TOXICITY OF CYANIDE

by

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SUMMARY

Cyanide is one of the most toxic chemicals to which fish are likely to be exposed. Dose levels as low as 0.03 mg/L HCN can be ultimately fatal to sensitive species, while 0.2 mg/L is lethal to most species. In each case, levels less than the lethal dose provoke physiological and pathological responses that not only reduce swimming ability, interfere with reproductive capacity and lead to seriously deformed offspring, but also leave the fish more vulnerable to predators.

The toxicity of the principal metal cyanide complexes may, in some cases, include toxicity due both to cyanide and to the complex ion.

Ferrocyanide, while relatively non-toxic itself, can dissociate under the influence of the ultraviolet in sunlight and this can result in a toxicity approaching that of the other cyanide compounds. Toxicity to land animals, including man, while still a matter for concern, is at least an order of magnitude less than that for fish.

Cyanide is not a persistent toxic chemical and under normal conditions will not permanently destroy a fish habitat. It may nevertheless be necessary to completely repopulate a devastated body of water.

TOXICITY OF CYANIDE

While cyanide is eventually toxic to all life forms, some microorganisms such as bacteria, algae and fungi can tolerate and even metabolize cyanide at fairly elevated levels (up to 200 mg/L). Higher organisms are less resistant and fish, in particular, are extremely sensitive to its action.

MECHANISM OF TOXICITY

Hydrogen cyanide is rapidly absorbed and carried in the plasma. It binds strongly to iron, copper and sulphur, key constituents of some of the compounds which are important in life processes. Not all such compounds are inactivated: hemoglobin, in particular, retains its ability to accept and transport oxygen. The principal compound affected is cytochrome oxidase, an enzyme contained within the cells of the body which is essential for the utilization of oxygen. Its inactivation leads to cellular asphyxiation and tissue death. Since the central nervous system of higher animals has the greatest oxygen requirement, it is the most strongly affected. Its suppression leads to suspension of all vital functions and death of the organism.

Table 1 summarizes some cyanide toxicity data.

TABLE 1 SENSITIVITY OF ORGANISMS TO CYANIDE

Organism	CN Conc'n, mg/L	Temp °C	Effect
Fish species			
rainbow trout	0.028	6.3	LC_{50} - 96 hrs
	0.042	12.3	LC_{50} - 96 hrs
	0.068	18.0	LC_{50} - 96 hrs
brown trout	0.08	15.5	LC_{50} - 24 hrs
small mouth bass	0.13	21.0	LC_{50}
bluegill	0.28		LC_{50} - 96 hrs
fat head minnows	0.23		LC_{50} - 96 hrs
mosquito fish	0.64		LC_{50} - 96 hrs
Crustaceans			
scud	0.17	18	LC_{50} - 96 hrs
Mammals			
Humans	0.06 - 0.09 gms total oral dose		fatal

Human Toxicity

Although cyanide in small amounts is also lethal to humans, their sensitivity to its action is very much less than that of fish; the National Drinking Water Standard for cyanide is 0.2 mg/L. This value, however, provides a very large safety factor.

Sub-lethal Toxicity

Continued exposure to less-than-lethal concentrations of cyanide affects reproduction, physiology and levels of activity of many fish species to an extent that can lead to destruction of the habitat as a viable fishery resource.

These effects are summarized in Table 2.

TABLE 2 ACUTE, CHRONIC AND SUBLETHAL TOXICITY OF CYANIDES TO FISH

LETHAL EFFECTS		SUBLETHAL EFFECTS		
ACUTE (Dynamic LC_{50} - 96 hrs) mg/L CN	CHRONIC (Juniors/ Adults) mg/L CN	Activity or Organ Affected	Nature of Effect	at mg/L CN
0.05 - 0.2 mg/L	0.019 - 0.07	Spawning	completely inhibited	0.005
		Egg Production	reduced 42%	0.01
		Egg Viability	Eggs infertile	0.065
		Spermatogenesis	permanent reduction	0.02
		Abnormal embry-onic development	severe deformities	0.07
		Hatching	up to 40% failure	0.01 - 0.1
		Swimming	reduced 90% at 6°C	0.015

Factors Influencing Acute Lethality of Cyanide to Fish

In addition to the total cyanide level of the water, a number of other factors associated with water chemistry exert a modifying effect on acute toxicity.

The susceptibility of fish to acute poisoning can be altered as a result of changes in these parameters either before or during their exposure to cyanide. Table 3

TABLE 3 EFFECT OF OTHER WATER PARAMETERS ON CYANIDE TOXICITY

PARAMETER	RANGE	EFFECT ON TOXICITY
Dissolved Oxygen	< Saturation	Increases toxicity
Temperature	18°C - 6°C	3-fold increase with 12° decrease in temperature
Salinity	8.8 - 17 parts per thousand	increases with increase in salinity
Zinc	1/4 of CN conc'n	25% increase
Ammonia	0.35 - 0.70 mg/L NH_3	more than doubled toxicity
pH	>8.5	slight decrease at higher pH

summarizes these factors. They include the dissolved oxygen concentration, temperature, pH, and the presence of certain other dissolved constituents.

Oxygen: Toxicity increases with any reduction of dissolved oxygen below 100%.

Temperature: Toxicity increases 3-fold with a 12°C decrease in temperature.

pH: pH values in the range 6.0 to 8.5 should have no effect on cyanide toxicity while pH's outside this range may themselves be detrimental to fish.

Salinity: Up to 8.8 parts per thousand of chloride ion has relatively little effect but an increase to 17 parts per thousand (full strength sea water) decreases survival time.

Other dissolved constituents: The presence of zinc and ammonia ions results in a greater-than-additive increase in toxic action.

EFFECT OF THE FORM OF CYANIDE COMPOUND PRESENT

The cyanide content of gold mill effluents is usually combined with metals (principally zinc, copper, nickel, cobalt and/or iron) in soluble metallocyanide complexes. As a result, the toxicity of the effluent does not bear a simple linear relationship to its total cyanide content.

In most (but not all) cases, the true measure of toxicity of such complexes is the extent to which they release hydrocyanic acid at the pH of the receiving water. However both cyanide ion and some metal cyanides exhibit an additional toxicity of their own. This is illustrated in Table 4, along with the conditions in receiving waters that promote formation of hydrocyanic acid.

TABLE 4 TOXIC FORMS OF CYANIDE

	FREE CYANIDE	METAL-COMPLEXED CYANIDES					
	CN^-, HCN	Zn	Cd	Ni	Fe	Cu	Ag
Source of Toxicity	HCN, (CN^- is ≃ 1/2 as toxic)	HCN	HCN	HCN	HCN	HCN and $Cu(CN)_2^-$	HCN and $Ag(CN)_2^-$
Conditions promoting HCN production	pH <8	pH <8	pH <8	low pH e.g. pH 6.5	U.V. light		

Influence of pH

At pH 9.3 about half of the cyanide in the alkali cyanides is present as HCN, increasing to 94% at pH values below 8. An analysis of toxicity data indicates that although hydrogen cyanide is the dominant toxic form, the cyanide ion itself has a toxicity, about 0.43 times that of hydrogen cyanide.

Thus the toxicity at higher pH's (around 9.0) is greater than would be predicted on the assumption that hydrocyanic acid is the only toxic form. At lower pH's the distinction becomes unimportant since almost all the free cyanide is in the hydrogen cyanide form.

Influence of Metal Content

The stability of the metal-cyanide complexes increases in the order:

$$Zn(CN)_4^{-2} < Cd(CN)_4^{-2} < Ag(CN)_2^{-} < Ni(CN)_4^{-2} < Cu(CN)_3^{-2} < Hg(CN)_4^{-2} < Fe(CN)_6^{-4} < Fe(CN)_6^{-3}$$

The relative cyanide concentrations in equilibrium with these complexes at pH 7 and at various dilutions is shown in Table 5. In almost all cases, however, the toxicity of a solution containing any of these complexes is greater than would be indicated on the basis of its free cyanide level. Thus, in the case of zinc, the combined toxicity of the zinc and cyanide is greater than the sum of their individual toxicities. Also, the undissociated cuprocyanides and argentocyanides are themselves toxic, while the dissociation of ferrocyanide is greatly enhanced under the influence of ultraviolet radiation. Some of these interactions are shown in Table 6.

TABLE 5 FREE CYANIDE CONCENTRATION RELEASED AT VARIOUS LEVELS OF COMPLEX CYANIDE, pH = 7, AND 25°C

COMPLEX	CONCENTRATION (mg/l) TOTAL CYANIDE AND RESPECTIVE FREE CYANIDE CONCENTRATIONS (mg/l)				
	1 mg/l	10 mg/l	100 mg/l	1,000 mg/l	100,000 mg/l
$Hg(CN)_4^{-2}$	0.00002	0.00003	0.000045	0.00007	0.00018
$Ag(CN)_2^{-}$	0.00009	0.0002	0.0004	0.0009	0.0041
$Cu(CN)_3^{-2}$	0.0003	0.00054	0.00097	0.0017	0.0054
$Fe(CN)_6^{-3}$	0.0002	0.0032	0.0004	0.0006	0.0012
$Fe(CN)_6^{-4}$	0.0012	0.0016	0.0022	0.0031	0.0061
$Ni(CN)_4^{-2}$	0.135	0.215	0.340	0.539	1.324
$Cd(CN)_4^{-2}$	*	2.30	3.64	5.77	14.49
$Zn(CN)_4^{-2}$	*	2.26	3.59	5.68	14.28

* Calculations indicate that at this dilution the two complexes are essentially completely ionized.

TABLE 6 TOXICITY OF CYANIDE AND CYANIDE COMPOUNDS TO FISH

Form	State in Water, pH 6.5 - 8.5	Toxicity Range as CN mg/L
HCN	No change	0.02 - 0.3
NaCN, KCN $Zn(CN)_4^{2-}$ $Cd(CN)_4^{2-}$	Converts completely to HCN	0.02 - 03 (Zn + Cd increase toxicity)
$Cu(CN)_3^{2-}$	Converts partially to HCN and $Cu(CN)_2^-$	0.4
$Cu(CN)_2^-$	No change	4.
$Ni(CN)_4^{2-}$	Releases HCN slowly at pH's below 7	pH 6.5: -0.4 pH 8.0: 730
$Fe(CN)_6^{4-}$	Toxicity depends on illumination - Converts to HCN in sunlight	In light: <0.2 In darkness: 300

LONG-TERM ENVIRONMENTAL IMPACT

Over the long-term, and if the source of the cyanide is eliminated, cyanide can be considered to be a non-persistent toxic chemical. Moreover its action is reversible and living organisms have mechanisms capable of eliminating it. Thus, provided exposure has not been so prolonged as to produce permanent physiological damage, complete recovery is possible.

Cyanide does not undergo either bioaccumulation or biomagnification (if one ignores certain plants which actually synthesize and store cyanogenic glucosides). In cases where there has been exposure to lethal levels, or a prolonged sub-lethal regime, however, recovery of the fishery resource may require recolonization, possibly with human intervention.