EVALUATION OF LOW EMISSION CYANIDE FORMULATIONS FOR CONTROLLING POSSUMS

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1. SUMMARY

1.1 PROJECT AND CLIENT
The emission rates, palatability, and toxicity of new and conventional formulations of potassium cyanide were assessed by the Forest Research Institute, under contract to the Animal Health Board, 1991-92 (AHB No:38/90).

1.2 OBJECTIVES
- To assess hydrogen cyanide (HCN) emission rates of new encapsulated formulations of potassium cyanide (KCN) and compare these with Trappers® cyanide gel.
- To assess the toxicity of encapsulated formulations when administered using oral intubation.
- To assess the palatability of the encapsulated formulations.
- To assess the toxicity of the encapsulated formulations when consumed in a bait.
- To assess the rate of degradation of the encapsulated formulations compared to Trappers® cyanide when exposed to known rainfall.

1.3 METHODS
- HCN emissions from commercially available gels and coated formulations supplied by DSIR were assayed using a vapour-capture technique and gas chromatography.
- Toxicity of wax-coated tablets was assessed by oral intubation and by ingestion in a flour/icing sugar bait.
- Palatability of toxic and placebo wax tablets was assessed by recording consumption of tablets offered in a flour/icing sugar bait.
- Environmental persistence of the wax tablets and standard Trappers® gel was assessed by sampling each product at regular intervals over an 8-week period. Rainfall was recorded throughout the test period.

1.4 INTERIM RESULTS
- All commercial cyanide products tested have high HCN emission rates. Reverse enteric polymer resins used for encapsulating cyanide did not significantly reduce HCN emission rates.
- A wax/petrolatum coating did prevent HCN emission.
- The wax coating decreased the bioavailability of HCN which resulted in the tablets being ineffective both when intubated and when consumed in a bait.
- Possums accepted plain and cinnamon flavoured placebo tablets but preferred cinnamon toxic tablets. Possums were reluctant to consume more than one toxic tablet.
- The standard Trappers® cyanide gel decayed rapidly after only 3 mm of rain, but the wax tablets remained intact and retained most of their original KCN concentration after 8 weeks and 180 mm of rain.

1.5 RECOMMENDATIONS
- Evaluate the emission rates of HCN from all gel formulations and assess the potential of incorporating gels into cereal baits.
- Further develop cyanide in tablets with special emphasis on optimising tablet size so that sufficient cyanide can be administered when the coating is fractured.
- Assess the potential of micro-encapsulated cyanide as a means of administering KCN into the stomach without the possum tasting it.
- Assess the potential of masks for overcoming cyanide shyness.
2. INTRODUCTION

This study was undertaken to assess the potential of new formulations of cyanide for overcoming the problem of cyanide shyness in possum populations. The project was a collaborative one between DSIR Grasslands and the Forest Research Institute, and the research involved a step-wise team approach starting with the chemical evaluation of the new formulations, then their toxicity, and finally the behavioral responses of possums to the formulations. The work described in this report was carried out by the Forest Animal Ecology section, Forest Research Institute, Christchurch, under contract to the Animal Health Board.

3. BACKGROUND

Cyanide poisoning is one of several control techniques used for killing possums in New Zealand. Sodium cyanide is the most commonly used form of cyanide, although potassium cyanide has also been used. The poison is administered in a variety of petrolatum gel carriers with about 60% wt/wt of cyanide. The amount of cyanide gel produced each year varies markedly as a result of fluctuating possum skin prices, which govern the number of hunters harvesting possums. In recent years about 1500 - 2000 kg of cyanide gel have been produced each year, but in 1985 and earlier, when skin prices were high, about 9000 kg were produced each year.

Cyanide provides a relatively cheap control method (<2 cents per bait) that enables the user to retrieve the poisoned animal because of the rapid action of the poison. Apart from the legal requirement for users to have a licence, there are few restrictions on its use. The light weight of the cyanide tubes and the number of baits obtained from each tube (approx. 800 - 900 baits per 250-g tube) allow the hunter to cover a large area without having to carry heavy loads of traps.

However, even with these advantages, cyanide is often not used because in some areas poor kills are achieved. Only about 50% of possums killed by commercial hunters are obtained using cyanide, the rest are taken with traps (Reid 1986; unpubl. data submitted to the Ministry of Agriculture and Fisheries leg-hold trap committee, 1989).

The reason for poor kills with cyanide is not well understood, but it is generally attributed to possums being "cyanide shy". Cyanide shyness has been used as a general term to describe the proportion of a population that appears difficult to poison. This could include neophobic possums and those with primary (innate) food aversion (immediate recognition and rejection of cyanide) or learned food aversion from past exposure to sublethal doses (Reidinger & Mason 1983).

4. OBJECTIVES

Overall objectives

- To develop new formulations of cyanide that will overcome cyanide shyness.
- To develop formulations of cyanide that can be used in a variety of bait types, including paste and cereal pellets, thereby providing a more flexible and effective tool for possum control.
Objectives for 1991-92

- To assess hydrogen cyanide (HCN) emission rates of new encapsulated formulations of potassium cyanide (KCN) and compare these with commercially available Trapper® cyanide gel.
- To assess the toxicity of encapsulated formulations when administered using oral intubation.
- To assess the palatability of the encapsulated formulations.
- To assess the toxicity of the encapsulated formulations when consumed in a bait.
- To assess the rate of degradation of the encapsulated formulations compared to Trappers® cyanide gel when exposed to known rainfall.

5. METHODS

5.1 Materials
Two types of tablet formulations of KCN were provided by Grasslands, DSIR: a 35-40-mg KCN tablet coated with a polymer resin, and a 110-120-mg tablet coated with a wax/paraffin product. Both tablet formulations contained about 30 mg of KCN, and a sample of tablets with and without cinnamon were provided. Placebo tablets with the wax coating were also supplied with and without cinnamon.

Initial HCN-emission tests showed the polymer resin coating on the tablets did not stop the HCN emission and consequently these products were not tested further. The wax coating, however, stopped HCN emissions. Further trials examining palatability and toxicity were confined to this product.

Carbopol gel formulations were prepared by the Forest Research Institute, and these included binding agents and various concentrations of either sodium or potassium hydroxide as buffering agents.

5.2 HCN emission
A method has been developed by the toxicology laboratory of FRI for measuring HCN emission, based on the work of Krynitsky et al. (1986). A tablet or quantity of the cyanide bait preparation is placed in an emission chamber, left for 12 h, and the volatile cyanide is trapped in an alkaline solution and measured by gas chromatography.

5.3 Oral toxicity
Caged possums were fed a vegetable/fruit and foliage diet. To administer the tabulated KCN, possums were anaesthetised using a carbon dioxide/oxygen mixture. Two or three tablets were placed at the top of the pharynx and the possum encouraged to swallow by massaging the throat. Trappers® cyanide gel (KCN) was intubated in flexible plastic tube, using a plunger to push the gel from the end of the tube into the stomach. The equivalent doses to two and three KCN tablets were administered. After dosing, possums were placed back into their cages to recover, and any post-dosing symptoms were checked at 60-second intervals until the possum either died or recovered.
5.4  Palatability
Free-ranging possums in pens were offered placebo, plain KCN and cinnamon flavoured KCN tablets in flour/icing sugar baits. No flavours were added to the bait material to act as a mask. Baits were checked each morning and the presence or absence of the intact or partly consumed tablets was recorded. All possums were given water and pellets ad libitum and an apple each day.

5.5  Toxicity of tablets consumed in a bait
Free-ranging possums on a vegetable diet were offered KCN tablets in flour/icing sugar baits. No flavours were added to these baits. Plain and cinnamon flavoured tablets were tested. Baits were checked each morning for consumption of the tablets and the possums were recorded as dead or alive.

5.6  Environmental degradation
A set of wax-coated cyanide tablets were placed on rocks and exposed to the weather for 8 weeks, along with extruded pea-sized baits of standard potassium and sodium Trappers® cyanide gel, to assess their relative rates of cyanide loss. A sample of tablets from the same batch had shown no HCN emission when tested previously. The cyanide gels used were; Sodium cyanide (NaCN), petrolatum gel, and potassium cyanide gel in oil/surfactant. Samples were taken in duplicate at the beginning of the study and after 1, 2, 4, and 8 weeks.

Rain gauges were set up to monitor rainfall throughout the study period. The study location (on the balcony outside the laboratory window) was exposed overhead and to the north, south, and east, but sheltered from the west. The site received sunlight until 11 am. The cyanide content of each tablet and gel sample was measured by gas chromatography.

6.  RESULTS

6.1  HCN emission
HCN emission was assessed for 26 formulations (Table 1). The four commercial gel products had emission rates ranging from 84 to 313 ug/g HCN/h, with the highest rates obtained from a KCN oil/surfactant gel. Trials with carbopol gels at different concentrations of NaOH to increase the pH reduced emissions with the best being 13 ug/g HCN/h (product 17, Table 1).

Uncoated tablets of KCN had high HCN-emission rates, and although encapsulating the tablets with a polymer resin did reduce emission, rates were still 3 times higher than that of the commercial gel formulations (products 7 & 8,9,10; Table 1).

Emissions of HCN were eliminated by the wax coating, at least to the level of detectability (products 21,22,25,26; Table 1).

6.2  Oral toxicity
Two of the three possums dosed with two KCN tablets died within 45 minutes whereas none of the five dosed with three tablets died (Table 2). Surviving possums were dissected 24 h post-dose, and some tablets were found to be still intact in the stomach contents. Intubated KCN gel proved to be considerably more toxic than the tablets with 12 of the 14 possums killed (Table 2).
Table 1. Cyanide (HCN) emission rates from a range of KCN and NaCN formulations.

<table>
<thead>
<tr>
<th>No.</th>
<th>DESCRIPTION</th>
<th>Wt</th>
<th>mg K/NaCN</th>
<th>ug/g/ HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Trappers 60% NaCN paste</td>
<td>0.119</td>
<td>71</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Trappers 60% NaCN in oil/surf.</td>
<td>0.124</td>
<td>74</td>
<td>202</td>
</tr>
<tr>
<td>3</td>
<td>Trappers 60% KCN in oil/surf.</td>
<td>0.115</td>
<td>69</td>
<td>313</td>
</tr>
<tr>
<td>4</td>
<td>Wanganui 50% NaCN paste</td>
<td>0.112</td>
<td>58</td>
<td>214</td>
</tr>
</tbody>
</table>

Uncoated and polymer coated tablets

<table>
<thead>
<tr>
<th>No.</th>
<th>DESCRIPTION</th>
<th>Wt</th>
<th>mg K/NaCN</th>
<th>ug/g/ HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Tablets, uncoated batch 3</td>
<td>0.036</td>
<td>18</td>
<td>2361</td>
</tr>
<tr>
<td>8</td>
<td>Tablets, uncoated batch 4</td>
<td>0.034</td>
<td>22</td>
<td>1706</td>
</tr>
<tr>
<td>9</td>
<td>Tablets, coated batch 3</td>
<td>0.038</td>
<td>31</td>
<td>974</td>
</tr>
<tr>
<td>10</td>
<td>Tablets, coated batch 4</td>
<td>0.040</td>
<td>23</td>
<td>1075</td>
</tr>
<tr>
<td>11</td>
<td>(a)Tablet, one coat sealant</td>
<td>0.038</td>
<td>34</td>
<td>1579</td>
</tr>
<tr>
<td>12</td>
<td>(b)Tablet, three coats sealant</td>
<td>0.041</td>
<td>34</td>
<td>1146</td>
</tr>
<tr>
<td>13</td>
<td>(c)Tablet,1 sealant,reverse enteric.</td>
<td>0.044</td>
<td>35</td>
<td>955</td>
</tr>
<tr>
<td>14</td>
<td>(d)Tablet,3 sealant,reverse enteric.</td>
<td>0.046</td>
<td>37</td>
<td>761</td>
</tr>
<tr>
<td>15</td>
<td>Tablet, uncoated in petrolatum</td>
<td>0.038</td>
<td>22</td>
<td>39</td>
</tr>
</tbody>
</table>

FRI Carbopol gels

<table>
<thead>
<tr>
<th>No.</th>
<th>DESCRIPTION</th>
<th>Wt</th>
<th>mg K/NaCN</th>
<th>ug/g/ HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Carbopol blend 4, 30% KCN/NaOH</td>
<td>0.105</td>
<td>32</td>
<td>67</td>
</tr>
<tr>
<td>17</td>
<td>Carbopol blend 5, 30% KCN/NaOH</td>
<td>0.176</td>
<td>53</td>
<td>13</td>
</tr>
<tr>
<td>18</td>
<td>Carbopol blend 6, 30% KCN/KOH</td>
<td>0.285</td>
<td>86</td>
<td>154</td>
</tr>
<tr>
<td>19</td>
<td>Carbopol blend 8, 30% KCN/NaOH</td>
<td>0.125</td>
<td>38</td>
<td>104</td>
</tr>
<tr>
<td>20</td>
<td>Carbopol blend 9, 60% KCN/NaOH</td>
<td>0.177</td>
<td>106</td>
<td>40</td>
</tr>
</tbody>
</table>

Wax coated tablets

<table>
<thead>
<tr>
<th>No.</th>
<th>DESCRIPTION</th>
<th>Wt</th>
<th>mg K/NaCN</th>
<th>ug/g/ HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Batch 13A-1, 30-34mg KCN</td>
<td>0.110</td>
<td>36</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>Batch 13A-2, 34-38mg KCN</td>
<td>0.119</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>Batch 15.1, 30-35mg KCN</td>
<td>0.128</td>
<td></td>
<td>141</td>
</tr>
<tr>
<td>24</td>
<td>Batch 15B, 30-35mg KCN/cinnamon</td>
<td>0.105</td>
<td></td>
<td>152</td>
</tr>
<tr>
<td>25</td>
<td>Batch 15C, 30mg KCN</td>
<td>0.118</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>Batch 15D, 30mg KCN</td>
<td>0.115</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2. Toxicity of KCN tablets and gel administered orally.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mortality</th>
<th>Time to death</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 KCN tablets</td>
<td>2/5</td>
<td>= 45 min</td>
</tr>
<tr>
<td>3 KCN tablets</td>
<td>0/5</td>
<td>NA</td>
</tr>
<tr>
<td>KCN gel = 2 tablets</td>
<td>7/9</td>
<td>15-30 min</td>
</tr>
<tr>
<td>KCN gel = 3 tablets</td>
<td>5/5</td>
<td>9-50 min</td>
</tr>
</tbody>
</table>

6.3 Palatability

Of 10 possums tested, nine accepted plain placebo tablets on their first encounter. On subsequent encounters some possums appeared to identify them within the flour-based baits and rejected them (Table 3). Four of the seven possums offered plain KCN tablets rejected them (Table 3). One of the rejected tablets was found to be emitting relatively high levels of KCN because of a fracture in the wax coating. Eleven possums were offered cinnamon-coated KCN tablets; nine of these ate one tablet and three ate half a tablet (Table 3).

Table 3. Palatability of placebo and flavoured and plain KCN tablets.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Number of possums treated</th>
<th>Number of possums accepting</th>
</tr>
</thead>
<tbody>
<tr>
<td>First encounters placebos</td>
<td>10</td>
<td>9 (90%)</td>
</tr>
<tr>
<td>Subsequent encounters placebos</td>
<td>20</td>
<td>16 (80%)</td>
</tr>
<tr>
<td>KCN plain</td>
<td>7</td>
<td>3 (43%)</td>
</tr>
<tr>
<td>KCN cinnamon</td>
<td>3</td>
<td>3 (100%)</td>
</tr>
<tr>
<td>KCN cinnamon</td>
<td>3</td>
<td>3 (100%)</td>
</tr>
<tr>
<td>1 tablet offered</td>
<td>8</td>
<td>6 accepted 1</td>
</tr>
<tr>
<td>2 tablets offered</td>
<td></td>
<td>2 accepted ½</td>
</tr>
</tbody>
</table>

6.4 Toxicity of tablets consumed in a bait

Results from this trial corroborated those from the oral-dosing trial with few possums dying from ingesting a tablet (Table 4). None of the possums died more than 12 h after ingestion. Very few possums offered two toxic tablets ate them both, suggesting the first tablet was fractured, the KCN tasted and the second tablet then rejected. Of the seven possums that ate two tablets, only two died (Table 4).
Table 4. Mortality from ingestion of plain and cinnamon flavoured KCN tablets. A = alive; D = dead.

<table>
<thead>
<tr>
<th>Plain</th>
<th>1 tablet</th>
<th>2 tablets</th>
<th>Cinnamon</th>
<th>1 tablet</th>
<th>2 tablets</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
</tr>
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<td>A</td>
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<td>D</td>
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<td>D</td>
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<td>D</td>
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<td>D</td>
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<td>D</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>Mortality 4/12</td>
<td>1/2</td>
<td>1/13</td>
<td>1/5</td>
<td></td>
</tr>
</tbody>
</table>

6.5 Environmental degradation

The cyanide content of tablets and gels showed significantly different rates of decay. The standard commercially available petrolatum-based gels rapidly lost their toxicity but the tablets retained more than 80% of their cyanide content even after 8 weeks and more than 180 mm of rain (Table 5).

The KCN gel was very soluble in water and even after 3 mm of rain the gel was completely degraded. The NaCN formulation, which is primarily petrolatum-based was more robust and even though the cyanide concentration had dropped to an insignificant level after the first week, part of the gel remained present throughout the 8-week trial period. Only two of the 10 tablets exposed to the weathering conditions showed any reduction of KCN from their initial concentrations.

Table 5. Environmental persistence of KCN in wax tablet and gel formulations.

<table>
<thead>
<tr>
<th>Week</th>
<th>Tablet mg KCN</th>
<th>KCN gel mg KCN</th>
<th>NaCN gel mg NaCN</th>
<th>Rainfall mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35</td>
<td>58</td>
<td>102</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>27.5</td>
<td>0</td>
<td>.24</td>
<td>56.5</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>72.2</td>
</tr>
<tr>
<td>4</td>
<td>29.5</td>
<td>0</td>
<td>0</td>
<td>105.8</td>
</tr>
<tr>
<td>8</td>
<td>28</td>
<td>0</td>
<td>0</td>
<td>&gt;180.3</td>
</tr>
</tbody>
</table>
7. CONCLUSIONS

- All commercially available cyanide formulations have relatively high HCN-emission rates, and field data suggest that emission rates of HCN of about 84 ug/g/h (i.e., the emission from NaCN gel) are sufficient for possums to detect and reject the toxin. HCN-emission rates therefore need to be reduced to some level below this. None of the reverse-enteric coating compounds stopped the HCN emission or even reduced it to levels comparable with the NaCN gel. A wax polymer coating, however, effectively stopped HCN emission, and future product development and testing will be aimed at optimising this product.

- Reductions in HCN emissions can also be achieved by increasing the pH of the carrier with the addition of alkalines such as NaOH. At this stage it is unknown whether this degree of reduction in HCN emission (80 down to 13) would have a significant impact on the ability of possums to detect the toxin.

- Results indicate that most, if not all possums, will eat placebo wax tablets on their first encounter. Plain KCN tablets were rejected by 4 out of 7 possums whereas most possums (80%) consumed at least one cinnamon-flavoured KCN tablet. It is recommended that all tablets should include cinnamon which may either act as a mask or by enhancing the palatability of the tablet.

- The wax tablets, when administered into the stomach without any physical damage to the coating, remained intact for at least 24 hours. The bioavailability of the HCN from these intact tablets was too low to be lethal. It is assumed that the two possums that died from receiving two tablets did so because some imperfection in the wax coating increased the rate at which HCN could become available. The wax tablets also proved ineffective when consumed in a bait. It appears from the high rejection rate of the second tablet that the possums were fracturing the coating of the first tablet consumed, tasting the cyanide and then rejecting the second tablet. If this is so, it is assumed that insufficient cyanide was being made available from the fractured tablet. Consequently, for this technique to work the tablet has to be of such a size that when fractured, a lethal dose of cyanide is released into the mouth.

- Cyanide in gel decays rapidly with small amounts (3 mm) of rainfall, however, the wax-coated tablets remain intact, with no significant reduction of KCN after 8 weeks and 180 mm of rain. It is likely therefore that the current tablet formulation will remain toxic for long periods of time unless the coating suffers some physical damage that allows moisture to penetrate into the KCN.

8. RECOMMENDATIONS

- The emission rates of HCN from all gel formulations should be evaluated and the potential of incorporating gels into cereal baits should be assessed.

- Cyanide in tablets should be developed with special emphasis on optimising tablet size so that sufficient cyanide can be administered when the coating is fractured.

- The potential of micro-encapsulated cyanide should be assessed as a means of administering KCN into the stomach without the possum tasting it.

- The potential of masks for overcoming shyness should be assessed.
9. ACKNOWLEDGEMENTS

We thank Dr. R. Welsh and M. Carter for providing cyanide formulations to test, G. Wright for assaying emission rates, R. Henderson, and S. Hough for running pen trials and J. Coleman and J. Orwin for comments on drafts of this report. The Animal Health Board and AGMARDT are thanked for supporting and funding this project.

10. REFERENCES

