STIMBR

Note prepared for the EPA DMC. August 2018

Wood Odour

Introduction:

In the STIMR submission to the EPA for the EDN application APP202804, STIMBR identified that d*uring containment field trials at Tokoroa in April 2016 following venting and on subsequent days, those involved in the trials and log logistics commented that the stacks smelled different [from fumigations with methyl bromide or phosphine] (Hall et al 2016). No EDN was detected in association with the vented stacks. Plant and Food Research (PFR) showed previously that EDN did not decompose to HCN during simulated log fumigations (Hall et al 2018). Because EDN is volatile and has a high sorption rate (Hall et al 2015), it is likely that EDN quickly decomposes to a number of compounds during and after fumigation (e.g., CO_2 and NH_3). Some of these compounds, particularly ammonia (NH_3), have a very strong odour that port workers and bystanders may notice once EDN is used commercially. The 'different smell' reported during the Tokoroa trial may have been the low levels of NH_3.*

In anticipation that similar observations may be made following the introduction of EDN, STIMBR commissioned PFR to develop a protocol to identify the compounds that are present in the treated space at the end of log fumigations with EDN. Unfortunately, due to technical reasons this work was unable to effectively identify and quantify the gases which remain in the treated space at the end of fumigation, particularly NH_3. STIMBR has undertaken this additional research in order to pre-empt questions which may arise around the different odour of logs after treatment with EDN, compared to methyl bromide, and whether or not it is safe.

To provide an outline of the potential cause of this smell the following information has been collated.

Preliminary Research

Plant & Food Research conducted a preliminary trial which aimed to identify and quantify the compounds which remain at the end of EDN fumigation and which may therefore have contributed towards the unusual odour.

At the end of 24-hour fumigations of Pinus radiata logs with EDN Plant and Food confirmed residues of EDN, HCN (hydrogen cyanide) and monoterpenes, principally α- and β-pinene. The concentrations of these compounds were measured in the headspace of the sealed treatment chambers at the end of a 24h fumigation period. No measurements were made in the period immediately following fumigation to determine possible volatile compounds that are flushed-out during the post-fumigation process. A ventilation period would normally follow fumigation and would result in dilution of such residues to very low levels as reported by Hall et. al. (2016).

This initial research to identify possible candidate compounds for the reported post fumigation smell associated with EDN fumigated logs has been unable to provide a definitive answer. The trial did show:

- Sorption of EDN by the logs was high (98%) during the fumigation with an average concentration of 3.4 gm^{-3} remaining at the end of the fumigation period
- HCN levels were low at the end of the fumigation period at 1.06 gm^{-3}, however they were higher than the initial level of 0.74 gm^{-3} at the start of the fumigation. The average increase was 0.32 gm^{-3}.
- Ammonia was not identified in the headspace above the EDN-treated log samples, implying a headspace concentration at or below 11 ppm (the limit of detection in the trial).
- there was no measurable change in levels of the seven terpenes/monoterpenes identified when comparing fumigated and non-fumigated logs
- The most prevalent gas present in the treatment chambers containing logs was carbon dioxide (CO_2), present as a consequence of respiration of the logs in a closed space.

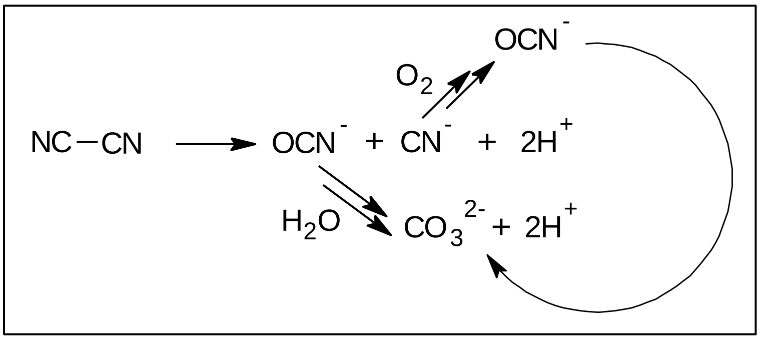
Both HCN and EDN have characteristic odours. Hydrogen cyanide is described as having a bitter almond smell, but it does not always give off an odour, and 20% of the population cannot smell it because of a recessive genetic trait. The odour threshold of HCN is 0.58 to 5 ppm (National Research Council 2002). EDN has a pungent, penetrating almond-like odour that some people can detect at a concentration as low as 10 ppm (National Research Council 2014). These compounds were present at the end of the treatment period at concentrations in excess of their published aroma threshold values. However, these values do not representative of the concentrations likely to be present at the end of ventilation.

STIMBR considers that at the time of making its submission it underestimated the challenge of identifying the molecular constituents of the change in smell following fumigation with EDN. When checked following the Tokoroa trial no EDN was found to be present.

At the request of STIMBR Plant and Food is considering how best it could identify a wider range of compounds (ammonia-based compounds, fatty acid degradation products, terpenoic substances and odorous substances resulting from the degradation of lignin) that would enable it to isolate the possible candidate odour compounds following EDN treatment.

Breakdown of EDN

EDN is a stable molecule and can only have an effect on living things if it comes into contact with water. EDN has a strong affinity at a molecular level for liquid water and rapidly reacts to form HCN which then breaks down to release CNO, O, and NO. The dominant reaction that occurs in the decomposition of EDN is summarized in the figure below.



In the presence of water this breakdown happens very rapidly on a molecular level. Appendix 1 provides details from the EDN application on the breakdown of EDN.

In the case of wood fumigation, the potential production of hydrogen cyanide (HCN) is suppressed by EDN absorption into the wood and interaction with wood components. Inside the wood EDN will potentially react with:

- tannin
- lignin
- cellulose structure, and,
- other substances associated with tree sap composition, such as terpenoids and isoprenoids

This contrasts to the situation in soil, where there is some HCN increase in the free HCN present after fumigation with EDN.

<u>Instances of reported odour</u>

The odour reported in New Zealand on fumigated logs appears to be specific to *Pinus radiata* (D.Don). It has been noted by researchers at Plant & Food Research that this smell is noticeable when the EDN's application rate exceeds approximately 50 g/m^3.

Draslovka has been involved in an extensive number of research trials internationally using both EDN and HCN and there have been no other reports of a post fumigation "smell" either at the end of treatment, or after several hours of ventilation. This includes a number of field trials in involving several thousand cubic meters of wood. EDN was approved in June 2018 by the Czech authorities (Central Institute for Supervising and Testing in Agriculture, Decree June 2018) as a critical use exemption (CUE) for the Czech Republic to control the bark beetle (*Ips typographus(L))* and the double spined bark beetle *(Ips duplicatus* (Sahlberg)). Since then, tens of thousands of cubic meters of Norway spruce *Picea abies* (L)) have been fumigated without any report of an unusual smell. None of those involved in the field trials outside of New Zealand or these recent fumigations in the Czech Republic have reported a post fumigation odour. We understand that there has been no change in the odour characteristics of either reference or fumigated samples when the sample have been stored following fumigation (Pers. Com. Draslovka).

Draslovka also has extensive experience in the production and use of cyanide-based chemicals. As a group these chemicals are used extensively in mill fumigations, buildings fumigations and for the treatments of wooden materials. Initial experimental work is also underway examining their potential use in the fumigation of grain and flour. Draslovka has not received any report of an unusual odour during or after these fumigations.

Potential cause of the odour

The odour commonly associated with conifer species, including *P. radiata*, is due primarily to terpenes. Terpenes are composed of carbon (C) and hydrogen (H) atoms where they are built from different numbers of isoprene molecules, which have a chemical formula of C_5H_8. Monoterpenes contain two isoprene units - chemical formula of $C_{10}H_{16}$. Pinene, which has a typical odour of pine, is a monoterpene. Limonene, which has citrusy odour, is also a monoterpene. These two molecules, among others, give conifer trees their distinctive scent. Larger terpenes are known as diterpenes, triterpenes, and so forth, and they can take the shape of long chains or rings. Many diverse types of organisms produce terpenes besides conifers, including insects, marine algae and sea slugs.

Recent research (Schreiner et.al. 2018), has been published studying the identity of odour constituents of pines (Resolving the smell of wood - identification of odor-active compounds in Scots pine (*Pinus sylvestris* L.). In *P. sylvestris* these researchers successfully detected 44 odour-active compounds. The majority of the identified odorants were fatty acid degradation products, plus some terpenoic substances and odorous substances resulting from the degradation of lignin. Although some of the detected substances have previously been reported as constituents of wood, 11 newly identified substances were reported for the first time as odour-active compounds in wood, amongst them heptanoic acid, γ-octalactone, δ-nonalactone and (E,Z,Z)-trideca-2,4,7-trienal. This paper underscores the difficulties in establishing volatile compound finger prints for pines species. Another five chemicals could not be named. Of the 39 named substances, only two are mentioned in the American Industrial Hygiene Association document 2013 which considers odor theresholds. These are acetic acid with an odor threshold of is 0.0004 – 204 ppm and vanillin .00000016-.929 ppm. https://www.nature.com/articles/s41598-018-26626-8

Lignins, tannins, cellulose will instantaneously react with EDN to form a succession of decomposition products. EDN, can also react with a system of conjugated double bonds (such as those found in pinenes and other terpenoids), with double bonds activated by functional groups in their proximity (such as those found in lignin, tannin, aromatic compounds).

In mammals, odours and the sense of smell are the result of a highly sensitive interaction between the environment and how the olfactory receptors are influenced by the molecular structure of the chemical creating the odour. In some cases, the responsiveness of the olfactory receptors is so sensitive that even minute concentration of the chemical in the atmosphere is enough for the olfactory receptors to record a signal. This “slightest concentration” (e.g., parts per billion) is often at the borderline for identification of the odour and small changes in the composition and/or ratio of the chemicals that create an odour can result in a difference in the odour that is perceived (or if the odour is perceived).

In the case of fumigation workers, sensitization by the molecule groups that create an odour is highly subjective because the structure and amount of the molecule itself play a role in perception combined with genetic predisposition of individual workers that affects their perception of the molecules. However, it is important to note here that neither EDN nor HCN has a specific odour that would generally be perceived as a “stench” but in fact both compounds have an odour that is more often described as a distinctive almond or bitter almond smell. The distinct characteristic of this smell must not be underestimated.

Identifying the chemical causing the odour

Schreiner et. al. (2018) used two methods to record the compounds that were produced by natural non-fumigated *P. sylvestris* (a closely related species to *P. radiata.*) and identified up to 44 compounds that may cause odours, including mercaptans, amines, esters, isothiocyanates, pinenes and terpenoids. Unfortunately, there is no evidence that specific odours can be related to specific combinations and amounts of the compounds that Schreiner et al. (2018) identified. Moreover, little is known about the relationship between the compounds that are produced by *Pinus* species, their molecular structure, the amounts produced, and the combinations required to elicit the optimum responses by insect in the field of insect attractants and trapping (Bockerhoff et al 2017). Hence, any attempt at research to identify the cause (i.e., the molecular compounds, their combinations, and specific amounts) of any odour that occurred after *P. radiata* was fumigated with EDN would require unlimited time and resources without any guarantee that the cause of the odour would ultimately be determined. And, moreover, it would be impossible to relate any results to individual olfactory responses among humans without trials at a clinical level of study with hundreds, if not more, individuals.

If research is undertaken to attempt to identify the cause of the post fumigation odour in *Pinus radiata* a study looking for a wide range of mercaptans, amines, esters, isothiocyanates, pinenes and terpenoids would be required with no guarantee that the cause of the odour will be determined.

Conclusion:

The identification of compound(s) which contribute towards the odour of *P. radiata* logs fumigated with EDN is technically difficult to determine (as analytical techniques do not currently exist) and at low concentrations is subjective (as it is dependent on the sensitivity of olfactory receptors). Given that EDN and HCN have a distinctive almond smell, it is highly unlikely that these compounds are involved in the reported odour of logs post fumigation. Taking into consideration the toxicity of EDN and HCN and all the other likely compounds and variables (including wood composition, moisture, temperature etc.), it is extremely unlikely that the odor is harmful. The cost of pursuing possibly elusive fractions within the volatile finger print would need to be considered against the derived benefits.

References:

1. Cicerone, R.J., Zellner R. 1983. The atmospheric chemistry of hydrogen cyanide (HCN). J Geophys Res 88:10689-10696.
2. Bockerhoff et al. (2017). Literature review: Traps and lures for bark beetles and Sirex. Scion confidential report to STIMBR
3. Fritz B, Lorenz K, Steinert W, et al. 1982. Laboratory kinetic investigation of the tropospheric oxidation of selected industrial emissions. EUR 7624:192-202
4. Hall, M., Adlam, A., Matich, A., Najar-Rodriguez, A., Pal, P., Brash, D. (2018). Quantification of hydrogen cyanide as a potential decomposition product of ethanedinitrile during pine log fumigation. *New Zealand Journal of Forestry Science*. **48**:7.
5. Hall, M.K.D., Najar-Rodriguez, A., Pranamornkith, T., Adlam, A.R., Hall A.J., Brash, D.W. (2015). Influence of dose, bark cover and end-grain sealing on ethanedinitrile (C_2N_2) sorption by pine (*Pinus radiata* D.Don) logs. *New Zealand Plant Protection*. 68:13-18.
6. Hall, M.K.D., Adlan, A., Najar-Rodriquez A., Zeng, F., Hall, A. 2016. Fumigation monitoring – Fumigas EDN™ commercial log trial to determine ethanedinitirle emissions. A Plant and Food Research report prepared for Draslovka. SPTS No 13576.
7. Hall, M.K.D., Pranamornkith, T., Adlam A.R., Hall, A.J., Brash, D.W. (2014). Simulated commercial fumigation of sawn timber and logs to verify the sorption and desorption model of ethanedinitrile. Plant & Food Research SPTS No. 10152.
8. Lyman, W. 1982. Atmospheric residence time. In: Lyman, WJ, Reehl, WF, Rosenblatt DH, eds. Handbook of chemical property estimation methods: Environmental behavior of organic compounds. New York, NY: McGraw Hill Book Company, 10-2-10-33
9. National Research Council (2002). Acute Exposure Guideline Levels for Selected Airborne Chemicals, Appendix 5, Volume 2. The National Academies Press. https://www.ncbi.nlm.nih.gov/books/NBK207604/pdf/Bookshelf_NBK207604.pdf.
10. National Research Council (2014). Acute Exposure Guideline Levels for Selected Airborne Chemicals, Appendix 3, Volume 17. The National Academies Press. https://www.epa.gov/sites/production/files/2014-11/documents/cyanogen_final_v17_jun2014.pdf
11. Schreiner, l. et al. 2018. Resolving the smell of wood - identification of odour-active compounds in Scots pine (Pinus sylvestris L.) Nature May 2018 https://www.nature.com/articles/s41598-018-26626-8

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