Appendix D: Ecotoxicity and Environmental Fate of Cyanide

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Key points

- Cyanide acts by disrupting oxygen metabolism.
- The acute toxicity to all trophic levels of aquatic life is <1 mg/l.
- Non-acclimatised soil bacteria are adversely affected at 0.3 mg HCN/kg, but acclimatised bacteria can degrade wastes containing up to 60 mg total CN/kg.
- No data are available on the toxicity of cyanide to soil macro invertebrates.
- There are no relevant data on the toxicity of cyanide to plants, but some plant species can degrade cyanide.
- The acute LD_{50} to mammals and birds is generally 1-10 mg/kg bw.
- The likely effects of Feratox pellets will depend on the organism's ability to break the pellet.
- Cyanide rapidly degrades in water and soil.
- Feratox pellets may be persistent for several weeks in both water and soil.
- Paste will degrade more rapidly than pellets at a rate largely determined by exposure to rainfall, moisture and humidity.
- Cyanide is unlikely to bioaccumulate.
- The persistence of cyanide baits is a factor of the persistence of cyanide itself and the persistence of the bait in the field.

D1 Formulations

Three formulations of cyanide are used in New Zealand: encapsulated pellets (Feratox®), micro-encapsulated pellets in a paste (Cyanara Ferapaste®) and non-encapsulated cyanide paste (Trappers Cyanide® and Cyanide Paste for Possum Destruction®).

Ferapaste contains 50% potassium cyanide. The tube containing the paste is clear and the paste is dyed green. Small white pieces of cyanide granules can be seen dispersed in the paste. The balance of 50% of the paste is petroleum jelly some oils and polymer encapsulates (Connovation 2002). All three cyanide pastes available on the market are 50–60% cyanide by weight. The standard amount of a cyanide paste per bait is 400 mg, equivalent to 200 mg of cyanide (Connovation 2007).

The active cyanide in both Feratox pellets and Cyanara Ferapaste is 'encapsulated' with a non-toxic moisture and air barrier.

Feratox pellets were previously produced with a cyanide concentration of 800 g/kg, but are now produced with a concentration of 475 g/kg. Toxicological information relating to the higher concentration is applicable to the lower concentration since the dose contained in a single pellet is the same (approximately 95 mg of potassium cyanide) (Connovation no date). The effects on an animal breaking the capsule are, therefore, likely to be the same.

This is not a reassessment of cyanide or trapping, so the following consideration of the effects of cyanide and trapping is not to the same depth as that performed for 1080.

D2 Toxicity

D2.1 Aquatic life

The application contains no information on the toxicity of cyanide formulations to aquatic life. Since cyanide is laid by hand and is readily degradable, exposure of aquatic organisms will not occur. The Agency concurs with this view but notes that potassium and sodium cyanide are acutely very toxic (acute LC_{50} less than 1 mg/l) to all trophic levels of aquatic life but in particular fish (IUCLID 2000; Eisler 2001).

D2.2 Soil micro-organisms

Cyanide is produced by a variety of microbes and more than 2000 species of plants (DoC no date). Eisler (1991) states that non-acclimatised soil bacteria are adversely affected at 0.3 mg HCN/kg, although acclimatised populations can degrade wastes containing up to 60 mg total CN/kg.

The applicants have provided indirect evidence as to the toxicity of cyanide to soil microbial communities (Eisler 2001, quoting Towill et al 1978, but attributed by the applicants to Knowles 1988):

> Cyanide seldom remains biologically available for long in soil because it is either metabolised by various micro-organisms, lost through volatilisation or forms complexes with other compounds, such as iron (Eisler 1991). These forms are relatively much less toxic and reactive than free cyanide ions (Shifrin et al 1996). Cyanide salts may be degraded by some bacteria. Under aerobic conditions microbial metabolism rapidly degrades cyanides to carbon dioxide and ammonia, while under anaerobic conditions cyanides are converted by bacteria to gaseous nitrogen compounds that escape to the atmosphere (Eisler 1991).

The Agency concurs with these statements.

D2.3 Soil macro-invertebrates

The applicants provided no information on the toxicity of cyanide to soil macro-invertebrates. The Agency has located no information.

D2.4 Plants

The applicants provided no information on the toxicity of cyanide to plants other than to say “Plants can take up cyanide (Eisler 1991) and toxic effects reported include inhibition of growth and phloem translocation (Eisler 1991)”.

Yu et al (2005) report that β-cyanoalanine synthase (CAS) is widely distributed in a range of higher plants and plays a crucial role in the conversion of cyanide plus cysteine to β-cyanoalanine and sulphide. They performed experimental work with hydroponic systems (concentration around 1 mg/l) and three species of Salicaceae that showed rapid uptake and degradation. The maximum concentration of cyanide (CN) in the plant was reached in the root and was around 1 mg/kg fresh weight.

Shifrin et al (1996) report that the phytotoxicity of cyanide complexes is directly related to the amount of free cyanide evolved. No data are presented in this paper, but they quote others who proposed a conservative soil threshold for complexed cyanides of 50 mg/kg that would be protective of vegetation at sites contaminated by gas-works.

D2.5 Cold-blooded animals

The only toxicity figure identified by the Agency is a lethal dose in frogs (species unknown) of 60 mg/kg (Eason and Wickstrom 2001).

D2.6 Birds

The toxicity of cyanide dosed orally using gelatin capsules was determined by Wiemeyer et al (1986). Six species were tested (see Table D1).

Table D1: Birds species tested for toxicity of cyanide dosed orally using gelatin capsules

Species	LD_{50} (mg/kg bw)
Black vulture *Coragyps atratus*	4.8
American kestrel *Falco sparverius*	4
Japanese quail *Coturnix japonica*	9.4
Domestic fowl *Gallus domesticus*	21
Eastern screech-owl *Otus asio*	8.6
European starling *Sturnus vulgaris*	17

Source: Wiemeyer et al 1986.

Wiemeyer et al noted that the LD_{50} values of the predator species *C. atratus, F. sparverius* and *O. asio* were lower than those for the herbivorous species. They also noted that the blood CN concentration of birds that died overlapped with that of birds that survived. They speculated this may be due to rapid metabolism of CN to thiocyanate and its subsequent excretion. Eisler (1991) noted that the predator species appeared to be more sensitive than the predominantly herbivorous species, but notes that the LD_{50} for mallard duck, which are herbivores, is 1.4 mg/kg bw (DoC no date).

The applicability of the toxicity of cyanide to Feratox will depend on the ability of exposed organisms to break or digest the pellets. Mehrtens and Gaze (2003) provide field observations that suggest that weka at least can be exposed, although it is unknown if they break the pellets or are exposed to pellets broken by rodents; nor is it known how or which other species may be exposed to cyanide through pellets (Appendix O).

The proportion of a Feratox pellet or paste bait required to kill different birds is shown in Table D2.

Table D2: Effects of cyanide pellets and paste on birds

	LD_{50}	Weight (g)	Number of Feratox pellets[1]	Number of paste baits[2]
Chicken	11.1	900	0.110	0.0004700
Mallard	1.43	1,100	0.017	0.0000910
Starling	17	85	0.015	0.0000065

Source: Adapted from Fisher and Fairweather 2004.

Notes

1 Based on 95 mg CN/pellet.

2 Based on 200 mg CN/bait.

Wiemeyer et al (1986) state that the first signs of toxicosis in birds dosed by gelatin capsule placed in the proventriculus appeared between 0.5 and 5 minutes after exposure. Death normally occurred from 15–30 minutes and birds still alive after 60 minutes usually survived.

D2.7 Mammals

No information is available on toxicity to bats. IUCLID (2000) quotes various studies looking at lethal doses of cyanide to dogs. None used a single or short-term oral route of exposure. Infusion and subcutaneous LD_{50} values were in the range of 2–5 mg/kg bw. LD_{50} values in the range of 3.5–5 mg/kg have been observed for deer, pig, goat, rabbit, hare and cattle (DoC no date). The LD_{50} of cyanide to possums is about 8.7 mg/kg bw (Fisher and Fairweather 2004).

Fisher and Fairweather (2004) refer to an average time to onset of ataxia of three minutes, the average time to overall loss of consciousness was 6.5 minutes and the time to cessation of breathing was 18 minutes.

LD_{50} values related to the size of Feratox pellets and Ferapaste baits.

The Agency has interpreted the above mammalian LD_{50} values for cyanide in terms of Feratox pellets and cyanide pastes (Table D3).

Table D3: Effects of cyanide pellets and paste on mammals

	LD_{50}	Weight (g)	Number of Feratox pellets[1]	Number of paste baits[2]
Cattle	3.5	170,000	6.3	5.3
Deer (not specified)	3.5	45,000	1.7	0.373026316
Coyote[3]	4.1	8,000	0.35	0.014
House mouse	6.44	20	0.0014	0.00000014
Pig	2.0	120,000	2.5	1.5
Rabbit	5.1	800	0.043	0.00017
Norway rat	8.5	220	0.020	0.000022
Sheep	2.3	50,000	1.2	0.30
Possum	8.7	2400	0.22	0.0026

Source: Adapted from Fisher and Fairweather, 2004.

Notes

1 Based on 95 mg CN/pellet (Connovation no date).

2 Based on 200 mg CN/bait (Connovation no date).

3 Assumed representative of dogs.

D2.8 Chronic effects

Exposure to cyanide is expected to be at worst occasional. Chronic effects are, therefore, not of great relevance. Nevertheless, Eisler (1991) showed that repeated sub-lethal dietary intake of 135 mg cyanide/kg resulted in reduced growth of young domestic chicken.

D2.9 Bait shyness

One feature of cyanide pertinent to a consideration of the effects of baits is the ability of animals to detect it. Bait shyness has been documented in possums 300 days after sub-lethal exposure (Morgan et al 2001*)* and may last for at least 24 months (O'Connor and Matthews 1997). Morgan et al (1995) report that cyanide paste used for possum operations emits hydrocyanic acid gas at a rate of 50–160 μg/g/h and compare this with possums' ability to detect the gas at emission rates as low as 1.3 μg/g/h.

D3 Fate of cyanide and cyanide baits

D3.1 Fate in water

Cyanide-based vertebrate toxic agents contain potassium cyanide or sodium cyanide. Potassium cyanide (KCN) and sodium cyanide (NaCN) are solids at environmental temperature. They ionise in water to form cyanide ions, which, depending on pH, will form hydrogen cyanide (HCN). HCN is a liquid or gas at environmental temperature (boiling point 25.7°C). Free cyanide is the term used to refer to the sum of HCN and CN^- and is the primary toxic agent referred to as cyanide (Eisler 2001).

Cyanide is highly soluble in water (NaCN, 480 g/L @ 15ºC; KCN, 716 g/L @20ºC (Eisler 2001)).

The disappearance of cyanide from water occurs through degradation and at acidic pH volatilisation of HCN into the atmosphere. It is most effective under conditions of high temperature and high dissolved oxygen concentration (Eisler 2001, quoting USEPA 1980). Eisler (2001) quotes Leduc (1984) as stating that in small, cold oligotrophic lakes treated with 1 mg NaCN/L, acute toxicity disappeared within 40 days, in warm, shallow ponds, toxicity disappeared within 4 days.

D3.1.1 Cyanide paste

No information is available on the fate of cyanide paste in water. The Agency assumes that it will be similar to that of cyanide itself, although the oily paste matrix and micro-encapsulation of cyanide may reduce the rapid degradation.

D3.1.2 Feratox

Wright and Manning (2003) looked at the loss of cyanide from pellets kept in circulating water. After 34 days the average loss of cyanide from the pellets was 89% but variability was great, with individual pellets showing 50–99.9% loss. By 64 days all pellets showed more than 97% decrease in cyanide concentration. The experimental method did not distinguish between evaporation and degradation, although the authors attribute the loss to evaporation.

D3.2 Fate in soil

Cyanide ions are not strongly absorbed or retained in soils (Eisler 2001; Eason and Wickstrom 2001) and leaching into the surrounding groundwater will probably occur (Eisler 2001).

Formation of iron complexes such as ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, immobilises cyanide in a relatively non-toxic form particularly under acid conditions. Dissociation of such iron complexes is pH dependent, but little free cyanide is evolved (Shifrin et al 1996). Ferricyanides and ferrocyanides do not release free cyanide unless exposed to ultraviolet light (Eisler 2001).

In experiments to look at the loss of cyanide from soil Wright and Manning (2003) sprayed cyanide solution onto soil at a rate of approximately 100 mg/kg and measured the concentration remaining in the soil over a 24 h period. A half-life of 1.1 h was derived.

D3.2.1 Cyanide paste

As in water, the fate of non-encapsulated cyanide in soil is largely extrapolated from the fate of cyanide itself, although it is noted that oil in the paste normally protects the cyanide from exposure to air and slows the release of hydrogen cyanide. How long baits remain toxic may well depend on how well they are protected from rainfall (Eason and Wickstrom 2001), but they remain potentially hazardous until broken down and unrecognisable (Rammell and Fleming 1978). In laboratory trials, emission rates of hydrogen cyanide have been recorded at 23.0–25.5 µg HCN/hr for non-encapsulated paste (Wright 1999). Details of the laboratory conditions for these trials, or even the amount of paste emitting the measured HCN are not known.

Morgan et al (1995) report higher rates, that is, that cyanide paste used for possum operations emits hydrocyanic acid gas at a rate of 50–160 µg/g/h. Encapsulated cyanide paste has reduced gas emission rates of 3.7 µg HCN/hr (Wright 2000), although, as for the non-encapsulated paste, the details of the studies are not known.

D3.2.2 Feratox

Wright and Manning (2003) buried Feratox pellets to a depth of 5 cm in soil plots, watered them at 13 mm/day and kept them at an average temperature of 15^{o}C. The pellets were removed at intervals up to 16 days, together with a 20 g soil sample from around the pellet. The authors report concentrations in the soil around the pellets that on day 16 reached

8 mg/kg, although the Agency notes that the data described in the text of the report do not correspond to the plot of those data. After 16 days, three of the four pellets sampled remained substantially intact and retained 71% of their initial cyanide concentration. The fourth pellet had largely broken down and contained only 1% of the initial cyanide concentration.

In a second similar experiment, pellets were sampled at intervals up to 64 days. On day 34 the pellets contained an average of 45% of the initial cyanide concentration (range 2.9–67%), by day 64 seven pellets lost more than 98% of the initial cyanide, an eighth retained 63%. The Agency concludes that cyanide pellets can remain largely intact in soil for periods of several weeks. The authors note that on removing the pellets on day 34, worms were observed close to the pellets, but it is not stated in the report whether this includes both the pellets that had disintegrated and those that had not. They also note that the soil had a background concentration of 0.48 mg/kg. Rainfall, humidity or environmental moisture and presence of soil micro-organisms increase the degradation of cyanide in soil (Eason and Wickstrom 2001).

D3.3 Bioaccumulation

Cyanide does not bioaccumulate and cyanide biomagnification in food webs has not been reported, possibly due to rapid detoxification of sublethal doses by most species and deaths at higher doses (Eisler 1991). In sub-lethally poisoned animals cyanide is metabolised to thiocyanate. Thiocyanate is approximately 120 times less toxic than cyanide, and is excreted over several days (Eason and Wickstrom 2001). During a US pen study of chickens, most of a sub-lethal cyanide dose was recovered as thiocyanate within six hours (Eisler 1991).

Residues of cyanide in possum carcasses are discussed in Appendix O.