Appendix 3

Toxicity Profile and Risk Assessment for Cyanide

(Total No. of pages including blank pages = 130)

(Note: A colour version of this Appendix is available on the Project CD)

This Appendix includes two reports prepared by ToxConsult.

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Toxicity profile for cyanide

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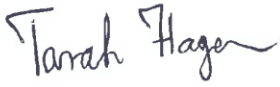

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Executive Summary

Big Island Mining Ltd has requested ToxConsult to consider the hazards, and assess the health risks associated with the use of cyanide to wildlife and residents in proximity of the mine. This toxicity profile provides an understanding of the chemistry and environmental fate of cyanide, and toxicological information that informs the risk assessment.

Chemistry and Environmental fate

- Analytical measurements of cyanide(s) in water typically report the following:
  - *'**Free' cyanide** includes only hydrogen cyanide (HCN) and cyanide ion (CN^-).*
  - ***WAD cyanide** includes both 'free' cyanide and any cyanide in metallo-cyanide complexes which can be liberated at a pH of 4.5 – 6. These include Cu, Cd, Ni, Zn, and Ag complexes which have low stability constants.*
  - ***Total cyanide** includes all 'free' cyanide, and all dissociable cyanide complexes (both WAD and strong metal cyanide complexes including Fe, Co, and Au cyanides). Cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from total cyanide.*
- *WAD CN is frequently considered the most appropriate indicator of biologically available cyanide for monitoring purposes.*
- *Cyanide seldom persists in surface waters because it is readily lost to air by volatilisation. It is also removed from water by complexing with metals to form less soluble forms that precipitate and by microbial biodegradation.*
- *The biodegradation half-life of cyanide at concentrations $\leq$6 mg/L in natural river waters is less than 24 days.*
- *At pH <9, cyanide in surface water readily forms HCN and evaporates.*
- *The volatilisation half-life of HCN from solutions at concentrations of 0.025-0.2 mg/L ranges from 22 to 110 hours, with shorter half-lives at lower pH.*
- *Although cyanide is potentially mobile in soils it rarely remains biologically available because it is either complexed with trace metals, microbially metabolised, or lost through volatilisation. It is rarely detected in groundwater.*
- *Cyanogenic glycosides in dietary plants is the greatest source of non-occupational exposure to cyanide. Similarly for animals. The potential toxicity of cyanogenic plants depends on the ease and rate at which HCN is released during preparation or digestion.*
- *In animals (including humans) low exposures to HCN either orally or by inhalation are easily detoxified. Primarily to thiocyanate. Toxicity occurs when the detoxification mechanisms are overwhelmed.*

Ecotoxicity

Birds and wildlife

- *There is a body of evidence from various anecdotal, scientific observations and incident reports at mine sites indicating significant avian mortalities have occurred when WAD CN concentrations are >50 mg/L, but relatively few or no mortalities at lower concentrations.*
- *Whether the exposure is by ingestion or inhalation cyanide the dose-response for mortality is steep.*
- *Animals fully recover from non-lethal acute exposures to cyanide.*

Oral toxicity:

- *From repeat oral exposure data in birds, according to Australian authorities (NICNAS) 50 mg/L WAD equates to an estimated overall bird lethality of approx 1% and provides acceptable protection for birds that may drink the water.*
- *Experimental studies where birds were exposed to cyanide in drinking water or via oral bolus doses give avian LD_{50} values ranging from 1.4 to 69 mg CN^-/kg bw. No Observed Effect Levels (at which no mortalities occurred) ranged from 0.53 mg CN/kg bw for mallard ducks to 6 mg CN/kg bw for domestic chickens.*
- *Experimental toxicity studies in birds indicate oral KCN is similarly toxic in terms of lethality as NaCN but other compounds, particularly metallo-cyanides such as copper cyanide, are significantly less toxic.*
- *Water WAD concentrations protective of birds are also considered by Australian and European authorities to be protective of bats and terrestrial vertebrates (e.g. reptiles and macropods).*

Inhalation toxicity:

- *There is little information available for the inhalation toxicity of HCN to birds.*
- *Several studies have determined LC_{50} values for HCN for a variety of exposure periods in rats, rabbits, and mice. Lethality is dependent upon the HCN concentration and time of exposure. LC_{50} values ranged from 133 (rat, 60 mins) to 3,800 mg HCN/m^3 (rat, 12 sec).*
- *No Observed Effect Concentrations (for lethality) were only available in a few studies, and ranged from 84 (rat, 60 mins) to 313 mg HCN/m^3 (rat, 5 mins).*
- *Other studies have investigated sublethal effects of inhaling HCN in monkeys, rats and mice. Sublethal effects were characteristic of respiratory depression and worsened with increasing HCN concentrations in air.*

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Dermal toxicity:

- *HCN readily penetrates intact and damaged mammalian skin. Data were not available for birds.*

Tolerable water concentrations:

- *ECETOC (2007) derived a "tolerable" water concentration for protecting wildlife of 2mg CN^-/L (free cyanide) by applying an assessment factor of 10 to the Low Observed Effect Level (for decreased water intake and decreased body weight) of 19.4 mg CN^-/L from an experimental study with mallard ducks exposed to NaCN in drinking water for 5 days.*
- *NICNAS (2010) used data from acute oral toxicity tests to derive a predicted no effect concentration (PNEC) for CN^- of ~1mg/L, but indicated this low PNEC may not be justified based on field evidence and difficulties with extrapolating acute toxicity data from laboratory studies to risk in the field. The derivation details for this PNEC is not described by NICNAS and therefore there is uncertainty in its appropriateness.*
- *The International Cyanide Management Institute developed the International Cyanide Management Code (ICMC), a voluntary initiative for the gold mining industry and for producers and transporters of cyanide used in gold mining. The guidance indicates that where birds, wildlife or livestock have access to water impounded in tailings storage facilities, leaching facilities or solution ponds, operations should implement measures to limit the concentration of WAD cyanide to a maximum of 50 mg/L. This concentration is typically viewed as being protective of most wildlife and livestock mortality other than aquatic organisms.*

Aquatic organisms

- *Aquatic organisms are sensitive to cyanide, with fish being the most sensitive, followed by invertebrates. Algae and aquatic plants are comparatively tolerant to cyanide.*
- *In chronic toxicity studies, reliable NOECs for free cyanide range from 1 to 29 µg/L for fish, 3.9 to 30 µg/L for invertebrates, and 3.9 to 700 µg/L for algae.*
- *The ANZECC freshwater trigger value for protection of 95% of aquatic species is 7 µg CN/L.*
- *ECETOC (2007) also used a species sensitivity distribution approach and selected the 5^{th} percentile of the distribution (i.e. 95% species protection level) to estimate a PNEC of 1 µg/L of free cyanide for freshwater and saltwater species.*

Terrestrial plants

- *By comparison to other organisms, terrestrial plants seem to be relatively resistant to cyanides and certain plants themselves may be sources of cyanide in the form of cyanogenic glycosides*

Human toxicity

- *Cyanide is a potent and rapid-acting chemical asphyxiant acting by inhibiting cytochrome C oxidase in mitochondria.*
- *The toxicity of individual cyanide compounds is dependent on the ease with which they release free CN^-. For example, stable Fe cyanide complexes are nearly non-toxic.*
- *After ingestion of cyanide salts or metal complexes cyanide is absorbed as HCN. Different amounts and rates of formation of HCN in the gastrointestinal tract depends on the form of cyanide.*
- *CN^- is readily and largely completely absorbed by humans after inhalation, dermal and oral exposure.*
- *HCN does not accumulate in blood or tissues following chronic or repeat exposure. HCN is metabolised by the enzyme rhodanase to thiocyanate, which is readily excreted in urine.*
- *In humans, the plasma half-life for cyanide to be metabolised to thiocyanate is ~20-60 minutes. The elimination half-life of orally administered thiocyanate is about 3 days in healthy human volunteers or 7-9 days in subjects with impaired renal function.*

Acute toxicity

- *Acute toxicity of cyanide in humans has a steep dose-response relationship. Exposure to lethal or nearly lethal doses rapidly (within seconds to minutes) leads to a series of respiratory, cardiovascular and neurological symptoms, followed by coma and death. Death is due to respiratory failure or cardiac arrest.*
- *After a single, brief exposure to a low concentration of HCN from which an individual recovers quickly, no long term health effects have been observed.*
- *However, serious acute cyanide poisoning that does not result in death may lead to severe and potentially irreversible neurotoxicity. There is no indication from the available data that repeated low dose exposure to cyanide could have similar effects. Substantial but sublethal intermittent doses of cyanide can be tolerated by many animals for long periods of time without adverse effects.*
- *FSANZ (2014) and JECFA (2011) have set acute reference doses for cyanide (80 and 90 µg HCN/kg bw, respectively). Both authorities used the same experimental study where pigs were fed the cyanogenic glycoside linamarin, but used different endpoints.*

Subchronic toxicity

- *ATSDR (2006) derived an intermediate-duration (15-364 days) minimal risk level (MRL) of 0.05 mg CN^-/kg/d from the NOAEL of 4.5 mg/kg/d for reduced epididymal weight in male rats in a 90-day oral study from the NTP (1993) with sodium cyanide.*
- *The same point of departure was used by the World Health Organisation (WHO 2009, 2011) to derive a drinking water quality guideline of 0.5 mg/L for total cyanide (for short term exposure, i.e. <5 days).*

Chronic toxicity

- *JECFA (2011) and US EPA (2010) have both established chronic guideline values for cyanide (20 and 0.6 µg CN/kg/d, respectively). Both values used the same point of departure ($BMDL_{10}$ or $BMDL_{1SD}$ of 1.9 mg/kg/d for decreased cauda epididymis weight in rats from the NTP study with sodium cyanide) but applied different uncertainty factors resulting in a 33-fold difference in the derived guideline values. Since the effect on which the guidelines are based are very sensitive (small decrease in cauda epididymis weight) and a 2-year feeding study in rats did not find adverse effects at treatments similar to those used in the NTP (1993) study, the high uncertainty factor used by the US EPA (2010) is not justified and too conservative. Thus the JECFA (2011) guideline is considered more appropriate.*
- *There is no evidence that cyanide is carcinogenic (although specific carcinogenicity studies are lacking). Studies assessing the genotoxicity of cyanide salts in vitro or in vivo have been negative.*
- *Cyanides are embryotoxic and teratogenic at maternally toxic doses.*

Contents

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1. Introduction and Scope

Dargues Gold Mine (the Mine) will recover gold with the aid of a well-developed and well understood cyanide extraction technique that has been used around the world for many decades. The owners of the Mine have requested ToxConsult Pty Ltd to provide them with a document that discusses the toxicology of cyanide(s) towards wildlife and humans. Much of the information in this toxicity profile has been gleaned from recent reviews produced by competent authorities (OEHHA 2000, ANZECC 2000, WHO 2004, ATSDR 2006, ECETOC 2007, NICNAS 2010, US EPA 2010, JECFA 2011) but heavily supplemented by reference to individual scientific publications.

Cyanides are compounds which contain the cyano group (this chemically designated as –CN). They are common industrial chemicals widely used in extracting gold and silver from ore, in manufacturing nitrile and methacrylate fibres, in electroplating and other metal production, and in some fumigants and pesticides. Hydrogen cyanide (HCN) is ubiquitous in nature. It is released into the atmosphere from biomass burning, volcanoes, and natural biogenic processes from higher plants, bacteria, algae, and fungi. Thus HCN is present in cigarette smoke, smoke from bushfires and burning buildings. Cyanide occurs naturally as cyanogenic glycosides in at least 2000 plants, including many used for food. It is found in cassava (tapioca), bitter almonds, lima beans, sorghum, sweet potato, corn, cabbage, linseed, millet, immature shoot tip bamboo, commercial fruit juices (cherry, apricot, prune), in pits of stone fruits, such as cherries, peaches, and apricots, and in apple seeds (ANZECC 2000, WHO 2004). Due to its dietary ubiquity many organisms, including humans, have evolved ways to metabolise cyanide. Toxicity occurs when these detoxification mechanisms are overwhelmed.

2. Environmental Fate

The environmental fate of cyanide is intimately tied to the complex chemistry of the substance. Consequently the sections below contain a lot of contextual chemistry.

2.1 Water

2.1.1 Chemistry

Cyanide in water may be present in different chemical forms (ANZECC 2000) including:

- hydrocyanic acid (HCN),
- cyanide ion (CN^-),
- various complexes with metals in the water, the stability of which is pH dependant,
- cyanogen $(CN)_2$,
- cyanates (containing –OCN),

- thiocyanates (-SCN),
- nitriles (RCN, where R is an alkyl group).

Measurements of cyanide in water may be reported as:

- 'Free' cyanide. This is cyanide present as HCN and ionic CN^-
- Weak Acid Dissociable (WAD) cyanide. This refers to cyanide weakly complexed with metals such as cadmium, copper, nickel, zinc and silver, plus the free cyanide. For these metallo-cyanide complexes the cyanide may be readily released when water is tested at a pH of 4.5. WAD does not include cyanide strongly bound to metals, e.g. iron or cobalt cyanide complexes.
- Total cyanide. This is the sum of the free cyanide, WAD and all other forms of cyanide from which free cyanide may be released.

These different cyanide measurement classifications are depicted in Figure 2.1 and different chemical forms further summarised in Table 2.1.

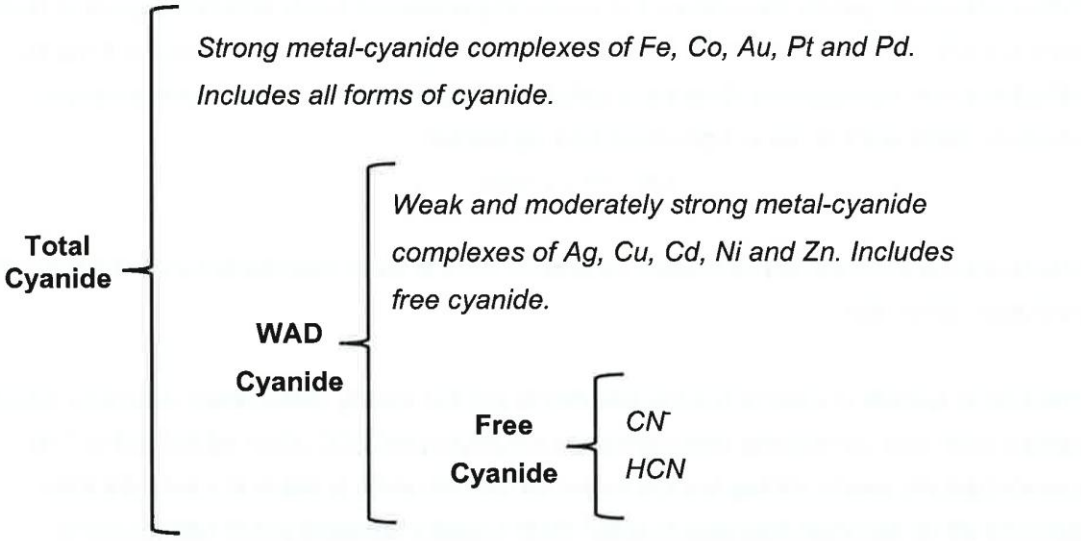

Figure 2.1: Classification of cyanide compounds according to measurement reporting
Adapted from Applikon Analytical (undated) and Mintek (undated).

Table 2.1: General description of different forms of cyanide (From Merg 2001).

Term	Description	Example
Cyanide ion	The free cyanide ion	CN^-
Molecular HCN	Hydrogen cyanide (hydrocyanic acid)	HCN
Free cyanide	includes the cyanide ion and hydrogen cyanide	CN^- + HCN
Simple cyanide	A salt which dissociates to form a cyanide ion.	NaCN
Complex cyanide	Dissociates to form another cyanide compound.	$Au(CN)_2$
WAD cyanide	Weak acid dissociable; cyanide that is readily released from cyanide containing compounds when tested at pH 4.5.	$Cd(CN)_2$
SAD cyanide	Strong acid dissociable, cyanide that is released from cyanide containing compounds under highly acidic conditions.	$Co(CN)_6^{4-}$
Total cyanide	The sum of all of the different forms of cyanide present in the water that can release free cyanide.	

Different forms of cyanide have different chemical properties and hence different degrees of toxicity. HCN and CN^- are the principal toxic forms, the former being the most toxic because it is readily diffusible across biological membranes, is volatile and highly reactive. In most environmental situations, HCN and CN^- are in a pH dependent equilibrium.

$$CN^- + H^+ \leftrightarrow HCN$$

Volatilisation is the dominant elimination process for HCN in water (see Section 2.2) (ANZECC 2000, HPA 2011, NPS 1997).

The form of cyanide in water is not only affected by pH, but also by temperature, dissolved oxygen, salinity, other ions, complexing metal agents, and sunlight (ANZECC 2000, MERG 2001). The cyanide typically used in mining is sodium cyanide (NaCN) which is stable in a solid dry state (NICNAS 2010) but when dissolved in water[1] HCN is readily formed at pH<9 (MERG 2001).

Cyanide binds with various metal ions to form metallo-cyanide complexes of varying degrees of stability. For example, Zn and Cd complexes are unstable and dissociate readily in aqueous solution, or gastric pH, releasing CN^- and thence HCN. Although less dissociation occurs from more stable complexes such as Ni, Cu and Ag they are still regarded as being easily dissociable and are included in WAD measurements. The degree of dissociation increases with decreasing pH and complex

[1] NaCN is highly soluble in water (48 g/100 mL at 10 °C) (ATSDR 2006). HCN is also highly soluble in water, however its solubility decreases with increased temperature and under highly saline conditions (ICMI undated, FAO 1965).

instability (ANZECC 2000, ATSDR 2006). Ferric-, ferro-, and cobalt- cyanides are relatively stable complexes but may slowly release cyanide when exposed to sunlight (ANZECC 2000, ATSDR 2006, MERG 2001, Little et al 2007). For example, diurnal changes in free cyanide concentrations in the drainage from 'heap' leachates were found to increase approximately 3-fold around midday due to the photodissociation of iron cyanocomplexes (Johnson et al 2002). Further information on the rate of photolysis of ferric cyanocomplexes in water was not found.

The stability of metal cyanide complexes with respect to dissociation is expressed by their formation, or stability, constants. The higher the value of the formation equilibrium constant (K), the greater the energy of formation and therefore stability of the metal-cyanide complex. Complexes with higher formation constants are thus often termed "strong metal cyanide complexes." The distinction between weak and strong complexes is environmentally relevant because strong complexes such as ferro-cyanide dissociate only under strong acidic conditions (pH<2). They are considered environmentally stable and relatively nontoxic, whereas weak metal cyanide complexes dissociate under mildly acidic conditions (pH 4-6) (Dionex 2003, Nsimba 2009). Table 2.2 lists a number of common metal-cyanide complexes and compounds and their equilibrium formation constants (as logK).

With the exception of thiocyanate in acidic media, thiocyanate, cyanate and nitriles do not form free cyanides, and hence are much less toxic (ANZECC 2000).

'Free' cyanide and the weak acid-dissociable complexes (e.g. copper, nickel, silver, zinc, and cadmium cyanide) are considered of potential toxicological significance.

Measurements of WAD cyanide[2] is frequently considered the most appropriate indicator of biologically available cyanide for monitoring purposes when determining toxicological and environmental impacts (ANZECC 2000, DRET 2008, NICNAS 2010)[3].

[2] Conventional WAD CN methods use a weak acid (pH 4 or 4.5) distillation method to release cyanide from defined metal complexes (Zn, Cd, Ag, Cu, Ni) for subsequent distillation and analysis. Following these methods cyanide is liberated from the weak acid dissociable complexes, and all free cyanide is then measured colourimetrically. Standard methods for WAD CN include ISO 6703/2 and ASTM Method D 2036-98.

[3] Conventional WAD cyanide analysis measures cyanide that dissociates at pH $\geq$ 4.5 or pH $\geq$4.0. However, it has been suggested by some authors that since a few common metal-cyanide complexes dissociate below pH 4.0, these may also present a hazard when ingested by some birds due to the pH of the gastric juices in some aquatic birds (pH 1.0-2.0) and some raptorial birds (pH 1.3). Nevertheless, other authors have suggested the effects may be counteracted by a potentially slower rate and degree of dissociation of the metal-cyanide complexes and by the alkalinity of the ingested solution (NICNAS 2010).

Table 2.2: Common metal-cyanide complexes and other compounds [a]

Compound class		Examples	Stability constant (logK)
Free cyanide		CN^-	
		HCN	-
Simple compounds	readily soluble	KCN	-
		$NaCN.2H_2O$	-
		$Ca(CN)_2$	-
	relatively insoluble	CuCN	-
		$Zn(CN)_2$	-
		$Ni(CN)_3$	-
Weak complexes		$Cd(CN)_4^{2-}$	18
		$Zn(CN)_4^{2-}$	17-19.6
Moderately strong complexes		$Ni(CN)_4^{2-}$	30.2
		$Cu(CN)_2^-$	24
		$Cu(CN)_3^{2-}$	23-28
		$Cu(CN)_4^{3-}$	23-28
		$Ag(CN)_2^-$	20.5
Strong complexes		$Fe(CN)_6^{4-}$	35.4-45.6
		$Fe(CN)_6^{3-}$	43.6-52.6
		$Au(CN)_2^-$	37-39
		$Co(CN)_6^{4-}$	64
Thiocyanate		SCN^-	-
Cyanate		OCN^-	-

- = none found.
log K = equilibrium formation (i.e. stability) constant at 25 °C. The higher the stability constant, the more stable the complex.
[a] Compiled from information in NICNAS (2010), Dionex (2003), Nsimba (2009), Nollet and De Gelder (2007).

2.1.2 Biodegradation

Biodegradation is an important transformation process for cyanide in natural surface waters, and is dependent on cyanide concentration, pH, temperature, availability of nutrients and acclimation of microorganisms (ATSDR 2006). Although the cyanide ion may be toxic to microbes at concentrations ≥ 5-10 mg/L, acclimation increases tolerance to the compound. For example, mixed microorganisms in sewage sludge acclimated to cyanide may biodegrade concentrations up to 100 mg/L (ATSDR 2006). From the information in Ludzack et al (1951), ATSDR (2006) estimated the biodegradation half-life of cyanide at concentrations ≤6 mg/L natural river waters to be less than 24 days. Biodegradation involves conversion of the cyanide ion to the less toxic thiocyanate, or nitrile derivatives of α-amino acids which are ultimately degraded to the corresponding amino acid or carboxylic acid and ammonia, formamide or formic acid, ammonia, and carbon dioxide (ATSDR 2006).

HCN and CN^- do not strongly partition to sediments or suspended adsorbents, primarily due to their high solubility in water. However binding to particulates and precipitation may be an important removal pathway for metal cyanide complexes in surface waters (ECETOC 2007). Figure 2.2 depicts the major processes influencing the fate of cyanide in water.

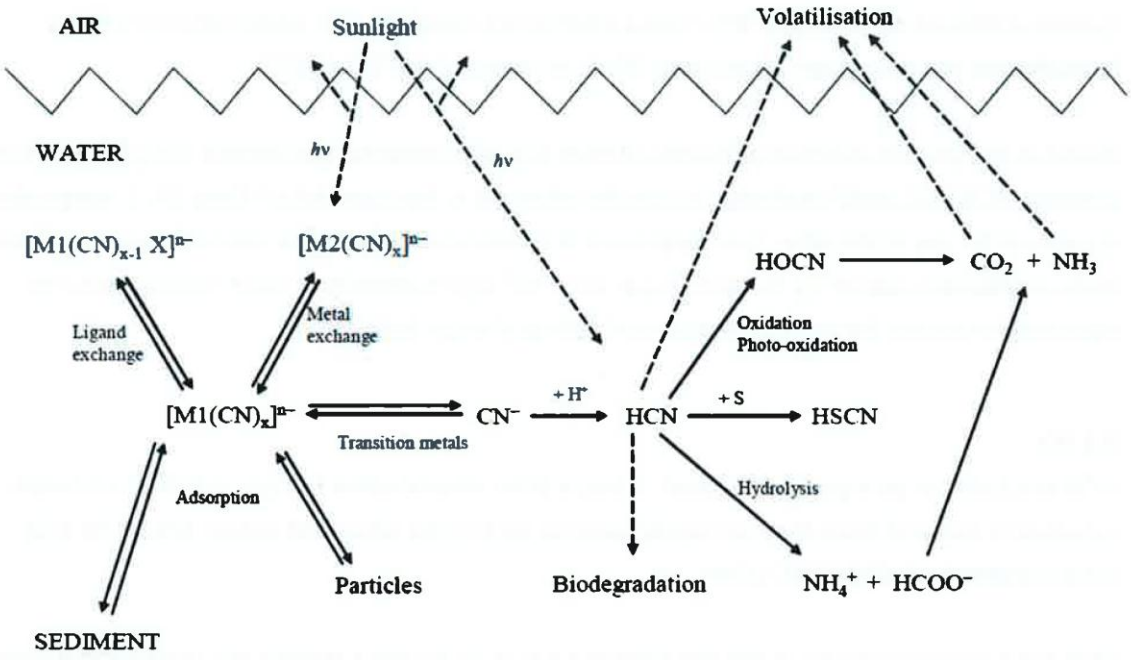

Figure 2.2: Fate of cyanides in water
M1 and M2 = transition metals; *hv* denotes light energy in the form of photons.
From ECETOC (2007)

2.1.3 Volatilisation

Cyanide seldom persists in surface waters because it is easily removed by volatilisation, complexation with metals, sedimentation of insoluble metal complexes, and microbial biodegradation (Eisler and Wiemeyer 2004, ECETOC 2007, NPS 1997).

At pH <9.2, most WAD cyanide in surface water forms HCN and evaporates. Volatilisation is low at high pHs, i.e. ~13. The volatilisation rate of HCN is affected by pH, temperature, wind speed and cyanide concentration (ATSDR 2006, NICNAS 2010). The volatilisation half-life of HCN from solutions (in the lab, without wind influence) at concentrations of 0.025-0.2 mg/L follows first order kinetics and

ranges from 22 to 110 hours, with shorter half-lives at lower pH (ECETOC 2007, ATSDR 2007). In outdoor experiments with moderate winds, the rate of HCN loss increased by a factor of 2-2.5 (ATSDR 2006, ECETOC 2007). Raef et al. (1977a,b) passed air (2 cm^3/min) through a solution of 10 mg CN^-/L at pH 7 and 30 °C. After 6.25 hours, about 42% of the cyanide had volatilised.

Significant volatilisation of HCN from cyanide-containing mine wastes has also been demonstrated in laboratory experiments. Within 24 hours, for a leachate from an oxide ore the majority (90%) of free cyanide volatilised as HCN, and 30% from a sulphide ore leachate, with volatilisation continuing thereafter but at a slower rate (Rubo et al. 2000, as cited in ECETOC 2007)[4].

Based on the physico-chemical properties of HCN and environmental calculations using the EPI Suite software, ECETOC (2007) estimated a cyanide solution (i.e. free cyanide) of 50mg CN^-/L evaporates at a rate of 0.1 mg HCN/cm^2/s. The Department of Environment (2006) has used in the past a much lower volatilisation rate of 1 g HCN/m^2/hr (i.e. 2.7 x 10^{-5} mg HCN/cm^2/s for each 100mg CN^-/L) for estimating emissions from the surface area of tailings storage facilities.

2.2 Air

HCN in solution or as a gas is colourless. It has a bitter almond odour but less than 50% of people can smell it; some of those that can rapidly become used to the odour and cannot smell it for long (Gezondheidsraad 2002, WHO 2004).

HCN has a vapour pressure of 100 kPa (750 mm Hg) at 26 °C and a Henry's law constant of 0.00544 (air/water; unitless) at 25 °C (ECETOC 2007). The Henry's law constant indicates HCN has high volatility from water. HCN is lighter than air (density of 0.94 relative to 1 for water) and therefore does not accumulate near the surface of treatment ponds or in hollows (NICNAS 2010).

Gaseous HCN is not easily removed from the air by wet or dry deposition (rain or snow, or by settling). It is also resistant to photolysis. Although HCN is highly reactive in biological systems it is stable in air with a half-life of about 1-3 years (Eisler and Wiemeyer 2004, ATSDR 2006, ECETOC 2007, RIVM

[4] The laboratory scale experiments used tailings obtained from cyanide leaching ore excavated from an oxide, a transition and a sulphide rich zone. The tests were performed in air-tight glass vessels at a mixture of 40% crushed ore and 60% water by weight. The pH was kept constant at 10.5 by addition of NaOH. After 24 hours, the pH was set to TSF pond conditions (pH 8-9) and air (20 l/h) was bubbled through the pulp and then through NaOH solution (1 mol/l) to trap cyanide. Samples of the NaOH solution and 24-hour pulp leach were filtered and analysed for HCN, total CN, WAD CN, free CN, SCN^- and OCN^-. For the oxide ore approximately 90% of the free cyanide in the leaching vessel had volatilised as HCN, and 30% for the sulphide ore. Even when free cyanide could no longer be measured (below the limit of detection of 0.2 ppm), HCN volatilisation was still observed, but at a much lower rate due to the stability of the cyanide complexes. The time course for removal was: free cyanide up to 9 weeks, WAD cyanide up to 6 months, total cyanide approximately 1 year (Rubo et al. 2000, as cited in ECETOC 2007).

2000). The most important reaction of HCN in air is with photochemically-generated hydroxyl radicals and subsequent oxidation to carbon monoxide and nitric oxide (ECETOC 2007).

2.3 Soil

In soils, cyanide rarely remains biologically available because it is either complexed with trace metals, microbially metabolised, or lost through volatilisation (Eisler and Wiemeyer 2004, NPS 1997). Although water soluble cyanides are potentially mobile in soil, they are not usually detected in groundwater, probably due to complexation and/or microbial transformation prior to reaching the groundwater (DEFRA 2002, ECETOC 2007). Upper limits of 200 and 2 mg CN^-/kg soil have been respectively reported for aerobic and anaerobic biodegradation of cyanide in soil without toxicity to microorganisms being observed (Fueller 1985, as cited in ATSDR 2006). Nevertheless, in soils where cyanide levels are high enough to be toxic to microorganisms they may leach into groundwater (ATSDR 2006). The mobility of cyanide is greater in soils with high pH, with high concentrations of free calcium carbonate (high negative charge), and low clay content (NICNAS 2010, ECETOC 2007).

2.4 Food

The primary cyanide source in food is cyanogenic glycosides (ATSDR 2006, NPS 1997). Food typically represents the greatest source of cyanide exposure to humans and animals (NPS 1997). The potential toxicity of cyanogenic plants depends on the ease HCN is released during food preparation or digestion. Over 2,600 plant species contain cyanogenic glycosides which can be hydrolysed to form HCN. These include almonds, pits from stone fruits, sorghum, cassava, soybeans, spinach, lima beans, sweet potatoes, maize, millet, sugarcane, cabbage, linseed and bamboo shoots (ATSDR 2006, Gezondheidsraad 2002, NICNAS 2010, WHO 2004).

Cyanogenic glycosides are stored in plant cell vacuoles. Consumption and maceration of plant parts leads to the release of the plant enzyme ß-glucosidase which hydrolyses the glycoside to the sugar aglycone and to HCN, particularly in alkaline rumen conditions of ruminant herbivores. The low amount of HCN usually produced is either detoxified or excreted as a gas. Adverse effects may however occur in animals if the capacity for detoxification is exhausted (NICNAS 2010). There are many well-documented examples of deaths from consumption of cyanogenic plants in humans, cattle, sheep, koalas, goats, other grazing mammals, and birds (Gleadow and Woodrow 2002, Woldemeskel and Styer 2010).

2.5 Key Points from Section 2

- *Analytical techniques for measurement of cyanides is typically for three different forms:*
  - *'**Free' cyanide** includes only HCN and CN^-.*
  - ***WAD cyanide** includes both 'free' cyanide and any cyanide in metallo-cyanide complexes which can be liberated at a pH of 4.5 – 6. These include Cu, Cd, Ni, Zn, and Ag complexes which have low stability constants.*
  - ***Total cyanide** includes all 'free' cyanide, and all dissociable cyanide complexes (WAD and strong metal cyanide complexes including Fe, Co, and Au cyanides). Cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from total cyanide.*
- *WAD CN is frequently considered the most appropriate indicator of biologically available cyanide for monitoring purposes.*
- *Cyanide seldom persists in surface waters because it is readily lost to air by volatilisation. It is also removed from water by complexing with metals to form less soluble forms that precipitate and by microbial biodegradation.*
- *The biodegradation half-life of cyanide at concentrations ≤6 mg/L in natural river waters is less than 24 days.*
- *At pH <9, cyanide in surface water readily forms HCN and evaporates.*
- *The volatilisation half-life of HCN from solutions at concentrations of 0.025-0.2 mg/L ranges from 22 to 110 hours, with shorter half-lives at lower pH.*
- *Although cyanide is potentially mobile in soils it rarely remains biologically available because it is either complexed with trace metals, microbially metabolised, or lost through volatilisation. For this reason it is rarely detected in groundwater.*
- *Cyanogenic glycosides in plants typically represents the greatest source of non-occupational exposure to cyanide. Similarly for animals. The potential toxicity of cyanogenic plants depends on the ease and rate at which HCN is released during preparation or digestion.*
- *In animals (including humans) low amounts of HCN are easily detoxified. Toxicity occurs when the detoxification mechanisms are overwhelmed.*

3. Ecotoxicity

Cyanides are not persistent in the environment, do not bioconcentrate and are not bioaccumulative (MPERG 2001, NPS 1997, ATSDR 2006, ECETOC 2007, Donato et al. 2008, NICNAS 2010).

3.1 Birds and wildlife

There have been incidents of migratory birds being poisoned with cyanide at heap leaching facilities or tailings ponds (MERG 2001). Although birds may absorb cyanide through their skin when wading or swimming, or inhale HCN as it evaporates, drinking the water is considered the main route of intoxication in birds (ECETOC 2007, NICNAS 2010).

Small mammals, such as rodents, rabbits, bats, etc. have also been found dead near cyanide containing tailings ponds. Fencing the area, screening or netting ponds, floating balls to scare wildlife, and ensuring the concentration of cyanide is low in ponds have been used to prevent bird and mammal deaths (MERG 2001).

3.1.1 Oral toxicity

3.1.1.1 Free cyanide (CN^-)

- Experimental studies where various birds were exposed to cyanide in drinking water or via bolus dose yield avian oral LD_{50} values[5] for different species that range from 1.4 to 69 mg CN^-/kg bw, with the mallard duck being the most sensitive (Table 3.3). NICNAS (2010) note No Observed Effect Levels for lethality ($NOEL_{mortality}$) from bolus dosing ranged from 0.53mg CN^-/kg bw for mallard ducks to 3.2 mg CN^-/kg bw for domestic chickens with the corresponding Low Observed Effect Level ($LOEL_{mortality}$) being 1.1 mg CN/kg and 6.3 mg CN/kg respectively[6]. ECETOC (2007) note *ad libitum* exposure to NaCN for 5 days in drinking water resulted in NOELs of 16.4 ($NOEL_{mortality}$) and 33 ($NOEL_{any\ effect}$) mg CN^-/kg bw for mallard ducks and Northern bobwhite quail, respectively.[7] The dose response for mortality is very steep.
- When birds were not killed they fully recovered despite other effects occurring[8].

[5] The LD_{50} is the dose associated with death in 50% of the treated animals.

[6] These doses are converted from NaCN to CN^-. It is unclear how NICNAS (2010) have determined the $LOEL_{mortality}$ for chickens from the information in the Wiemeyer et al (1986) paper.

[7] It is noted there is significant uncertainty with these doses. The assumptions used by ECETOC (2007) for calculating the dose from the measured water concentrations were not provided.

[8] See Table 3.2 and text below for effects descriptions.