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Quantification of hydrogen cyanide as a potential decomposition product of ethanedinitrile during pine log fumigation

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Abstract

Background: The Stakeholders in Methyl Bromide Reduction (STIMBR) are evaluating ethanedinitrile (EDN) as an alternative fumigant to methyl bromide for use as a phytosanitary treatment for pine logs (*Pinus radiata* D.Don). Ethanedinitrile is hypothesised to decompose into hydrogen cyanide (HCN) in the presence of water. This process, if it occurs, is of particular interest because it may influence the efficacy and emissions data needed for commercialisation.

Methods: The concentrations of EDN and HCN were measured in the treated space (28 L fumigation chambers) without ($n = 1$) and with pine log sections ($n = 3$; 46 ± 1.4% load factor) at 10 or 20 °C in a simulated commercial fumigation.

Results: On average, the cylinder of EDN tested contained 34.6 g m^{-3} HCN (or 3.1%), which corresponds to a concentration of 0.8 g m^{-3} (or 0.07%) in the treated space for a 50 g m^{-3} EDN dose (commercial rate in Australia). This level of HCN is likely a result of the manufacturing process, whereby HCN is oxidised to produce EDN. During fumigation, HCN was detected in the treated space at relatively low concentrations, which did not significantly change over time. This indicates that HCN is not produced in substantial amounts during fumigation and that, as a result, insect efficacy is unlikely to be affected by low unchanging ($P = 0.055$) concentrations of this compound in the treated space.

Conclusions: The results of this work support the statement that EDN is not significantly converted to HCN during the treatment of recently harvested pine logs.

Keywords: Cyanogen, Fate, Temperature, Fumigas™, Breakdown, Sorption, Sterigas™

Background

The treatment of commodities with fumigants is the most economic method of disinfestation to kill insects and pathogens (Duarte-Sierra et al. 2016; Fields et al. 2004). Methyl bromide (MB) is currently the most effective fumigant used for quarantine and pre-shipment (QPS) purposes internationally. As MB is an ozone-depleting compound, its use has largely been restricted globally to QPS treatments. In New Zealand, MB used after 2020 will require its recapture or destruction to limit emissions to the atmosphere (Hall et al. 2017). The search for alternative fumigants to MB identified a relatively new fumigant, ethanedinitrile (EDN), as a potential chemical treatment of pine (*Pinus radiata* D.Don) logs (Brash et al. 2013; Hall et al. 2015). The Stakeholders in Methyl Bromide Reduction (STIMBR) endorsed the collection of data to support the use of EDN as a QPS treatment for export logs.

Sorption is a term used to refer to the adsorption and absorption of fumigant molecules by the commodity being treated, thereby reducing its concentration in the treated space over time (Hall et al. 2017). Brash et al. (2013) reviewed EDN as a potential quarantine disinfestation treatment for logs and sawn timber. They concluded that EDN had potential as a phytosanitary treatment, particularly for sawn timber, where sorption rates were estimated to be lower than that of logs due to the lower moisture content of sawn timber. However,

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EDN is water soluble (Emekci 2010), with 4.5 L of gas dissolvable in 1 L of water and the decomposition pathway of EDN to HCN was unresolved because the patent (O'Brien et al. 1999) states that HCN is produced in water and high humidity environments. High humidity is expected to occur when recently harvested logs are covered with a tarpaulin and fumigated. Consequently, it was hypothesised that these circumstances would facilitate the decomposition of EDN to HCN. Also, the higher sorption rates of EDN into logs would potentially render this fumigant ineffective for commodities with a high moisture content. The fate of EDN must be considered by the New Zealand Environmental Protection Authority (EPA) during the registration process (EPA-NZ 2012) that will permit the use of EDN in New Zealand.

Park et al. (2014) did not detect HCN in the treated space during the fumigation of Korean red pine (*Pinus koraiensis* Siebold and Zucc.) logs with EDN. Their results indicated either that the predicted decomposition of EDN to HCN may not occur during the fumigation of logs or that the production of HCN occurred at levels that were undetectable with the gas chromatography system they used. Moreover, if HCN is not produced or produced only at inconsequential concentrations, then the impacts on chemical efficacy, environmental emissions and worker safety issues should be negligible. Also, Pranamornkith et al. (2014b) showed that the moisture content of wood did not significantly influence the sorption rate of EDN over a typical treatment period (10 h) despite the solubility of EDN in water.

Sorption rates vary depending on a number of factors such as the fumigant, temperature, load factor, moisture content and commodity being treated (Hall et al. 2015; Pranamornkith et al. 2014b). The mode of insecticidal action of EDN is respiratory so a high sorption rate is undesirable (Pranamornkith et al. 2014b) as less of the fumigant is available in the treated space to affect the insects. The results of Pranamornkith et al. (2014b) indicate that EDN may have more potential as a fumigant for the disinfestation of logs than Brash et al. (2013) suggested. Although EDN does have a higher rate of sorption than MB (Hall et al. 2017; Hall et al. 2015), it is highly toxic to forest insects (Pranamornkith et al. 2014a) and more toxic to the burnt pine longhorn beetle (*Arhopalus ferus* [Mulsant]) than MB (Najar-Rodriguez et al. 2015). Thus, any negative effects of a higher rate of sorption may be offset by the greater toxicity of EDN to insects.

If HCN is produced during fumigation by the decomposition of EDN as hypothesised (Brash et al. 2013), then this process may either positively or negatively affect the efficacy of EDN as a fumigant. Hydrogen cyanide is also toxic and could, therefore, have insecticidal activity that may either supplement or interfere with the effectiveness of EDN. For example, the CT (concentration × time) value of HCN required to kill larvae of the Asian longhorn beetle (*Anoplophora glabripennis*) is 17.67 g h m^{-3} at fumigation temperatures of 23–24 °C (Stejskal et al. 2014), while the CT value of EDN required to kill larvae of *Arhopalus ferus* is 19.50 g h m^{-3} at 20 °C (Najar-Rodriguez et al. 2015). Thus, determining the toxicity of both these chemicals to various insects and assessing whether or not their concentrations change in the treated space over time are important factors in understanding the efficacy of EDN as a fumigant. The current study focused on the second of these factors. The concentrations of both EDN and HCN were measured during simulated fumigations to determine if a significant proportion of HCN is produced as a breakdown product of EDN when used to treat recently harvested pine logs with a high moisture content.

Methods

Source and physical characteristics of logs

Pine (*Pinus radiata* D.Don.) logs were sourced near Palmerston North, New Zealand (latitude – 40.41°, longitude 175.67°), on 5 May 2015. Logs were collected from a commercial stand of 18-year-old trees. Timber sections were cut from the upper trunk of six randomly selected trees to fit into 28 L fumigation chambers (Labconco Desiccators, Kansas City, Missouri, USA) with internal dimensions of 305 × 305 × 305 mm. These sections were stored at 4 ± 1 °C for up to 4 weeks before they were used in experiments. This was done to allow enough time to arrange for the resources required for this experiment. Prior to fumigation, each of these six sections were further cut into smaller sections (≈ 270 mm long, ≈ 250 mm diameter) to ensure a load factor ≅ 50% was established during fumigations. Load factor is the proportion of the treated volume occupied by the material being treated and is typically close to 50% for logs treated commercially under tarpaulin.

Source of EDN

The EDN used for these experiments was manufactured by Draslovka, Czech Republic, in May 2010 using a pilot plant. The concentration of HCN in the cylinder used in this work was determined using the method described below. Draslovka does not expect any decomposition of EDN in the cylinder over 5 years of storage until its use for the current study (Adam Jonas, Draslovka; personal communication).

Experimental design

A two-factor, randomised block design was used to determine the relationship between EDN and HCN during fumigations, with temperature (at two levels, 10 or 20 °C) and time since fumigation (at six levels, viz. 0, 2, 4, 6, 8,

and 10 h) as factors. Chambers each at 10 and 20 °C without logs ($n = 1$, i.e. the control) and with logs ($n = 3$) were used to monitor EDN and HCN concentrations over time. Moisture content of the log sections were calculated on a dry weight basis using the following formula as described by Hall et al. (2017): [(wet weight – oven dry weight) × 100/(oven dry weight)]. Average moisture content of the log sections was 141 ± 9% ($n = 6$).

The registered dose of EDN Fumigas™ for the treatment of logs and timber in Australia is 50 g m^{-3} for a treatment period of 10 h [(BOC n.d.), Australia]. These conditions were replicated in the laboratory to simulate commercial practices by employing a 50 g m^{-3} dose of EDN in either an empty chamber or a chamber with a log (46 ± 1.4% load factor). This dose was used to determine the influence of log moisture on the potential production of HCN.

A gas-tight 1-L syringe connected to an EDN delivery system was used to transfer 625 mL of EDN to each treated chamber to produce a dose equivalent to 50 g m^{-3}. A fan provided circulation during fumigation to ensure complete gas mixing. The fumigation chambers were housed in temperature-controlled rooms maintained at either 10 or 20 ± 1 °C.

Measurements and analysis

Using an airtight gas syringe, gas samples were drawn from the treated space of each chamber at 0, 2, 4, 6, 8, and 10 h after fumigation. At each sampling occasion, two separate samples were simultaneously collected from each chamber: (1) a 1-mL sample that was analysed by direct injection on a gas chromatograph with a mass-spectrometer detector (GC–MS) to determine the concentration of HCN and (2) a 3-mL sample that was analysed on a gas chromatograph with a flame ionisation detector (GC–FID) with a 250-μL sample loop to determine the concentration of EDN. The MS detector was used to quantify HCN because the amounts of this compound in the samples were small and the MS detector was more sensitive than the GC–FID detector.

The concentration of EDN in each sample was measured using an Agilent 7890A GC (Santa Clara, CA) equipped with a FID following isothermal separation (at 150 °C) on a 30 m × 0.53 mm internal diameter GS–Q, fused-silica PLOT column (Agilent J&W). The GC oven, inlet, and detector temperatures were 150, 150, and 300 °C, respectively. The hydrogen, air, and make-up (nitrogen) flow rates were 100, 400, and 0.5 mL min^{-1}, respectively, and the total run time was 0.6 min. A seven-point calibration using dilutions of a newer, purer supply of EDN (Draslovka, Kolín, Czech Republic, > 99.5% pure) in air was performed at the beginning of each measurement period. Concentrations of 0, 10, 25, 35, 45, 55, and 90 g m^{-3} were used in preparing calibration curves. Measurement of HCN was performed using static headspace sampling and GC–MS, based on the methods of Murphy et al. (2006) and Eaton (2009). Separations were performed on an Agilent 6890N GC coupled to a Waters GCT time-of-flight MS with an electron ionisation energy of 70 eV and a scan time of 0.4 s. A gas-tight syringe was used to make 1-mL split-less injections (over c. 30 s) onto a HP–PLOT/Q column (30 m × 0.32 mm, Agilent Technologies Inc., Santa Clara, CA). The injection port was maintained at 40 °C, and the front of the GC column at – 30 °C with a liquid nitrogen cryotrap (GL Sciences Optic3–SC, Veldhoven, the Netherlands). After 90 s, the injection port was ramped from 40 to 150 °C at 25 °C s^{-1}; at 120 s, the injection port was changed from a split less to a split flow of 25 mL min^{-1}. At 125 s, the cryotrap was heated to 150 °C at 50 °C s^{-1} and the oven temperature ramp and MS were triggered. The oven temperature programme was 0.5 min at 60 °C, 11 °C min^{-1} to 200 °C, which was held for 1.5 min. A HCN standard (Air Liquide, Melbourne, Australia) was used to determine the response of the GC–MS system. Under these conditions, EDN was eluted at 4.6 min and HCN at 5.8 min (Fig. 1).

Statistical analysis

The concentrations of EDN and HCN during the fumigation of log sections were analysed with residual maximum likelihood (REML) repeated measurements using GenStat (14th edition, VSN International, Hemel Hempstead, UK). Temperature and time after fumigation were analysed as factors. The P values and Wald/d.f. values were used to identify those factors (temperature and time) that significantly influenced the concentration of gases during fumigation. Differences between means were expressed as the standard error of the mean.

Results and discussion

Identification of HCN and EDN

The mass-to-charge ratios (m/z) of 27 and 52 for HCN and EDN, respectively, are shown in Fig. 2. The relative sensitivity of the GC–MS system combined with the m/z of these compounds demonstrated that HCN was appropriately separated from EDN identified from the gas samples taken from the treated space during fumigations.

Purity of EDN

The concentration of HCN in the cylinder used for fumigations was found to be 3.1% v/v, which is equivalent to 34.6 g m^{-3}. When the gas was diluted to supply an EDN dose of 50 g m^{-3}, this value equated to 0.8 g m^{-3} (or 0.07%) HCN in the treated space. It is most likely a residue contaminant from the manufacturing process in which HCN is oxidised to produce EDN. The manufacturer of the EDN (Draslovka) has since constructed a

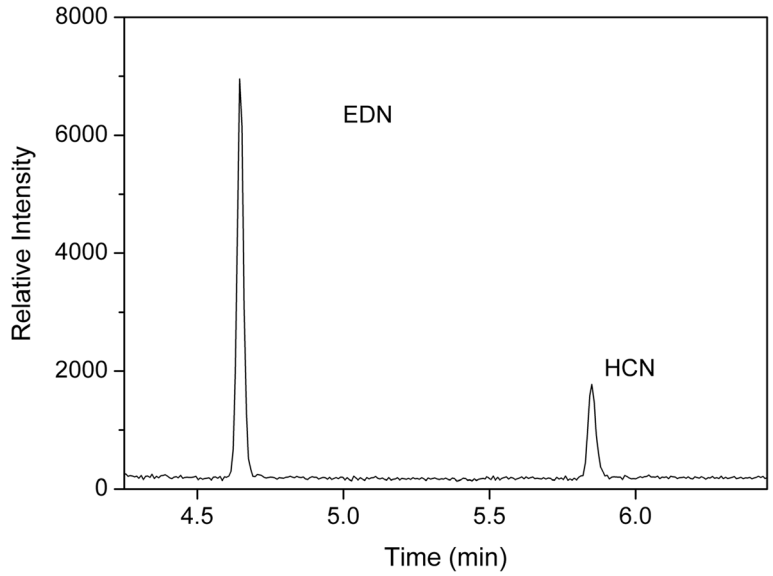

Fig. 1 Retention time and relative intensity of ethanedinitrile (EDN) and hydrogen cyanide (HCN) under the conditions used in this study

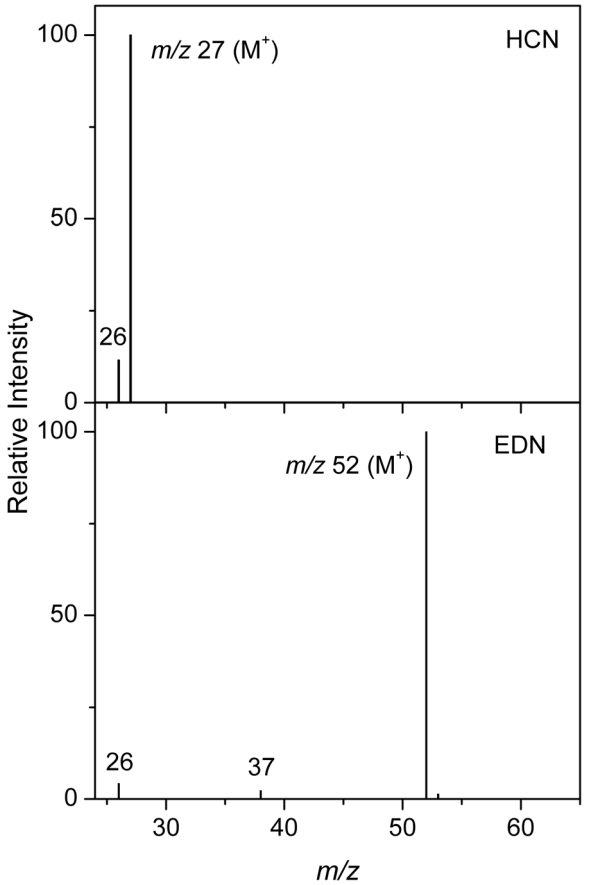

Fig. 2 Mass-to-charge ratio (*m/z*) of hydrogen cyanide (HCN) and ethanedinitrile (EDN) showing their respective *m/z* and relative intensity

production plant that is capable of supplying EDN with < 0.9% HCN, so the concentrations of HCN in the treated space and environment post-application should be lower than those reported here.

Concentration of HCN during fumigation

Hydrogen cyanide was detected in the samples from the treated space of chambers that only contained EDN (i.e. devoid of a log). This was to be expected given that the source of EDN contained HCN. Following an EDN dose of 50 g m^{-3}, the concentrations of HCN in the empty chamber at each temperature did not significantly change over time, and hence, data has been averaged over the measurement period that equated to 0.76 ± 0.04 g m^{-3} ($n = 6$) at 10 °C and 0.86 ± 0.03 g m^{-3} at 20 °C (Fig. 3d). Compared to the empty chambers above, lower HCN concentrations were detected in the treated space of chambers containing log sections (Fig. 3c). The lower concentrations were evidently due to sorption since HCN has a relatively higher wood penetration ability compared to other fumigants (Douda et al. 2015; Stejskal et al. 2014). At 10 °C, the concentration of HCN in the treated space ranged from 0.45 to 0.55 g m^{-3} (averaging 0.5 ± 0.01 g m^{-3}) during fumigation of log sections with no clear trend over time, whereas at 20 °C, the HCN concentrations ranged from 0.41 to 0.99 g m^{-3} (averaging 0.75 ± 0.09 g m^{-3}; Table 1). However, concentrations did not change significantly (P value = 0.055) during fumigation (Table 1). Temperature did significantly (P value < 0.001, Wald/d.f. 17) influence the concentration of HCN in the treated space when logs were present, with a higher average concentration measured at 20 °C than 10 °C (Table 1). Although statistically significant, this difference in average

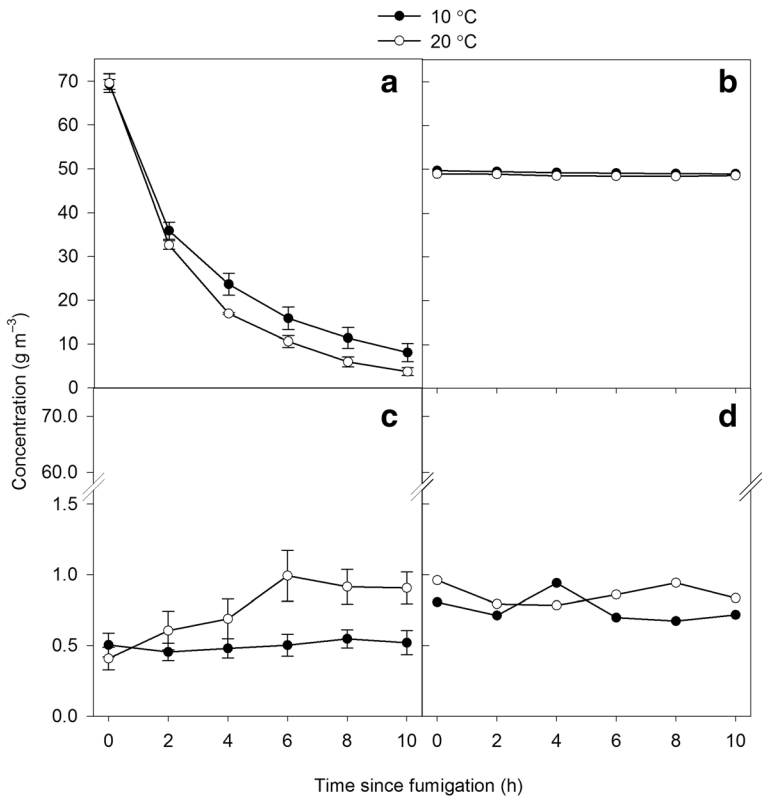

Fig. 3 Average concentrations of ethanedinitrile in the chambers **a** with log sections ($n = 3$) and **b** without log sections ($n = 1$) and hydrogen cyanide **c** with log sections ($n = 3$) and **d** without log sections ($n = 1$), during the fumigation of pine (*Pinus radiata* D.Don) log sections at 10 or 20 °C. Error bars represent the standard error of the mean

HCN concentration between treatment temperatures is commercially inconsequential as it equated to a difference of 0.25 g m^{-3}.

The results of these tests demonstrate that HCN is not a significant breakdown product of EDN when used to treat commodities with high moisture contents, such as pine logs.

Park et al. (2014) used 48 to 158 g m^{-3} of EDN to fumigate Korean red pine logs with an approximate load factor of 50%. Moisture content of the logs was 55.5 and 68.2% for the winter and spring trials, respectively, while 3-d average temperatures were 4.4 and 6.1 °C, respectively. The EDN used in that study had a 99% purity in balanced air and was also manufactured by Draslovka and marketed by BOC Australia. These authors did not detect HCN during their fumigations. Differences between the current results and those of Park et al. (2014) may be explained by the sensitivity of the analytical instrument used to measure HCN, i.e. GC–MS (current study) vs. GC–FID (Park et al. 2014) and/or a higher purity of EDN reagent. Because Park et al. (2014) did not detect HCN, these authors concluded that EDN is not converted to HCN during low-temperature fumigations. The results of the current study are consistent with this conclusion.

Concentration of EDN during fumigation

The initial concentration (0 h) of EDN in the treated space of empty chambers was 49.7 and 49.0 g m^{-3} at 10 and 20 °C, respectively, which did not change

Table 1 Average concentration (g m^{-3}) of hydrogen cyanide in the treated space during simulated fumigation of pine (*Pinus radiata* D.Don) logs at 10 or 20 °C

	Time (h)						
Temperature (°C)	0	2	4	6	8	10	Average
10	0.50 ns	0.45 ns	0.48 ns	0.50 ns	0.55 ns	0.52 ns	0.50b
20	0.41 ns	0.61 ns	0.69 ns	0.99 ns	0.91 ns	0.91 ns	0.75a

For average concentrations at respective temperatures ($n = 3$), values followed by a different letter are significantly different (P value < 0.001), REML and LSD 5% (0.13). At respective temperatures, concentrations over time were not significantly (ns) different (P value 0.055)

significantly over time at either temperature (Fig. 3b). Initial concentrations of EDN in the chambers with log sections were ≈ 70 g m^{-3} (influenced by the load factor of 46 ± 1.4%). The concentration of EDN in the treatments using log sections decreased exponentially over time at both temperatures (Fig. 3a) while it remained constant in the chambers' devoid of logs. Previous fumigant studies have showed that these decreased concentrations over time occur due to sorption (Hall et al. 2017; Hall et al. 2015). At 10 °C, 8.0 ± 2.0 g m^{-3} remained in the treated space after 10 h, whereas only 3.7 ± 0.9 g m^{-3} remained at 20 °C. During fumigation, time was the most significant (P value < 0.001, Wald/d.f. 1842) factor influencing the concentration of EDN in the treated space. The decrease in concentration over time is due primarily to the adsorption and absorption of molecules onto and into the wood.

A higher rate of EDN loss was measured at 20 °C than at 10 °C (P value < 0.001, Wald/d.f. 16), whereby 5.3 ± 1.4% and 11.6 ± 3.2% of the initial concentration remained in the treated space after 10 h of fumigation, respectively (Fig. 3). This temperature-related difference in concentration is similar to that shown by Hall et al. (2015), who found that 9.4 ± 0.4% of the initial EDN concentration remained in the treated space after 10 h for logs treated at 15 °C. Hence, under these simulated commercial conditions, any decomposition of EDN to HCN is not likely to occur.

Very little is known about the breakdown products of EDN during or after fumigation. Various studies, such as Hwang et al. (1989), Hemminger et al. (1979) and Kingsley et al. (1984), have quantified the bonding and surface chemistry of EDN with single crystal metals such as Pt, Ni and Cu. These studies focused on the adsorption, desorption and decomposition of EDN on metal surfaces, and hence, the results are not transferable to the conditions that occur during the fumigation of commodities such as logs and sawn timber. While gaps remain in our knowledge about all the breakdown products of EDN during and after fumigation, our study clearly demonstrates that HCN is not produced in measurable amounts under the experimental conditions used in this current study.

Higher temperatures generally increase the sorption rate of fumigants because the activity of molecules increases, so their ability to diffuse and penetrate into the material improves (Dumas and Bond 1977; Hall et al. 2017; Ren et al. 2006). The results of the current study confirm that greater sorption rates can be expected during EDN fumigations of recently harvested pine logs at higher temperatures, with sorption of EDN increasing as the fumigation temperature increases. This is the first time that a temperature-dependent response has been reported for the treatment of logs with EDN. This temperature-dependent response differs from the results reported by Hall et al. (2017) for MB, where sorption rates were similar at both 10 and 20 °C. These authors suggested that this difference in temperature was not sufficient to induce a measurable change in the activity of MB molecules, whereas this temperature difference does result in a measurable change in the activity of EDN molecules. In contrast, Ren et al. (2011) reported differences in the sorption rates of EDN and MB at 23–25 °C with 36% of the EDN and 30% of the MB remaining in the treated space after 48 h. However, the results of Ren et al. (2011), Hall et al. (2017) and those reported in this current study cannot be compared directly because the treatment parameters of temperature, load factor, tree species, the treated wood (log or sawn timber) and the moisture content were different.

The variation in sorption rates at different temperatures affects the development of fumigation schedules because sorption rates must be factored into the amount of EDN applied to ensure an efficacious QPS treatment. Hall et al. (2017) suggested that the temperature-dependent differences in sorption rates can reduce the concentration in the treated space over time to directly influence the CT product required to kill the target insect at a given concentration.

Pranamornkith et al. (2014b) and Hall et al. (2015) proposed formulae that can be used to predict the rate of fumigant sorption for EDN under different temperature conditions in the development of QPS fumigation schedules for further testing. In addition, higher treatment temperatures generally require lower doses to achieve efficacy (Najar-Rodriguez et al. 2015), indicating that an understanding of the chemical activity and efficacy of a fumigant at different temperatures is critical in the development of fumigation schedules. The sorption results presented here can be combined with data from similar studies (Hall et al. 2015; Park et al. 2014; Ren et al. 2011) and the EDN toxicity data for forest insects (Najar-Rodriguez et al. 2015; Pranamornkith et al. 2014a) to select concentrations for testing to identify the minimum dose required to control forest insects at different temperatures and times.

By comparing the CT values for larvae of two longhorn species, *A. ferus* and *A. glabripennis*, to EDN (19.50 g h m^{-3}) and HCN (17.67 g h m^{-3}), respectively (Najar-Rodriguez et al. 2015; Stejskal et al. 2014), it can be speculated that the toxicity of these compounds to larvae of these species may be similar. Therefore, the HCN impurity of 3.1%, reported in this work, equates to a CT of 2.4 g h m^{-3} HCN for a 50 g m^{-3} dose of EDN over a 3-h fumigation. By extrapolation of this data to the toxicity of these compounds to larvae of *A. ferus*, assuming equal toxicity, approximately 1.6% (0.3/19.50 g h m^{-3}) of the efficacy may be achieved by HCN under the conditions tested by Najar-Rodriguez et al. (2015). The effect of

fumigation on the mortality of different types of insects and the relationship between the toxicity of insects to EDN and HCN warrant further investigation.

Conclusions

Our study, for the first time, demonstrates that either fumigation of pine logs with EDN does not result in the production of HCN or the concentration of HCN produced is not detectable as it is masked by the HCN that is endogenous to the EDN. Impacts on chemical efficacy, environmental emissions and worker safety due to the presence of HCN are therefore likely to be negligible. The concentration of HCN in the cylinder tested was 3.1% (or 34.6 g m^{-3}). The manufacturer is now able to supply EDN with < 0.9% HCN, which will result in concentrations of HCN that are lower than those reported here. Furthermore, our results advance the knowledge required for the registration and commercialisation of EDN as a fumigant for the treatment of export logs.

Abbreviations

CT: Concentration × time; EDN: Ethanedinitrile; EPA: Environmental Protection Authority; GC: Gas chromatograph; HCN: Hydrogen cyanide; MB: Methyl bromide; MS: Mass spectrometer; PLOT: Porous layer open tubular; QPS: Quarantine and pre-shipment; REML: Residual maximum likelihood; STIMBR: Stakeholders in Methyl Bromide Reduction

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Authors' contributions

All authors contributed substantially to the work reported here. MH and AA conducted the study. MH, AA and PP wrote the manuscript. All authors read and approved the final manuscript.

Ethics approval and consent to participate

Not applicable

Competing interests

The authors declare that they have no competing interests.

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