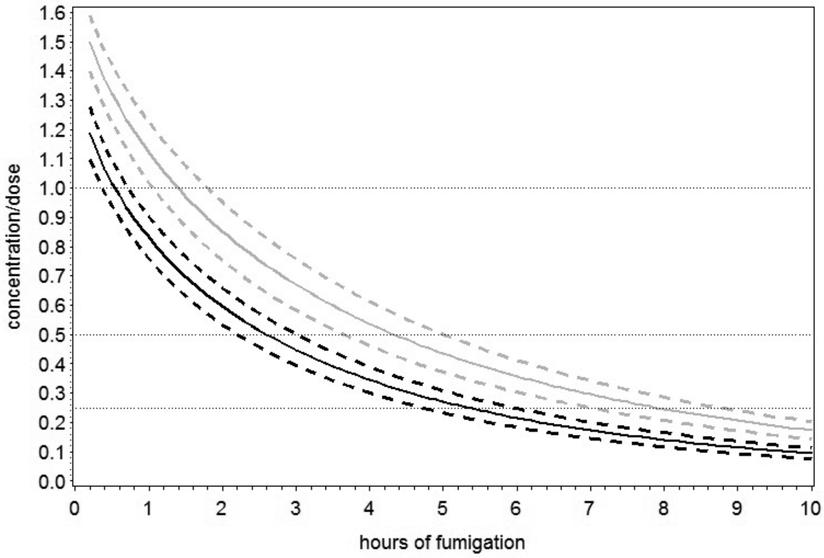

Figure 1 The ratio of headspace concentration to initial dose of ethanedinitrile (EDN) during fumigation of *Pinus radiata* logs at 15°C for 10 h at a 50% ± 2 load factor, for all treatments with sealed (grey) or unsealed (black) ends. Mean values (solid lines) and values one standard deviation ± from the mean (dashed lines) are shown (n=18). The horizontal dashed lines can be used to estimate the time at which the headspace concentration dropped below the applied dose, or below one-half or one-quarter of the applied dose.

of the drop with unsealed ends. For both the 20 and 50 g/m^3 doses, it was found that the drop in headspace concentration in the first 0.5 h of the treatment was 30% less when ends were sealed. This is very close to the 29% calculated if all surfaces absorbed EDN at the same rate.

CONCLUSIONS

The present work indicates that EDN sorption by pine logs is influenced by the dose applied and end-grain sealing, whereas bark cover did not significantly influence EDN sorption. The amount of EDN fumigant lost through sorption was proportional to the applied dose or dependent on the surface area of the log which was sealed. A new sorption model for EDN, which is better able to describe the transitional zone of a previously defined two-phase exponential decay model, has been proposed. This sorption model, in combination with insect toxicity studies, will help with predictions of the fumigant doses needed to control forest insects under certain conditions.

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