Justification for not using Scrubbing, Destruction, or Recapture Equipment during the ventilation of Ethanedinitrile

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1. Purposes

The purpose of this document is to outline the key occupational health and safety issues, environmental issues and hazards associated with the use of scrubbing or recapture equipment during the ventilation of Ethanedinitrile (EDN™). Note throughout the text “scrubbing” will be used as a term to cover the use of a scrubbing, destruction or recapture technology unless it is listed without inverted commas i.e. scrubbing.

2. Background

In 2017 Draslovka applied to register EDN™ for use in New Zealand as a fumigant for export logs and timber. This application provided modelling to show the potential levels of EDN associated with fumigation and ventilation. The subsequent EPA assessment cast doubt on the validity of the modelling submitted and recommended that perceived atmospheric levels should be inflated to ensure that risks were not underestimated.

In June 2018 Worksafe New Zealand produced a report based on this assessment that recommended that EDN™ fumigations should be “scrubbed” during ventilation to protect workers on the port.

Since June 2018 a series of 9 commercial scale log stack fumigations were undertaken that have confirmed the levels of EDN™ required to control the pests of concern on New Zealand logs and the levels of EDN™ that are released to the atmosphere at the time of ventilation. Draslovka has also confirmed that based on the results of these trials it has revised the proposed controls for its use of EDN™ to

- A maximum treatment rate of EDN™120 gm/m³ for 24 hours. Note MPI will be asking trading partners to approve a phytosanitary treatment for imported New Zealand logs of 100 gm/m³ but until we have confirmation of this lower rate the application for registration will ask for approval of 120 gm/m³
- Ventilation only to commence once the concentration under the tarpaulin averages 1000ppm.
- A buffer zone for unprotected workers of 20m, and.
- Re-entry to the buffer zone for non-protected workers permitted once the atmospheric level of EDN™ is at or below 3 parts per million (ppm) following ventilation (field trials show this can be achieved in under three hours).

During an “average” fumigation of a 1000m³ stack at a fumigation rate of 120 gm/m³ 120kg of product will be applied to the stack to provide a concentration of approximately 54,500 ppm at 15 deg. C.

The field trials mentioned above confirmed earlier laboratory testing show that 20 hours after treatment the total EDN under the tarpaulin will have dropped to approximately 1.1% of the initial application. Table 1

1 With review by Derek Miller Occupational Hygienist and Dr Jack Armstrong Quarantine Scientific
2 EDN™ is the form of Ethanedinitrile patented and trademarked by the manufacturer Lučební závody Draslovka (Draslovka).
provides the data from the field trials for the replicates that were treated with 120 gm/m$^3$ for either 16 or 20 hours. In all cases the end of fumigation concentration was under 1000ppm. Our proposed dose rate and treatment time for registration as mentioned above will be 120 g/m$^3$ for 20 hours.

Table 1 Field trial results from the trials conducted in Tokoroa 2019

<table>
<thead>
<tr>
<th>Gas Chromatograph readings</th>
<th>120</th>
<th>120</th>
<th>120</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EDN Rate gm/m$^3$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fumigation treatment time - hours</strong></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>replicate</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Under the tarpaulin after application ppm</td>
<td>52,855</td>
<td>61,485</td>
<td>58,381</td>
<td>77,169</td>
</tr>
<tr>
<td>Under the tarpaulin prior ventilation ppm</td>
<td>700</td>
<td>992</td>
<td>483</td>
<td>483</td>
</tr>
<tr>
<td>% EDN at end of fumigation</td>
<td>1.32%</td>
<td>1.61%</td>
<td>0.83%</td>
<td>0.63%</td>
</tr>
<tr>
<td>Highest reading 20 m – ventilation ppm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Highest reading 5 m – ventilation ppm in first half hour</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>12</td>
</tr>
</tbody>
</table>

Note from the nine replicates that were conducted between February and May 2019 (application rates varied from 80 to 120gm/m$^3$ and the length of fumigations varied between 16 and 24 hours) end point concentration varied between 0.2 to 3.9% or 182 ppm to 2816 ppm. The average end point concentration from the nine trials were 833 ppm or 1.8 g/m$^3$. It is as a consequence of this variation that Draslovka has asked that a control be imposed that limits the pre-ventilation under tarpaulin concentration to 1000 ppm.

Draslovka has undertaken a review of the globally available “scrubbing” technologies and has been unable to identify any technology that can effectively provide 100% “scrubbing” of any fumigant. It is also recognised that “scrubbing” adds additional processes and hazardous substances to fumigation and such technologies come with their own inherent risks and safety concerns. From an economic perspective a requirement for “scrubbing” increases the cost not only for the process of “scrubbing” but also the disposal of the “scrubbing” waste. Albeit that the primary concern should always be the health and safety of those involved, it should be noted that both costs will come straight off the bottom line and primarily affect the price paid to growers.

Draslovka recognises that the full elimination of the risks associated with the release of any fumigant can only be achieved by not using that fumigant. 8 years of research in New Zealand by STIMBR has been unable to identify any other non-fumigant alternative to support the export of New Zealand’s timber and logs (Appendix 1 of https://www.epa.govt.nz/assets/FileAPI/hsno-ar/APP202804/ed8b925769/EDN- appendices-27-2-2018.pdf).

There is an imperative to perform any work activity as safely as possible, with a vision of zero harm. However, the fact of the matter remains that whatever methodology is employed to overcome the risks associated with fumigation they must be based on a risk analyses to ensure that risks are mitigated as far as reasonably practicable. To do this for EDN it is imperative that any analyses of “scrubbing” provide a nett risk that balances the release of 1000ppm of EDN to the atmosphere with the risks to workers and environment associated with the equipment and materials used in the “scrubbing” process and the subsequent disposal of the “scrubbing” effluent.
This document considers only the “scrubbing” of EDN post fumigation of logs and timber in New Zealand. The method used to fumigate these products is essentially the same as that used to fumigate logs and timber with methyl bromide. A brief description of EDN and comparison with methyl bromide is documented Appendix 1.

3. New Zealand’s Health and Safety Legislation

The sections of New Zealand’s Health and safety regulations that will primarily influence how Worksafe New Zealand must approach the formulation of workplace controls for the use of EDN are documented below:

3.1. Health and Safety at Work

There are three key sections of the Health and Safety at Work legislation which should be taken into account:

HSWA Section 22: Meaning of reasonably practicable\(^4\)

In this Act, unless the context otherwise requires, reasonably practicable, in relation to a duty of a PCBU set out in subpart 2 of Part 2, means that which is, or was, at a particular time, reasonably able to be done in relation to ensuring health and safety, taking into account and weighing up all relevant matters, including—

(a) the likelihood of the hazard or the risk concerned occurring; and

(b) the degree of harm that might result from the hazard or risk; and

(c) what the person concerned knows, or ought reasonably to know, about—

(i) the hazard or risk; and

(ii) ways of eliminating or minimising the risk; and

(d) the availability and suitability of ways to eliminate or minimise the risk; and

(e) after assessing the extent of the risk and the available ways of eliminating or minimising the risk, the cost associated with available ways of eliminating or minimising the risk, including whether the cost is grossly disproportionate to the risk.

HSW(GRWM) Regulation 6 – General Risk & Workplace Risk Regulations: Hierarchy of Control Measures\(^5\)

(1) This regulation applies if it is not reasonably practicable for a PCBU to eliminate risks to health and safety in accordance with section 30(1)(a) of the Act.

(2) A PCBU must, to minimise risks to health and safety, implement control measures in accordance with this regulation.

(3) The PCBU must minimise risks to health and safety, so far as is reasonably practicable, by taking 1 or more of the following actions that is the most appropriate and effective taking into account the nature of the risk:


(a) substituting (wholly or partly) the hazard giving rise to the risk with something that gives rise to a lesser risk:

(b) isolating the hazard giving rise to the risk to prevent any person coming into contact with it:

(c) implementing engineering controls.

(4) If a risk then remains, the PCBU must minimise the remaining risk, so far as is reasonably practicable, by implementing administrative controls.

(5) If a risk then remains, the PCBU must minimise the remaining risk by ensuring the provision and use of suitable personal protective equipment.

3.2. HSW (Haz Subs) Regulations 2017

Section 14 of the HSWA regulation covers the use of fumigants and in particular subsection 14.16 deals with ventilation of fumigants

14.16 Ventilation of fumigation area and safety of risk area

(1) This regulation applies to the following types of fumigation:

   (a) space fumigation:

   (b) fumigation of—

      (i) a glasshouse; or

      (ii) a ship; or

      (iii) commodities on a ship; or

      (iv) an aircraft; or

      (v) a silo; or

      (vi) grain or other loose material in small bins, or in bulk on the floor of a building or other structure:

   (c) fumigation in a fumigation cell:

   (d) fumigation in a shipping container:

   (e) fumigation under sheets:

   (f) fumigation of soil or compost in a glasshouse, building, or other enclosed structure.

(2) A PCBU with management or control of fumigation must—

   (a) ensure, so far as is reasonably practicable, that the fumigation area is properly ventilated so that, at the completion of fumigation,—

      (i) in the opinion of a certified handler, the fumigant used to carry out the fumigation has dispersed from all parts of the fumigation area (including all confined spaces in the fumigation area), and

   

(ii) the maximum concentration of the fumigant used in the fumigation that is in the risk area is reduced to the lower of the following:

(A) the maximum level of exposure permitted in the prescribed exposure standard set in relation to the fumigant or any component of it (if any);

(B) the lowest level practicable: and

(b) before allowing any person access to the risk area, ensure that the certified handler referred to in subclause (2)(a)(i) is satisfied that the risk area is safe for the person to enter.

(3) However, if a relevant safe work instrument prescribes modified requirements for proper ventilation of the fumigation area or safety of the risk area (or both), the PCBU must ensure that the modified requirements are complied with.

(4) A PCBU who contravenes subclause (2) or (3) commits an offence and is liable on conviction,—

(a) for an individual, to a fine not exceeding $10,000:

(b) for any other person, to a fine not exceeding $50,000.

Compare: Gazette 2004, p 3471, Schedule 3 cl 9

4. Hierarchy of Controls – EDN Specifics

Under section 30(1)(a) of HSWA the PCBU must eliminate risks to health and safety so far as reasonably practicable. If this is not reasonably practicable, the PCBU must minimise the risks so far as is reasonably practicable following the hierarchy of controls. The hierarchy of controls is set out in regulation 6 of the GRWM Regulations (see section 3). Table 2 summarises the Hierarchy of controls

Table 1 The Hierarchy of controls as per the HSWA regulations

<table>
<thead>
<tr>
<th>Elimination</th>
<th>removes the cause of danger completely.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substitution</td>
<td>controls the hazard by replacing it with a less risky way to achieve the same outcome.</td>
</tr>
<tr>
<td>Isolation</td>
<td>separates the hazard from the people at risk by isolating it.</td>
</tr>
<tr>
<td>Engineering Controls</td>
<td>using engineering controls. i.e. making physical changes, to lessen any remaining risk. e.g. redesign a machine by adding safeguards.</td>
</tr>
<tr>
<td>Administrative Controls</td>
<td>use administrative controls to lessen the risk. e.g. install signs, rotate jobs.</td>
</tr>
<tr>
<td>Personal Protective Equipment</td>
<td>require your employees to wear PPE, e.g. provide gloves, earplugs, goggles, iridescent vests</td>
</tr>
</tbody>
</table>

The hierarchy of controls creates a systematic approach to managing safety in the workplace by providing a structure to select the most effective control measures to eliminate or reduce the risk of certain hazards that have been identified as being caused by the operations of PCBU.
The hierarchy of controls has six levels of control measures, the most effective measure is at the top of the hierarchy and the least effective is at the bottom.

The key issue with employing the Hierarchy of Controls in isolation is that it can sometimes exclude auxiliary risks which can potentially cause even greater health and safety issues outside the key process that is being considered.

Table 3 lists EDN specific characteristics with regard to each control

**Table 3 Hierarchy of Controls applied to the use of EDN**

<table>
<thead>
<tr>
<th>Control</th>
<th>Description</th>
</tr>
</thead>
</table>
| Elimination | Pre-export phytosanitary treatments of timber and logs are required by the importing country according to their phytosanitary requirements. Only two (relatively small) markets for New Zealand timber and logs do not require fumigation – Japan and Korea.  
As noted above the STIMBR research programme has looked at all possible approaches to ensure the New Zealand logs are pest free. This includes the assessment of a systems\(^7\) approach.  
Research by Scion has shown in the case of New Zealand logs it is not possible to prevent infestation in the forest or at the port because of the high number of insects present and the huge hectarages of forest involved. This is compounded by New Zealand’s benign climate which does not provide a period of winter dormancy when pests of concern are not present. |
| Substitution | Efforts to find a substitute for EDN™ have been unsuccessful. It should be noted that EDN™ is in fact the recommended substitute for methyl bromide.  
There are a number of potential substitutions for the use of EDN™ for the treatment of timber and logs – all of which carry their own associated risks. Any substitution would need to be approved by trading partners. Currently China allows 10% of export logs to be debarked to reduce risk. China is not prepared to increase this percentage. A number of debarking plants have been built to fill this demand. India does not recognise debarking as a phytosanitary treatment and currently is only prepared to accept fumigation with methyl bromide.  
Fumigation has become the accepted practice to treat timber and wooden structures globally (ISPM, 2009). Fumigants can reach the surface and penetrate the timber and logs that other pesticides/physical methods do not easily reach. This is particularly important for the bark boring insects which constitute two of the three insects of concern found on New Zealand logs.  
The fumigant phosphine is currently used to treat in hold logs to China (on an experimental permit) but no other country allows the use of phosphine. All top stow to China and logs to India must currently be fumigated with methyl bromide.  
In an international review of potential fumigants for use on logs STIMBR reviewed 15 significant chemical candidates and 18 minor chemicals. This review identified EDN™ as the only timber fumigant alternative to methyl bromide and supported further study and registration |

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\(^7\) A system approach utilises cultural control of pests in the field (prior to harvest) potentially in combination with periods of low pest activity to ensure product ready for export is essentially pest free.
| **Isolation** | Isolation is used for unprotected workers. The isolation of risks associated with EDN™ can be achieved by the use of restricted entry areas and buffer zones. The proposed buffer zone for unprotected workers during an EDN™ fumigation is 20 metres for a log stack with no re-entry to that space until the level falls below 3ppm. This buffer is supported by the field trial data. |
| **Engineering Controls** | It is difficult to develop engineering controls for the ventilation of EDN™ fumigated log or timber stacks. It should be noted however that tarpaulin removal or ship hold opening is not a totally uncontrolled process with operators having significant control over the speed at which both processes take place. With EDN™'s high volatility slowing release allows EDN™ already released to dilute to lower concentrations before more EDN™ is released. In the case of ship holds the hatches can be temporarily closed with no additional risk to workers. Monitors are available to monitor EDN levels in the stack at the end of fumigation and the level of EDN in the air during ventilation. |
| **Administrative Controls** | The primary administrative control that Draslovka has planned for the use of EDN™ is its Services Group Product Stewardship, Training, and Certification Process. Currently Draslovka is the sole producer of EDN™ globally. With the product's high purity, it is unlikely any other producer will supply EDN™ to New Zealand at the purity which is currently requesting registration. As the provider of 100% of EDN™ in New Zealand Draslovka will control the supply pathways and will only provide product to those companies that operate under its Product Stewardship scheme. Under this scheme all users involved in the application of EDN™ are individually trained, certified, and audited by Draslovka Services Specialists. Certification will be revoked or suspended at any time the substance is misused and if any controls are broken. Administrative controls referred to in HSNOCOP31 - The Control and Safe Use of Fumigants must be followed. and in addition, the nominated fumigation company who undertakes the fumigation process must hold all necessary licenses. including but not limited to the Controlled Substances Licenses necessary for the safe handling and transportation of a Class 2.3/2.1 fumigant. |
It is recognised that Personal Protective Equipment (PPE) should be the last line of defence.

It is noted that EDN™ can only have a significant effect on humans via inhalation. EDN™ will cause lacrimation (tears) at above 15ppm but this effect is instantaneous and does not have any negative long-term effect. Note the estimated LC50 for EDN is 136 ppm for 4 hours.

As such the appropriate PPE for use within the buffer zone will be a full-face mask using an A2B2 filter. This filter provides excellent long-term protection even at high concentrations. The filters have been tested well above 1000 ppm – i.e. up to 5000 ppm. The corresponding service lives are noted in table 4.

<table>
<thead>
<tr>
<th>(CN)₂</th>
<th>A2B2E2K1 Hg P3 R D 6738815</th>
<th>A2B2 6738775</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>2500</td>
<td>22</td>
<td>16</td>
</tr>
<tr>
<td>1000</td>
<td>59</td>
<td>39</td>
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<td>500</td>
<td>124</td>
<td>76</td>
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<td>150</td>
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<tr>
<td>100</td>
<td>693</td>
<td>348</td>
</tr>
<tr>
<td>50</td>
<td>1453</td>
<td>674</td>
</tr>
<tr>
<td>10</td>
<td>8106</td>
<td>3124</td>
</tr>
</tbody>
</table>

Draslovka recommends that for applicators working in and around the log stacks during application and ventilation, air purifying filters should be changed every day to ensure the maximum protection limits. This is standard practice for filter management.

5. Scrubbing, Destruction, and Recapture Equipment Considerations:

This section builds on a document submitted as part of the methyl bromide reassessment process “Revised Review of Proposed Concepts and Technologies to Recapture and/or Destroy Residual Methyl Bromide (MB) after Log Fumigations at New Zealand Ports” by Dr Armstrong. The document provides detail on the different scrubbing, recapture, and destruction technologies available for other fumigants and in particular methyl bromide.

For EDN™ there are four approaches to managing the release of the air from the treated structure (i.e. from in a container, from under a tarpaulin of from a ship hold) which contains a maximum concentration of 1000 ppm of EDN™. These include:

- Release to the atmosphere i.e. Environmental Hydrolyzation and Degradation.
- Burning i.e. Combustion of the remaining EDN™.

- Chemisorption i.e. liquid scrubbing, and.
- Carbon recapture i.e. absorption onto activated carbon

The four processes and their advantages and disadvantages are outlined below.

5.1. Environmental Hydrolyzation and Degradation

The easiest, simplest, and safest approach in terms of minimizing subsidiary risks is to release any remaining concentration of EDN™ into the atmosphere post the treatment period. This can be achieved in a controlled way (i.e. by monitoring atmospheric levels at a set distance within the buffer zone and slowing down release if levels start to rise). It ensures that no additional risks are introduced to the site.

The field trials described in Section 2 have shown that at 120gm/m³ with less than 1000ppm released to the atmosphere 0 ppm was recorded at the edge of the 20m buffer zone and a maximum of 12 ppm was measured at 5 meters in the first half hour.

It is also noted that the AERMOD dispersion modelling platform was used to simulate multiple stack scenarios of 30 log stacks treated at a maximum treatment rate of 150 g/m³ for 24 hours. EDN™ dose rates between 80 and 120 g/m³ for 16 to 24 hours were used in the large-scale trials conducted at Tokoroa. The parameters used in the model were, in most cases, similar to those tested at Tokoroa:

- In the modelling, the log stack size was 750 m³ similar to the commercial log volume and the trials conducted at Tokoroa (680 m³).
- Stack height of 3.3 m was used in the modelling which is similar to the large-scale trials conducted at Tokoroa (3 m).
- The tarpaulin material tested in the laboratory permeation trial as modelling input had been used in the large-scale trials.
- A loading factor of between 45 to 55% was used in the modelling compared with loading factors between 58 and 59 % calculated for the large-scale trials.
- Residual EDN concentrations of 376 ppm to 660 ppm were used as ventilation emission at the end of the treatment period in the modelling. In the large-scale trials, the average endpoint concentration was 833 ppm. We propose 1000 ppm as endpoint concentration.

AERMOD was conducted with 5-years of hourly 24/7 meteorological data with randomized emissions. A 40 simulation runs over the 5-years is equivalent to 200-years of modelled randomized emissions. A maximum downwind EDN concentration of 0.016 ppm (24-hour average) was estimated at 20 m from the stack at 95th percentile at the highest dose rate (150 g/m³).

Of the nine large scale trials monitored for the EDN emission during ventilation at Tokoroa, no EDN was found at 20 m from the log stack in the seven trials. 2 and 5 ppm were found in the two trials. The maximum EDN concentration (i.e.) 2 & 5 ppm were spot sampling and not 24 hours average. During the application and treatment period, no EDN was found at 20 m from the log stacks. Hence averaging this concentration (2 & 5 ppm) over 24 hours would provide 0.08 ppm and 0.20 ppm respectively which could be related to modelling results (0.016 ppm) as it was determined at the 95th percentile and not 99.99 or 100%. Nevertheless, those average values were lower than 3ppm recommended by Work Safe.

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### Advantages

- Natural breakdown of the product in the environment and in log stack so that approximately of 1% of EDN™ is left after 20 hours. Measurement of the atmosphere in the fumigation space will ensure the concentration does not exceed 1000 ppm
- Controlled release of fumigant through isolation, engineering, and administrative controls (i.e. the hierarchy of controls can be applied)
- No additional equipment or logistics considerations on site
- No additional chemicals or substances added to the site
- No additional training is required to conduct any scrubbing
- No additional cost added to the fumigation process
- Buffer zones provide adequate protection for bystanders based on comprehensive data points. Note buffer zones are monitored in real time to allow the buffer to be adjusted if required
- Will not increase the overall treatment time minimizing the effect on normal port operations and logistics optimising export efficiency
- Fumigation can be conducted at the existing ports and in ship holds
- Cost effective method, commercially competitive with current fumigant treatments which will optimize return to growers
- Can be applied equally to small size (shipping container) and large-scale fumigation (ship in-hold)
- Modelling shows acceptable levels of EDN™ over time for up to 30 log stacks per day

### Disadvantages

- Uninformed Public Perception about fumigation practices and risks to health
- Need to achieve a minimum of 1000 ppm as end point concentration may lengthen the treatment and have a limited effect on port logistics

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#### 5.2. Combustion of the remaining EDN™

In 2015 Draslovka investigated the development of a mobile burning unit to “scrub” EDN™. The work was initiated because this approach is used to treat effluent emission at the manufacturing facility in Kolin, Czech Republic.

Draslovka built a prototype of a scalable burning unit. The unit uses LPG burner technology as the fuel. The LPG consumption is considerable at 750 Liters LPG/hour with an air flow of 2000 Nm3/hour.

Typically, 10 air passes are needed to burn off all the EDN. In a 1000 m³ log stack this will need 10,000 m³ of air to be moved through the machine requiring 5 hours to scrub 1000ppm, and consuming 3.75 tonnes of LPG. If every log stack is to be scrubbed this will have a significant effect on New Zealand carbon footprint and so damage to the atmosphere.

The unit is ‘portable’ but would require cranes and trucks to move the equipment from point A to point B on the port.
- Acceptable destruction of the free-air emissions of EDN
- Large Technology Unit (Footprint)
- Equipment includes an LPG tank with sufficient capacity to fuel the burner. This tank would need to be refilled in-situ.
- In many of New Zealand’s ports an emissions consent would need to be granted by the local council before the technology could be used.
- Limited mobility due to rigid connections that must be dismantled before transportation.
- This unit could only be made mobile with the use of a crane and a rigid truck.
- The use of a large LPG burner on port introduces an additional flammability risk to the port.
- A concrete base must be built beneath the technology in advance and the line must be fixed to it. An asphalt surface cannot be used because of melting and ignition issues from the heat output of the burner. This would require a number of concrete bases to be poured on the port with large flexible pipes laid from the log stack to these hubs.
- The technology would require multiple recapture points for a large stack due to variable air movement within the stack.
- As this technology is only semi mobile ducting from the individual stacks will need to be connected to a central scrubbing system. This would impede the movement of vehicles and workers at the port or require a major port modification to place the ducts below the port surface. Any need for such structural changes to the log yard would significantly increase the cost and delay the uptake of EDN as a fumigant until both a resource consent can be gained for the project and the ducts installed.
- The need to burn off all the EDN™ will take approximately 5 hours increasing the total treatment time, impacting port operations and increasing cost.

### 5.3. Chemisorption

EDN™ can be captured from the atmosphere by scrubbing with a solution of NaOH. The air containing EDN is passed through the solution and the following reaction occurs:

\[
C_{2}N_{2} + 2 \text{NaOH} + \text{NaOCI} \rightarrow 2 \text{NaOCN} + \text{NaCl} + \text{H}_{2}\text{O}
\]

Disposal of 1 kg of EDN requires 1.5 kg Sodium Hydroxide and 1.5 kg Sodium Hypochlorite.

Theoretically 650 Liters of 12% NaOH solution will be required to recapture 50 kg of EDN. Based on 2.2 kg remaining in a 1000 m³ stack at the end of fumigation this would require 28.6 liters per stack. At the rate of 30 stacks per day this would require disposal of 858 liters of toxic waste per day. A similar approach is discussed in Dr Armstrong’s report where sodium thiosulphate is used to remove methyl bromide.

A trial undertaken in Australia (appendix 2) with an average concentration of 4539 ppm at the start of ventilation scrubbing dropped the concentration to an average of 193 (4.3%) ppm after 4 hours and then did not fall any further over the next 8 hours. A similar decrease takes place naturally over
approximately 10 hours in a log stack\textsuperscript{10} between 10- and 20-hours post fumigation. The Australian trial concluded that the EDN concentration inside the timber tarpaulin with a liquid scrubber would be similar to the concentration by extending the treatment time without scrubbing.

Apart from machinery related risks the main risk associated with this process is the potential for workers to have contact with the scrubbing solution pre and post scrubbing. Handling and exposure of sodium hydroxide, sodium hypochlorite, sodium cyanate and sodium chloride by the fumigators/workers creates safety concerns for workers. Disposal of the waste (sodium cyanate and sodium chloride) will potentially also cause environmental issues and public health concerns.

Sodium hydroxide is a highly caustic base and alkali. It readily decomposes proteins, lipids in living tissues and consequently causes chemical burns and may induce permanent blindness upon contact with eyes. Sodium hydroxide can dissolve in water. A high concentration in water will result in toxic effects for aquatic organisms e.g. fish.

NZ WorkSafe exposure value for Sodium salts – 1 to 5 mg/m\textsuperscript{3} TWA

NZ WorkSafe exposure value for Sodium hydroxide – 2 mg/m\textsuperscript{3} TWA

Sodium hypochlorite has a TWA value of 1 ppm. Sodium hypochlorite is a strong oxidizer. Oxidation reactions are corrosive. Solutions burn the skin and cause eye damage. Additionally, fumes from the substances causes respiratory irritation. It is also very toxic to aquatic organisms.

Sodium cyanate is toxic to humans and aquatic environment.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td>• Proven effective on a small scale in New Zealand for the handling of EDN emissions at Plant &amp; Food Research in Palmerston North. Total recapture per annum of up to 10kg of EDN™ emissions equivalent to less than 5 log stacks.</td>
<td>• The NaOH in its own right can be a risky chemical to use</td>
</tr>
<tr>
<td>• It is scalable technology that can be used to scrub a range of fumigation structures</td>
<td>• Disposal of the dangerous waste (a mixture of NaOH and NaCN) must be done by authorized person</td>
</tr>
</tbody>
</table>

\textsuperscript{10} https://www.epa.govt.nz/assets/FileAPI/hsno-ar/APP202804/d36c434dd5/Further_information_Efficacy_Data_June_2019.pdf
5.4. Carbon Recapture

Activated carbon can be used to recapture EDN emissions post-fumigation. Here the EDN is removed by being absorbed onto the activated charcoal. This method is used to scrub a range of fumigants. For any fumigant the approach is considered very ineffective and merely transfers the issue from one location to another location since over time the fumigant will desorb off the activated carbon to the atmosphere – there is a possibility to use chemicals to actively desorb the product, but there is no cradle-to-cradle approach on how to mitigate the subsidiary risks associated with this. For carbon recapture no estimate can be given of the time required to scrub with activated carbon.

The use of carbon recapture systems such as those developed by NORDIKO is an expensive form of recapture which has not be proven at any scale in New Zealand. As with Chemisorption the site for disposal of the contaminated carbon is yet to be identified.

The ability of an activated carbon filter to function efficiently depends on a number of factors including temperature, humidity, residence time, filter age, evaporation rate and chemical concentration.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Somewhat portable and scalable</td>
<td>• The use of activated carbon filters to recapture free-air emissions is merely a transference of the issues from one location to another location.</td>
</tr>
<tr>
<td></td>
<td>• There is no technology that will show when the carbon has to be changed it is purely based on breakthrough monitoring</td>
</tr>
<tr>
<td></td>
<td>• There is no safe method for the destruction of activated carbon, with the current proposed solution being to bury the toxic laden carbon in landfill.</td>
</tr>
<tr>
<td></td>
<td>• The calculated volume of activated carbon per kilogram of EDN™ is 20kg, (similar to methyl bromide) requiring approximately 44 kg of activated carbon for each 1000m³ log stack.</td>
</tr>
<tr>
<td></td>
<td>• Activated carbon systems have inherent issues with moisture ingress and subsequent unknown quantities of degradation by-products.</td>
</tr>
<tr>
<td></td>
<td>• Although scaling is possible, scaling to large size fumigations like a ship could be a challenge</td>
</tr>
<tr>
<td></td>
<td>• Increase the overall time for treatment that will impede port operations, logistics and export efficiency and have significant economic impact</td>
</tr>
<tr>
<td></td>
<td>• Require multiple recapture points for a large stack due to variable air movement within the stack</td>
</tr>
</tbody>
</table>

6. Conclusion:

There is no known or current viable scrubber for a fumigant in New Zealand that is commercially available, cost effective, portable, efficient, and suited to local conditions for log fumigation. STIMBR and more recently the largest fumigator in New Zealand, Genera, have spent millions of dollars on testing and developing “scrubbing” technologies over the last 8 years to satisfy the EPA’s controls which become mandatory on the 29th October 2020. This control requires that the level of methyl bromide in air released after fumigation is dropped from approximately 5000ppm to 5 ppm. Methyl bromide has proven environmental effects and its use causes significant anxiety across sectors of the community. EDN is the industries proposed substitute for methyl bromide.

Promising technologies identified in STIMBR’s research programme that have performed well in the lab or on container size stacks have proven that they cannot be easily scaled. With just over one year to the deadline an 80% reduction in the methyl bromide present at the end of fumigation using a chemisorption
technology has been shown to be just achievable. Disposal of the relatively toxic waste from this technology is proving to be an issue. The cost of a single unit is over a million dollars. The costs of running and maintaining a unit have not been calculated since all work to date has been viewed as research and improvement. At the moment at the Port of Tauranga scrubbing doubles the cost of a fumigation but the long-term cost may be higher depending on wear and tear on the machine and waste disposal costs.

Three potential EDN “scrubbing” technologies are discussed in this document; however, they have not been commercially tested for log fumigation as they are considered to only add and multiply risk to workers in and around the port. To date no work has been undertaken to develop a commercial sized scrubber since it does not make commercial sense and the recent EDN field trials show that the natural break down of EDN (i.e. self-scrubbing) occurs in the log stack to the extent that the nominated level of 1000 ppm can be reached within commercially acceptable treatment times. Monitoring equipment is available that will measure EDN levels both in the stack and in the atmosphere.

As described in section 5.1 field trial data from commercial sized log stacks showed that an application of 120gm/m³ for 20 hours the use of buffer zones and atmospheric monitoring at key points of the ventilation process will allow EDN to be safely used.

Table 3 systematically describes how the hierarchy of controls is applied to use of EDN so that the residual risk that remains within the buffer zone at the time of ventilation is managed with PPE.

Draslovka notes that with the natural break down of EDN (self-scrubbing) risks can be reduced by using this attribute to allow the level released to the atmosphere to be less than 1000ppm so that the process:

- Doesn’t require the introduction of any additional risk in the form of chemicals, equipment, training and disposal
- It will not increase the overall fumigation time hence normal port operations, logistics and export efficiency can be maintained without having a significant economic impact
- Fumigation can be conducted at the existing ports and ship in-hold
- Cost effective method, commercially competitive with current fumigants treatment
- Can be applied to small size (shipping container) and large-scale fumigation (ship in-hold)

Draslovka is confident that ventilation informed by the use of the available monitoring equipment and the Draslovka stewardship programme will allow EDN to be used safely without scrubbing in a way that will not expose workers to significant risk. It is concerned that the requirement to introduce another process, machinery and “scrubbing” substance will result in additional risk on the port, impede port logistics, have a negative effect on the environment and decrease the return to New Zealand Inc.

References:


NZ EPA Methyl bromide reassessment report (2010)
Appendix 1 EDN™ Background:

Introduction

EDN™ is not a new molecule. It was discovered in 1815 but was not manufactured on a large scale until the late nineteenth century.

- EDN™ was patented in 1960 for use in the nitrate fertiliser industry
- EDN™ is used in the production of nitrocellulose
- In medicine as an active ingredient in wart remover
- In molecular biology to help detect gene sequences
- In cosmetics industry in nail polish

EDN™ was identified as a possible fumigant in 1996 and was patented by CSIRO, an Australian government research organisation. The patent was later transferred to Draslovka.

Scientific research has shown that EDN™ can be used as a soil fumigant to kill soil borne pathogens, soil borne insects, nematodes and weeds prior to planting vegetable and fruit crops.

EDN™ is also very effective on insect pests and pathogens of forest products.

Based on these characteristics, EDN™ is considered as a suitable replacement for ozone depleting methyl bromide.

STIMBR NZ reviewed 15 significant chemical candidates and 18 minor chemicals. They identified EDN™ as the only timber fumigant alternative to methyl bromide and supported for further study and registration.

Key Differences when compared with methyl bromide:

Ozone depletion since the 1970s has been attributed to an increase in chlorine and bromine in the stratosphere. While chlorine exists in the stratosphere at approximately 3.5 ppb, bromine is present at 15-20 ppt (WMO, 2003).

Reactions involving bromine are approximately 50 times faster than reactions involving chlorine. Therefore, the smaller amount of bromine in the stratosphere still represents a significant danger to the ozone layer. Bromine reacts with the reservoir chlorine species, freeing the chlorine to react with additional chlorine (WMO, 1994). Methyl bromide is the major carrier of bromine to the stratosphere and breaks down to form bromine which reacts with ozone molecules. Reactions involving bromide are considered to contribute 50% of the loss of ozone over Antarctica each year (Chipperfield & Pyle, 1998).

Based on its ability to deplete ozone (referred to as the ozone depletion potential (ODP)) of 0.38 and lifetime of 0.7 years, methyl bromide has been classified as a Class 1 stratospheric ozone depletor (WMO, 2003).

Ozone is known to play a key function in moderating the climate of the earth by absorbing ultraviolet radiation from the sun (UV-B) and essentially acts as a sunscreen for the planet.

Methyl bromide is listed as an ozone-depleting substance under the Montreal Protocol (UNEP, 1996) and had been banned in Europe. less than 5 ppm should be released into the environment in NZ from 2020 (NZEPA 2010) and for domestic treatment in many countries. Although methyl bromide uses for domestic treatment have been restricted or significantly reduced. QPS use have been significantly increased due to increase of trade which is contributing a significant danger to the ozone layer. For logs use, New Zealand is the third highest methyl bromide user in the world.
Ozone layer depletion results in an increased incidence of human disease, in particular, skin cancer, cataracts and immune suppression due to the increased exposure to ultraviolet (UV) radiation experienced by the population.

A guide published by the World Health Organization indicates that some 220 deaths in New Zealand in 2002 were attributable to exposure to ultraviolet radiation (NZEPA, 2010)

Comparative Properties:

<table>
<thead>
<tr>
<th>Properties</th>
<th>EDN</th>
<th>Methyl Bromide</th>
<th>EDN Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>-21 °C</td>
<td>3.6 °C</td>
<td>EDN can be applied as a gas and is effective against target pests at very low temperatures.</td>
</tr>
<tr>
<td>Vapour Pressure</td>
<td>515 kPa (@21°C)</td>
<td>214 kPa (@21°C)</td>
<td>EDN has a high vapour pressure hence it will penetrate quickly and distribute easier than methyl bromide.</td>
</tr>
<tr>
<td>Density in Air</td>
<td>2.2</td>
<td>3.27</td>
<td>Both fumigants are heavier than air but EDN is lighter than methyl bromide hence ventilation can be quicker than methyl bromide.</td>
</tr>
<tr>
<td>Spec. Volume @ 25 °C and 1 atm</td>
<td>462L/kg</td>
<td>256L/kg</td>
<td>This is the comparative volume of each product – EDN creates much more gas per kg.</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>52.04</td>
<td>94.94</td>
<td>EDN has a low molecular weight which means it can move quickly from areas of high concentration to low concentration and achieve equilibrium faster.</td>
</tr>
<tr>
<td>Van der Waals radii</td>
<td>160 pm</td>
<td>185 pm</td>
<td>Smaller molecule hence greater penetration into timber and logs</td>
</tr>
</tbody>
</table>

Comparative use:

In New Zealand, under current Ministry of Primary Industries (MPI) protocols during Methyl Bromide fumigation, it is mandatory that the End Point Concentration (EPC) after the treatment time is 50% of the starting concentration.

Therefore, if we take a worked example of a 1000m3 log stack for Methyl Bromide fumigation:

Treated Volume: 1000 m3
MB Dose Rate: 120 g/m³
Applied Product: 120 kg
EPC (50 %): 60kg

Hence for every 1000 m³ of Methyl Bromide treated volume, 60kg of Methyl Bromide is initially released to the environment upon ventilation – this does not take into consideration the desorption of Methyl Bromide from timber and logs which will continue beyond the ventilation period.
In comparison, during EDN™ treatment - efficacy studies conducted by Plant & Food Research have shown that less than 1.8% (833ppm) of the initial concentration is remaining at the end of the treatment period. This 1.8% of the applied EDN™ dose remaining in the treated environment can be slowly and safely released into the environment without any risks to the environment and community.

Treated Volume: 1000 m³
EDN™ Dose Rate: 120 g/m³
Applied Product: 120 kg
EPC (1.8%): 2.2 kg

Hence for every 1000 m³ of EDN™ treated volume, only 2.2 kg of EDN™ is released to the environment upon ventilation - scientific studies have shown that no detectable concentrations of EDN™ were measurable after 1.5 hours of ventilation (Hall et al., 2014). Field trial results show acceptable levels of EDN (less that 3ppm was found on the logs after 2.5 hours).

Although both methyl bromide and EDN are considered as effective log fumigants both have different physical, chemical properties and break down pathway. Methyl bromide used to fumigate the logs does not break down during fumigation or immediately after it is released into the environment. Methyl bromide is sorbed into the wood and released over time. The released methyl bromide from fumigation breaks down in the ozone layer.

EDN™ breaks down rapidly in the presence of moisture during fumigation of logs to ammonia and carbon dioxide by the end of 24 hours with only insignificant amounts of original molecule remaining in the treated space. This insignificant amount subsequently breaks down to carbon dioxide and ammonia. Hence, EDN™ is a self-scrubbing fumigant which doesn’t require a recapture or destruction method at the end of the fumigation.
Appendix 2 Australian trial work as a case study

A timber tarp trial was conducted in 219 m$^3$ tarp filled with logs according to commercial fumigation condition.

The trial was conducted at a grain storage facility Regan’s ford, Perth Western Australia in 2012. A dose rate of 75 g/m$^3$ was applied and the EDN levels inside the tarp were monitored at the top, middle and bottom.

The fumigation was conducted for 6 hours followed by 12 hours of scrubbing then ventilation. During application, treatment, scrubbing and ventilation period, environmental air samplings were collected at 0, 5, 10, 25, 50, 100, 150 and 210 m head height. See results in Table 6. Note no EDN or HCN were found in the area around the trial site during application, treatment, scrubbing or during ventilation period.

At the start of the application period, an average of 34,533 ppm of EDN was found inside the tarp. At the end of the treatment period (6 hours) 13.13% (4539 ppm) of the initially applied dose rate remained in the tarp. Scrubbing was started at the end of the treatment period.

A liquid scrubber was used which contained an IBC filled with a solution of sodium hydroxide and sodium hypochlorite.

The reaction procedure is shown below:

$$C_2N_2 + 2 \text{NaOH} + \text{NaOCl} \rightarrow 2 \text{NaOCN} + \text{NaCl} + \text{H}_2\text{O}$$

Disposal 1 kg of EDN requires 1.5 kg Sodium Hydroxide and 1.5 kg Sodium Hypochlorite.

An extraction tube was connected to the tarp to withdraw the remaining EDN and attached to the IBC scrubber.

At the start of the scrubbing, an average concentration of 4539 ppm was found inside the tarp. Scrubbing continued for 12 hours however it did not scrub 100% of the EDN. After 4 hours of scrubbing the EDN reached an average of 193 ppm and remained at that level for the next 8 hours, steady state equilibrium.

It was also noted that breakthrough in the liquid scrubbing system occurred during that period and the air needed to be passed through another IBC containing activated carbon. As a consequence, after breakthrough was identified EDN collected from the treatment structure was first passed through a liquid scrubber and then passed through a 2nd IBC containing carbon.

Table 6 EDN levels during scrubbing

<table>
<thead>
<tr>
<th>Scrubbing started</th>
<th>1 hour</th>
<th>2 hours</th>
<th>3 hours</th>
<th>4 hours*</th>
<th>6 hours</th>
<th>8 hours</th>
<th>10 hours</th>
<th>12 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>21:30</td>
<td>22:00</td>
<td>22:30</td>
<td>23:00</td>
<td>0:30</td>
<td>1:30</td>
<td>3:30</td>
<td>5:30</td>
</tr>
<tr>
<td>Top ppm</td>
<td>3232</td>
<td>1000</td>
<td>488</td>
<td>322</td>
<td>265</td>
<td>245</td>
<td>66</td>
<td>60</td>
</tr>
<tr>
<td>Middle ppm</td>
<td>4833</td>
<td>2213</td>
<td>920</td>
<td>1005</td>
<td>461</td>
<td>381</td>
<td>180</td>
<td>252</td>
</tr>
</tbody>
</table>
The Draslovka proposal is for 20 hours treatment time. If we compare the EDN level after scrubbing to the levels obtained from the NZ PFR end-point concentration study (Table 7 for 24 hours the levels are more or less similar. Hence using a treatment time to 24 hours or setting a maximum concentration for the end of fumigation could be used as a strategy to avoid the use of scrubbing. The use of a scrubber has shown to be only as effective as extending the fumigation treatment time and does not come with the additional expenses and risks associated with a scrubber.

Table 7 Laboratory results for the concentration at the end of 24 hours fumigation

<table>
<thead>
<tr>
<th>EDN dose rate</th>
<th>End point concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 g/m3</td>
<td>670 ppm</td>
</tr>
<tr>
<td>120 g/m3</td>
<td>536 ppm</td>
</tr>
<tr>
<td>100 g/m3</td>
<td>446 ppm</td>
</tr>
<tr>
<td>80 g/m3</td>
<td>357 ppm</td>
</tr>
<tr>
<td>60 g/m3</td>
<td>268 ppm</td>
</tr>
<tr>
<td>50 g/m3</td>
<td>223 ppm</td>
</tr>
</tbody>
</table>

* APVMA recommendation is 4 hours scrubbing