BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:

WATER QUALITY AMENDMENTS TO	)
35 Ill. Adm. Code 302.208(e)-(g), 302.504(a),	)
302.575(d), 303.444, 309.141(h); and	)
PROPOSED 35 Ill. Adm. Code 301.267,	)
301.313, 301.413, 304.120, and 309.157	)

R02-11
(Rulemaking - Water)   P.C.#27

NOTICE OF FILING

Dorothy Gunn, Clerk
Pollution Control Board
100 West Randolph Street
Suite 11-500
Chicago, Illinois 60601

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Springfield, Illinois 62701-1787

Attached Service List

PLEASE TAKE NOTICE that I have today filed with the Office of the Clerk of the Pollution Control Board the **COMMENTS OF ILLINOIS ENVIRONMENTAL PROTECTION AGENCY**, copies of which are herewith served upon you.

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

By:_____
Sanjay K Sofat
Assistant Counsel
Division of Legal Counsel

Dated: September 6, 2002
Illinois Environmental Protection Agency
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THIS FILING PRINTED ON RECYCLED PAPER

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WATER QUALITY AMENDMENTS TO	)	
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P.C.c # 27

AGENCY'S COMEMNTS

THE ILLINOIS ENVIRONMENTAL PROTECTION AGENCY (the "Agency" or "Illinois

EPA") respectfully submits these comments on the hearing held on July 25, 2002, in the Illinois

Pollution Control Board's (the "Board") R02-11 rulemaking proceeding. The Agency files the

comments to provide additional information on the Agency's proposed cyanide standard and address

the issues raised by Albert Ettinger, attorney for the Environmental Law & Policy Center, the Sierra

Club, and Prairie Rivers Network at this hearing. The Agency is thankful to the Board for holding

the third hearing on this important rulemaking proceeding and providing this opportunity to file

comments.

In rulemaking proceedings, the Agency has always ensured that the Board has access to the

necessary and available information for its consideration. This rulemaking proposal was no

different. To ensure that the Agency has the most current information, it contacted several

organizations including industry groups, agencies, and environmental groups for their comments on

the Agency's draft proposal. (See Public Participation section of the Original Petition) Based on

the comments received, the Agency made essential changes to its draft before filing it with the

Board. The first time the Agency heard about the USEPA's new laboratory method for cyanide was

at the July 25 hearing. At that hearing, Albert Ettinger introduced the document, <u>Method OIA-1677</u>

<u>Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry,</u> EPA-821-R-013,

August 1999, into the hearing record as Exhibit 18. The Agency wishes that in the future

rulemakings, the stakeholders bring the new information to the Agency's attention at the earliest

possible time rather than wait until the First Notice period. However, since the hearing, the Agency

has been gathering facts regarding this new laboratory method.

<div align="center"><u>NEW LABORATORY METHOD FOR CYANIDE</u></div>

The new method was promoted several years ago by USEPA as the solution to the difficulties of

cyanide laboratory analysis and correlation to the USEPA national criteria for cyanide. Within

USEPA Region V (the six Westernmost Great Lakes states), Michigan is the only state to adopt this

method. For some reason, Region V water quality coordinator, who usually passes such information

down to the states, was not aware of this new method. The Michigan representatives indicated that

the new method, in theory, was attractive for use in cyanide standards, but due to budgetary

concerns, the state had not proceeded to use the method. Further, the representatives did not know

of any discharger using the new method in Michigan, nor were they aware of any consulting

laboratories capable of performing the analysis.

To find out about the capabilities of the new method, the Agency contacted two sources that

were key players in the development, testing, and USEPA adopting process. Mr. Jim Boiani of

Dyncorp participated in the testing process as a USEPA contractor. Ten laboratories were given the

instruments and reagents necessary for the new method and were instructed in its use. The

laboratories also participated in an evaluation process. USEPA found that the new method did

indeed have fewer problems with interferences and had a better minimum detection limit than

previously approved methods. As the method passed USEPA criteria for reliability, it was adopted

as an approved method.

<div align="center">3</div>

The Agency also contacted Mr. Jason Gray of OI Analytical Co., the company that actually developed the method. According to Mr. Gray, the new method measures the same forms of cyanide as does the weak acid dissociable method. Essentially, both methods, the new method and weak acid dissociable method, exclude the iron-cyanide complexes that are not toxic to aquatic life, but commonly are found in cyanide solutions. The tightly bound iron-cyanide complexes do not revert to free cyanide, the toxic form, unless strong-acidic conditions are present or, as explained later, they are exposed to ultraviolet light. All other cyanide present in the solution, i.e., the cyanide directly toxic to aquatic life or what may be conceivably be converted to a toxic form, is measured by both methods. Both methods measure the bound forms of cyanide present in other metal complexes, e.g., copper, zinc, silver, etc.

OI Analytical makes the propriety reagents for the test and sells the instruments needed to run the test. Mr. Gray indicated that these instruments are also available from other manufacturers. According to Mr. Jim Boiani of Dyncorp, the cost of the instrumentation is about $34,500 before discounts. The reagent cost for approximately 100 samples is $320. Mr. Boiani believes that that private laboratories would charge about $50 per sample analyzed. The approximate cost for analyzing a sample with the weak acid dissociable method is about $35.

The City of New York and Cincinnati Metro Water District and a number of industrial laboratories are currently using the new method. The new method is said to be much easier to perform than the old weak acid dissociable or cyanide amenable to chlorination methods. The minimum detection limit of 2 µg/L has been achieved with this new method. Mr. Pfeifer, Region V standards coordinator, has indicated that USEPA would have no objection to states adopting the new method since it came from USEPA's research arm.

One practical problem that exists with the new method, as well as with all new methods, is that most commercial laboratories in Illinois are not equipped to run the test. The Agency surveyed

three major commercial laboratories (Suburban Labs, EMT, Inc., and PDC Laboratories, Inc.) in Illinois and found that none of these laboratories conduct the cyanide test using this new method. In fact, these laboratories do not even have the necessary equipment to do so. All echoed the sentiment that unless their clients ask for this method or show a tremendous interest in the new method, the laboratories would not be making such a considerable investment.

It is clear from the above discussion that sufficient benefits exist from the use of the new method. Therefore, the Agency supports the use of this new method. The Agency recommends that both the weak acid dissociable method and the new cyanide method should be referenced as appropriate tests in the Board's cyanide standard. As the new method provides less interference and a lower detection limit, the dischargers, given the option of the new method, may begin to demand that laboratories use this method instead of the weak acid dissociable method. As the demand grows for the new method, the commercial laboratories may consider it worthwhile to invest in the necessary equipments to run the cyanide test.

ENVIRONMENTAL IMPACTS OF IRON-CYANIDE COMPLEXES

At the July 25 hearing, Albert Ettinger raised issues concerning the impact of iron-cyanide complexes on the aquatic system. Neither the weak acid dissociable method nor the new method measure the iron-complexed forms of cyanide. A publication by the US Fish & Wildlife Service addresses the issues raised by Mr. Ettinger at the hearing. (Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review, Ronald Eisler, Biological Report 85 (1.23) December, 1991). The author reports that cyanide in general does not persist very long in surface waters, at most a few days. Volatilization and microbial decomposition are two of the main ways that waters are naturally cleansed of cyanide. The publication refers to the ferricyanides and ferrocyanides as "sparingly decomposable" and that these iron complexes "do not release free cyanide unless exposed to ultra violet light." Further, the author states, "[t]he much lower toxicities of the ferrocyanide and

5

ferricyanide complexes- which are of high stability but subject to extensive and rapid photolysis, yielding free cyanide on direct exposure to sunlight- and the nickelocyanide ion complexes are not likely to be of practical importance." (See Attachment A)

Clearly, the iron-cyanide complexes are more persistent in the environment than other forms of cyanide. Any cyanide that becomes free from the iron-cyanide complexes due to extensive exposure to ultra violet light would not persist very long in surface waters. As the author indicates, the iron forms of cyanide are not likely to be of practical importance because actual photolysis (chemical decomposition due to exposure to sunlight) would occur at relatively slow rates. The National Criteria Document for cyanide explains that "[r]lease of cyanide ion by photodecomposition might be important in relatively clear waters." Apparently, the relative clarity, depth, and exposure to sunlight (i.e., degree of shading) all would be significant factors in photolysis. Since most waters in Illinois are not sufficiently shallow, clear and unshaded, photolysis is probably not 'rapid' in Illinois waters. Therefore, there is no need to consider the impact of the iron-cyanide complexes on the aquatic system. The Agency recommends the use of weak acid dissociable standard, the existing standard. This recommendation is further supported by the fact that even the USEPA's new cyanide method does not measure the iron form of cyanide.

HUMAN HEALTH IMPACTS OF CYANIDE

The issues related to human health impacts of cyanide were also raised at the July 25 hearing. The USEPA MCL for total cyanide is 0.2 mg/L, several times the level of the proposed aquatic life standards.

CONCLUSION

The Agency wishes to remind the Board that this rulemaking concerns the proposing of new standards for cyanide. The Agency has explained in detail the process for updating the General Use standards for cyanide, a process that has nothing to do with laboratory analytical methods. The

6

addition of a better laboratory method does not change the appropriateness of the numeric values of a standard that have been found to be protective of aquatic life. While supplemental reasons for changing the water quality standard for cyanide no longer exist, given the existence of new laboratory method, the primary reason is still pertinent. The warm water aquatic organisms found in General Use waters are not as sensitive to cyanide as the existing standard implies; and therefore, the cyanide standards should be updated to reflect "the latest scientific knowledge."

Proposed Update:

Constituent	STORET Number	AS (µg/L)	CS (µg/L)
Cyanide (Weak acid dissociable or Available [Method OIA-1677])	00718	49	11

The Agency appreciates this opportunity to comment in this proceeding. As set forth in detail above, the Agency urges the Board to adopt the proposed cyanide standard.

Respectfully Submitted

ILLINOIS ENVIRONMENTALPROTECTION AGENCY

By:_____

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Exhibit A

Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review
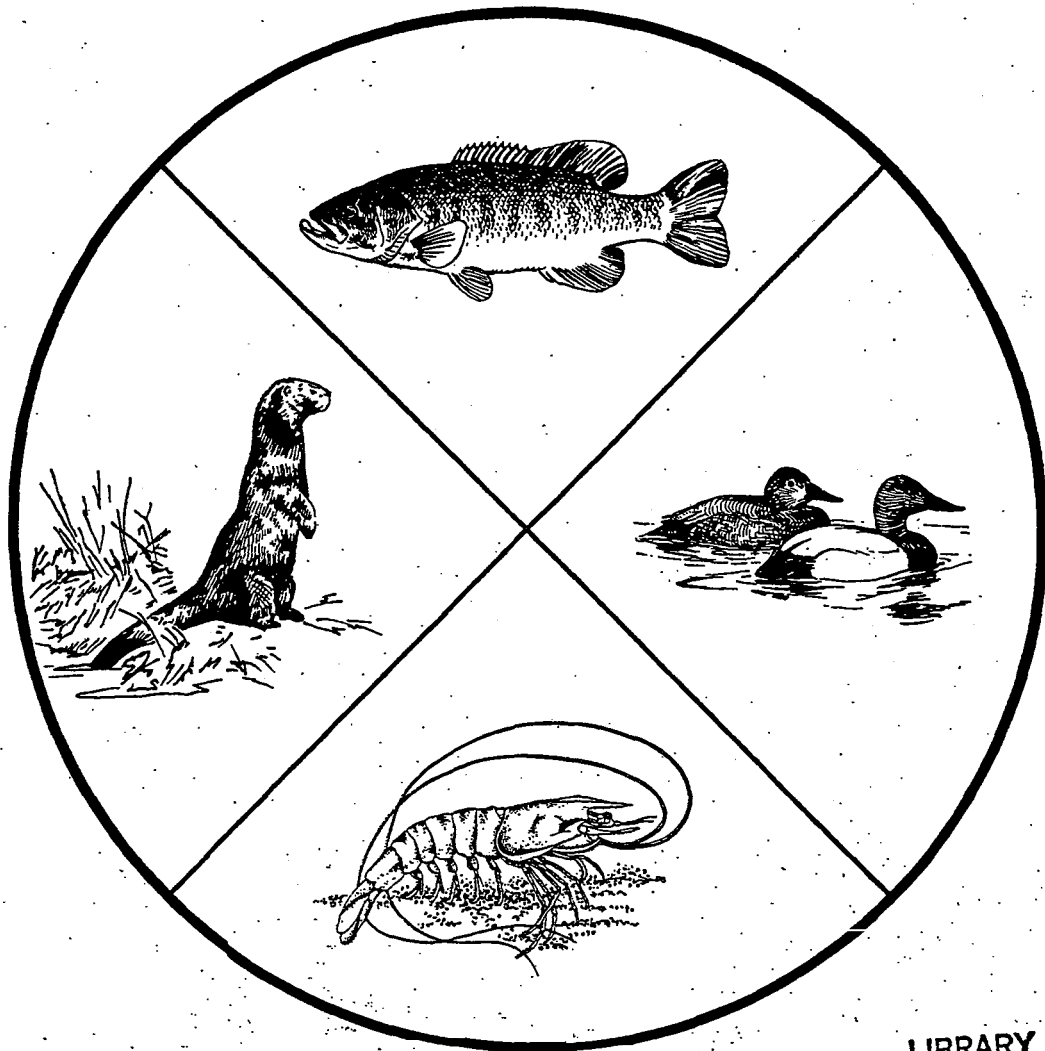
sh and Wildlife Service

S. Department of the Interior

and is also one of the most toxic cyanide species, it is noteworthy that the toxicity of simple cyanides will not be affected measurably below pH 8.3. Acidification of dilute (milligrams per liter) cyanide solutions will not intiate any greater release of HCN, but acidification of concentrated (grams per liter) solutions promotes HCN formation and release.

Complex cyanides are compounds in which the cyanide anion is incorporated into a complex or complexes; these compounds are different in chemical and toxicologic properties from simple cyanides. In solution, the stability of the cyanide complex varies with the type of cation and the complex that it forms. Some of these are dissociable in weak acids to give free cyanide and a cation, while other complexes require much stronger acidic conditions for dissociation. The least-stable complex metallocyanides include $Zn(CN)_4^{2-}$, $Cd(CN)_3^-$, and $Cd(CN)_4^{2-}$; moderately stable complexes include $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, and $Ag(CN)_2^-$; and the most stable complexes include $Fe(CN)_6^{4-}$ and $Co(CN)_6^{4-}$. The toxicity of complex cyanides is usually related to their ability to release cyanide ions in solution, which then enter into an equilibrium with HCN; relatively small fluctuations in pH significantly affect their biocidal properties.

Cyanogen $[(CN)_2]$ is the simplest compound containing the cyanide group. Cyanogen is an extremely toxic, flammable gas that reacts slowly with water to form HCN, cyanic acid, and other compounds; it is rapidly degraded in the environment. Cyanogen and its halide derivations are comparable in toxicity to hydrogen cyanide.

Nitriles are defined as organic compounds (RCN) containing the cyanide group. Cyanide bound to carbon as nitriles (other than as cyanogenic glycosides) are comparatively innocuous in the environment, and are low in chemical reactivity and are biodegradable. For simple mononitriles there is a clear progression, with more cyanide being released as chain length increases. A similar pattern exists in dinitriles, but corresponding compounds require a longer carbon chain than mononitriles before free cyanide is produced. Based on studies with chicken liver homogenates (Davis 1981), mononitriles were more toxic than dinitriles, and within each group the order of toxicity was $CH_3 > C_2H_5 > C_3H_7 > C_4H_9 > C_5H_{11} > C_7H_{15}$. Cyanohydrins $[R_2C(OH)CN]$ and cyanogenic glycosides $[R_1R_2C(OR_3)CN]$ are special classes of nitriles, in that under appropriate conditions they will decompose to HCN and cyanide ions. Cyanogens (not to be confused with cyanogen), such as

acrylonitrile, propionitrile, and succinonitrile, are nitrile-containing materials of varying complexity and lability, and can liberate free and toxicologically available amounts of cyanide. But the non-nitrile portion of the cyanogen molecule may exert an independent or interactive toxicity, causing a complex response.

Cyanates contain the OCN group. Inorganic cyanates that are formed industrially by the oxidation of cyanide salts hydrolyze in water to form ammonia and bicarbonate ion. Alkyl cyanates are insoluble in water and form cyanurates. Alkyl isocyanates contain the OCN radical, are formed from cyanates, and, like cyanates, are readily hydrolyzed. Thiocyanates (SCN group) are formed from cyanides and sulfur-containing materials and are relatively stable.

Total cyanides refers to all cyanide-containing compounds, including simple and complex cyanides, cyanoglycosides, and free cyanide. Total cyanides is a chemical measurement of free cyanide present in solution or released by acidification or digestion. Only free cyanide is considered to be a biologically meaningful expression of cyanide toxicity. Under most circumstances, the concentration of total cyanide will exceed that of HCN. In some waters, however, the total cyanide concentration may consist almost entirely of free cyanide, or it may contain cyanides that readily photodecompose or dissociate to yield HCN. The relation between total cyanide and free cyanide in natural waters varies with receiving-water conditions, type of cyanide compounds present, degree of exposure to daylight, and presence of other chemical compounds.

Hydrogen cyanide has frequently been associated with the odor of bitter almonds (Ballantyne 1983; Gee 1987). The threshold odor for olfactory detection of atmospheric HCN is 1 mg/L, but the odor may not be detected for various reasons, including the presence of other odors and the fact that only 20% to 40% of those tested could detect a cyanide odor.

Analytical methods for determining free and bound cyanide and cyanogenic compounds in biological materials are under revision. Current methods include chromatography; enzymic post-column cleavage; electrochemical detection; and ultraviolet, infrared, proton, and carbon-13 nuclear magnetic resonance spectroscopies (Brimer 1988). Proposed newer analytical methodologies include chemiluminescence (Wu et al. 1989); deproteinization techniques (Krynitsky et al. 1986); thin film dissociation coupled with prefer-

low in winter owing to dilution by high runoff, but peaked in summer because of cyanide production by plants (Leduc 1984). Cyanides do not seem to persist in aquatic environments. In small, cold oligotrophic lakes treated with 1 mg NaCN/L, acute toxicity was negligible within 40 days. In warm shallow ponds, toxicity disappeared within 4 days after application of 1 mg NaCN/L. In rivers and streams, toxicity rapidly disappeared on dilution (Leduc 1984). Cyanide was not detectable in water and sediments of Yellowknife Bay, Canada, between 1974 and 1976, although the bay receives liquid effluents containing cyanides from an operating gold mine. Nondetection was attributed to rapid oxidation (Moore 1981). Several factors contribute to the rapid disappearance of cyanide from water. Bacteria and protozoans may degrade cyanide by converting it to carbon dioxide and ammonia. Chlorination of water supplies can result in conversion to cyanate (EPA 1980). An alkaline pH favors oxidation by chlorine, and an acidic pH favors volatilization of HCN into the atmosphere (EPA 1980).

Persistence in Water, Soil, and Air

In water, cyanides occur as free hydrocyanic acid, simple cyanides, easily degradable complex cyanides such as $Zn(CN)_2$, and sparingly decomposable complex cyanides of iron and cobalt; complex nickel and copper cyanides are intermediate between the easily decomposable and sparingly degradable compounds (Towill et al. 1978). Cyanide has relatively low persistence in surface waters under normal conditions but may persist for extended periods in groundwater (Way 1981). Volatilization is the dominant mechanism for removal of free cyanide from concentrated solutions and is most effective under conditions of high temperatures, high dissolved oxygen levels, and at increased concentrations of atmospheric carbon dioxide (Leduc et al. 1982; Simovic and Snodgrass 1985). Loss of simple cyanides from the water column is primarily through sedimentation, microbial degradation, and volatilization (Leduc et al. 1982; Marrs and Ballantyne 1987). Water-soluble strong complexes, such as ferrocyanides and ferricyanides, do not release free cyanide unless exposed to ultraviolet light. Thus, sunlight may lead to cyanide formation in wastes containing iron-cyanide complexes (Towill et al. 1978; Leduc et al.

1982; Simovic and Snodgrass 1985; Marrs and Ballantyne 1987).

Alkaline chlorination of wastewaters is one of the most widely used methods of treating cyanide wastes. In this process, cyanogen chloride, (CNCl) is formed, which at alkaline pH is hydrolyzed to the cyanate ion (CNO^-). If free chlorine is present, CNO^- can be further oxidized (Way 1981; Leduc et al. 1982; Simovic and Snodgrass 1985; Marrs and Ballantyne 1987). Other methods used in cyanide waste management include lagooning for natural degradation, evaporation, exposure to ultraviolet radiation, aldehyde treatment, ozonization, acidification–volatilization–reneutralization, ion exchange, activated carbon absorption, electrolytic decomposition, catalytic oxidation, and biological treatment with cyanide-metabolizing bacteria (Towill et al. 1978; EPA 1980; Way 1981; Marrs and Ballantyne 1987). In the case of Canadian gold-mining operations, the primary treatment for cyanide removal is to retain gold mill wastewaters in impoundments for several days to months; removal occurs through volatilization, photodegradation, chemical oxidation, and, to a lesser extent, microbial oxidation. Microbial oxidation of cyanide is not significant in mine tailing ponds, which typically have pH >10, a low number of microorganisms, low nutrient levels, large quiescent zones, and cyanide concentrations >10 mg/L (Simovic and Snodgrass 1985).

Cyanide seldom remains biologically available in soils because it is either complexed by trace metals, metabolized by various microorganisms, or lost through volatilization (Towill et al. 1978; Marrs and Ballantyne 1987). Cyanide ions are not strongly adsorbed or retained on soils, and leaching into the surrounding ground water will probably occur. Under aerobic conditions, cyanide salts in the soil are microbially degraded to nitrites or form complexes with trace metals. Under anaerobic conditions, cyanides denitrify to gaseous nitrogen compounds that enter the atmosphere.

Volatile cyanides occur only occasionally in the atmosphere, due largely to emissions from plating plants, fumigation, and other special operations (Towill et al. 1978). Under normal conditions cyanide has relatively low persistence in air, usually between 30 days and 1 year (Way 1981), although some atmospheric HCN may persist for up to 11 years (Marrs and Ballantyne 1987). Data are lacking on the distribution and transformation of cyanide in the atmosphere (Towill et al. 1978) and should be acquired.

resistant to 65 mg KCN/L at low temperatures (13° C) than were seedlings from cold-susceptible cultivars (25° C), as judged by respiratory activity of mitochondria (Van De Venter 1985). Results suggest that cyanide-resistant respiration may play a role in cold resistance in maize seedlings, although more evidence is needed to demonstrate that cold-resistant plants actually use their greater potential for alternative respiration at low temperatures (Van De Venter 1985).

The cyanogenic system comprising cyanogenic glycosides, cyanohydrins, betaglucosidases, and nitrile lyases is widespread in plants, but also occurs in several species of arthropods, including the tiger beetle (*Megacephala virginica*), leaf beetle (*Paropsis atomaria*), zygaenid moths, and certain butterflies (Nahrstedt 1988). In *Zygaena trifolii*, cyanide compounds seem to function as protection against predators (Nahrstedt 1988). Defensive secretions of cyanide have also been reported in polydesmid millipedes, and these organisms seem to be more tolerant than other species when placed in killing jars containing HCN (Towill et al. 1978). In a millipede (*Apheloria* sp.), cyanide is generated in a two-compartment organ by hydrolysis of mandelonitrile; cyanide generation occurs outside the gland when the components of the two compartments are mixed during ejection (Towill et al. 1978).

Highly toxic substances, such as cyanides, are sometimes feeding cues and stimulants for specialized insects. For example, instar larvae of the southern armyworm (*Spodoptera eridania*) strongly prefer cyanogenic foods, such as foliage of the lima bean, a plant with comparatively elevated cyanide content—up to 31 mg/kg in some varieties—in the form of linamurin (Brattsten et al. 1983). Feeding was stimulated in southern armyworms at dietary levels up to 508 mg KCN/kg (208 mg HCN/kg) for first to fourth instar larval stages, and between 1,000 and 10,000 mg KCN/kg diet for fifth and sixth instar larvae (Brattsten et al. 1983). Sixth instar larvae preexposed to diets containing 5,000 mg KCN/kg showed no adverse affects at dietary levels of 10,000 mg KCN/kg; however, previously unexposed larvae showed reversible signs of poisoning at 10,000 mg/kg diet, including complete inhibition of oviposition and 83% reduction in adult emergence (Brattsten et al. 1983). Experimental studies with southern armyworm larvae and thiocyanate—one of the in vivo cyanide metabolites—showed that 5,000 mg thiocyanate per kilogram diet reduced pupation by 77%, completely inhibited oviposition, and re-

duced adult emergence by 80% (Brattsten et al. 1983), strongly suggesting that thiocyanate poisoning is the primary effect of high dietary cyanide levels in southern armyworms.

Resistant species, such as southern armyworms, require injected doses up to 800 mg KCN/kg BW (332 mg HCN/kg BW) or diets of 3,600 mg KCN/kg for 50% mortality (Brattsten et al. 1983), but data are scarce for other terrestrial invertebrates. Exposure to 8 mg HCN/L air inhibits respiration in the granary weevil (*Sitophilus granarius*) within 15 min and kills 50% in 4 h; some weevils recover after cessation of 4-h exposure (Towill et al. 1978).

Aquatic Organisms

Numerous accidental spills of sodium cyanide or potassium cyanide into rivers and streams have resulted in massive kills of fishes, amphibians, aquatic insects, and aquatic vegetation; sources of poisonings were storage reservoirs of concentrated solutions, overturned rail tank cars, or discharge of substances generating free HCN in the water from hydrolysis or decomposition (Leduc 1984). Data on the recovery of poisoned ecosystems are scarce. In one case, a large amount of cyanide-containing slag entered a stream from the reservoir of a Japanese gold mine as a result of an earthquake (Yasuno et al. 1981). The slag covered the streambed for about 10 km from the point of rupture, killing all stream biota; cyanide was detected in the water column for only 3 days after the spill. Within 1 month flora was established on the silt covering the above-water stones, but there was little underwater growth. After 6–7 months, populations of fish, algae, and invertebrates had recovered, although species composition of algae was altered (Yasuno et al. 1981).

Fish were the most sensitive aquatic organisms tested under controlled conditions. Significant adverse nonlethal effects, including reduced swimming performance and inhibited reproduction, were observed in the range of 5.0–7.2 µg free cyanide per liter; deaths were recorded for most species between 20 and 76 µg/L (Table 3). Among invertebrates, adverse nonlethal effects were documented between 18 and 43 µg/L, and lethal effects between 30 and 100 µg/L—although some deaths were recorded in the range 3–7 µg/L for the amphipod *Gammarus pulex* (Table 3). Algae and macrophytes were comparatively tolerant; adverse effects were reported at >160 µg free cyanide per liter (Table 3).
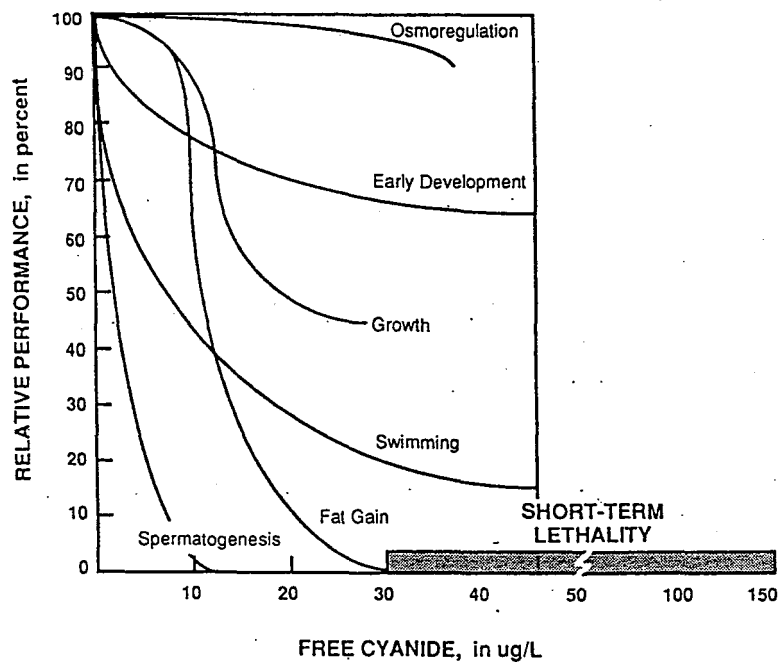
Figure. Summary of lethal and sublethal effects of free cyanide on freshwater fish. Modified from Leduc et al. (1982).

hepatic damage. Exposure of fish for 9 days to 10 μg HCN/L was sufficient to induce extensive necrosis in the liver, although gill tissue showed no damage. Intensification of liver histopathology was evident at dosages of 20 and 30 μg HCN/L and exposure periods up to 18 days (Leduc 1984). Cyanide has a strong, immediate, and long-lasting inhibitory effect on the swimming ability of fish (Leduc 1984). Free cyanide concentrations as low as 10 μg/L can rapidly and irreversibly impair the swimming ability of salmonids in well-aerated water (Doudoroff 1976). Osmoregulatory disturbances recorded at 10 μg HCN/L may affect migratory patterns, feeding, and predator avoidance (Leduc et al. 1982; Leduc 1984). In general, fish experience a significant reduction in relative performance (based on osmoregulation, growth, swimming, and spermatogenesis) at 10 μg HCN/L, and although fish can survive indefinitely at 30 μg HCN/L in the laboratory, the different physiological requirements necessary to survive in nature could not be met (Leduc 1978, 1981; Leduc et al. 1982; Figure). Increased predation by green sunfish (*Lepomis cyanellus*) on fathead minnows (*Pimephales promelas*) was noted at sublethal concentrations of HCN, but it was uncertain if fatheads became easier prey or if green sunfish had greater appetites (Smith et al. 1979).

Sodium cyanide has stimulatory effects on oxygen-sensitive receptors in lungfish, amphibians, reptiles, birds, and mammals (Smatresk

1986). Facultative and aquatic air breathers appear to rely on air breathing when external chemoreceptors are stimulated, whereas obligate air-breathing fish are more responsive to internal stimuli (Smatresk 1986). Gill ventilation frequency of longnose gar (*Lepisosteus osseus*), for example, was little affected by external cyanide application, but responded strongly when cyanide was administered internally by injection (Smatresk 1986). Cyanide, like many other chemicals, can stimulate growth of fish during exposure to low sublethal levels. This phenomenon, referred to as hormesis, is little understood and warrants additional research (Leduc 1984).

The observed toxicity to aquatic life of simple and complex cyanides was attributed almost entirely to molecular (undissociated) HCN derived from ionization, dissociation, and photodecomposition of cyanide-containing compounds. The toxicity of the cyanide ion, CN^-, which is a minor component of free cyanide ($HCN + CN^-$) in waters that are not exceptionally alkaline is of little importance (Doudoroff 1976; Towill et al. 1978; Smith et al. 1979; EPA 1980). The acute toxicity of stable silver cyanide and cuprocyanide complex anions is much less than that of molecular HCN, but is nevertheless important; these ions can be the principal toxicants, even in some very dilute solutions. The much lower toxicities of the ferrocyanide and ferricyanide complex ions—which are of high stability but subject to extensive and rapid photolysis

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▬▬▬▬▬▬▬▬▬ Doudoroff
1976). Toxicity to aquatic organisms of organic
cyanide compounds, such as lactonitrile, is similar
to that of inorganic cyanides because they usually
undergo rapid hydrolysis in water to free cyanide
(Towill et al. 1978) ▬▬▬▬▬▬▬▬▬▬
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▬▬▬▬▬▬▬▬▬▬▬▬
▬▬▬▬▬▬▬ d that the analytically de-
termined HCN concentration in cyanide-polluted
waters is considered to be the most reliable index of
toxicity (Doudoroff 1976; Smith et al. 1979; EPA
1980; Abel and Garner 1986).

Cyanide acts rapidly in aquatic environments,
does not persist for extended periods, and is highly
species selective; organisms usually recover
quickly on removal to clean water. The critical
sites for cyanide toxicity in freshwater organisms
include the gills, egg capsules, and other sites
where gaseous exchange and osmoregulatory proc-
esses occur. On passing through a semipermeable
membrane, the HCN molecules are usually dis-
tributed by way of the circulatory system to vari-
ous receptor sites where toxic action or
detoxification occurs (Leduc 1984). Once in the
general circulation, cyanide rapidly inhibits the
electron transport chain of vital organs. Signs of
distress include increased ventilation, gulping for
air at the surface, erratic swimming movements,
muscular incoordination, convulsions, tremors,
sinking to the bottom, and death with widely ex-
tended gill covers (Leduc 1981, 1984). The acute
mode of action of HCN is limited to binding those
porphyrins that contain Fe^{+3}, such as cytochrome
oxidase, hydroperoxidases, and methemoglobin.
At lethal levels, cyanide is primarily a respiratory
poison and one of the most rapidly effective toxi-
cants known (Leduc et al. 1982). The detoxi-
fication mechanism of cyanide is mediated by
thiosulfate sulfur transferase, also known as
rhodanese. This enzyme is widely distributed in
animals, including fish liver, gills, and kidney.
Rhodanese plays a key role in sulfur metabolism,
and catalyzes the transfer of a sulfane–sulfur
group to a thiophilic group (Leduc 1984). Thio-
sulfate administered in the water with cyanide re-
duced the toxicity of cyanide to fish, presumably by
increasing the detoxification rate of cyanide to
thiocyanate (Towill et al. 1978).

Additive or more-than-additive toxicity of free
cyanide to aquatic fauna has been reported in com-
bination with ammonia (Smith et al. 1979; Leduc

et al. 1982; Alabaster et al. 1983; Leduc 1984) or ar-
senic (Leduc 1984). However, conflicting reports
on the toxicity of mixtures of HCN with zinc or
chromium (Towill et al. 1978; Smith et al. 1979;
Leduc et al. 1982; Leduc 1984) require clarifica-
tion. Formation of the nickelocyanide complex
markedly reduces the toxicity of both cyanide and
nickel at high concentrations in alkaline pH. At
lower concentrations and acidic pH, solutions in-
crease in toxicity by more than 1,000 times, owing
to dissociation of the metallocyanide complex to
form hydrogen cyanide (Towill et al. 1978). Mix-
tures of cyanide and ammonia may interfere with
seaward migration of Atlantic salmon smolts un-
der conditions of low dissolved oxygen (Alabaster
et al. 1983). The 96-h toxicity of mixtures of sodium
cyanide and nickel sulfate to fathead minnows is
influenced by water alkalinity and pH. Toxicity de-
creased with increasing alkalinity and pH from
0.42 mg CN/L at 5 mg $CaCO_3$/L and pH 6.5; to 1.4
mg CN/L at 70 mg $CaCO_3$/L and pH 7.5; to 730 mg
CN/L at 192 mg $CaCO_3$/L and pH 8.0 (Doudoroff
1956).

Numerous biological and abiotic factors are
known to modify the biocidal properties of free cya-
nide, including water pH, temperature, and oxygen
content; life stage, condition, and species assayed;
previous exposure to cyanide compounds; presence
of other chemicals; and initial dose tested. There is
general agreement that cyanide is more toxic to
freshwater fish under conditions of low dissolved
oxygen (Doudoroff 1976; Towill et al. 1978; Smith
et al. 1979; EPA 1980; Leduc 1984); that pH levels
within the range 6.8–8.3 had little effect on cya-
nide toxicity but enhanced toxicity at acidic pH
(Smith et al. 1979; EPA 1980; Leduc et al. 1982;
Leduc 1984); that juveniles and adults were the
most sensitive life stages tested and embryos and
sac fry the most resistant (Smith et al. 1978, 1979;
EPA 1980; Leduc 1984); and that substantial in-
terspecies variability exists in sensitivity to free
cyanide (Smith et al. 1979; EPA 1980). Initial dose
and water temperature both modify the biocidal
properties of HCN to freshwater teleosts. At slowly
lethal concentrations (i.e., <10 µg HCN/L), cyanide
was more toxic at lower temperatures; at high, rap-
idly lethal HCN concentrations, cyanide was more
toxic at elevated temperatures (Kovacs and Leduc
1982a, 1982b; Leduc et al. 1982; Leduc 1984). By
contrast, aquatic invertebrates were most sensi-
tive to HCN at elevated water temperatures, re-
gardless of dose (Smith et al. 1979). Season and
exercise modify the lethality of HCN to juvenile

STATE OF ILLINOIS	)	
	)	
	)	SS
COUNTY OF SANGAMON	)	
	)	

PROOF OF SERVICE

I, the undersigned, on oath state that I have served the attached **COMMENTS OF THE ILLINIOS ENVIRONMENTAL PROTECTION AGENCY** upon the person to whom it is directed, by placing a copy in an envelope addressed to:

Dorothy Gunn, Clerk Pollution Control Board 100 West Randolph Street Suite 11-500 Chicago, Illinois 60601	Marie E. Tipsord Illinois Pollution Control Board James R. Thompson Center 100 West Randolph Street, Suite 11-500 Chicago, Illinois 60601
(OVERNIGHT MAIL)	**(OVERNIGHT MAIL)**
Mathew Dunn Illinois Attorney General's Office Environmental Control Division James R. Thompson Center 100 West Randolph Street Chicago, Illinois 60601	Legal Service Illinois Department of Natural Resources 524 South Second Street Springfield, Illinois 62701-1787
(FIRST CLASS MAIL)	**(FIRST CLASS MAIL)**
Attached Service List **(FIRST CLASS MAIL)**	

and mailing it from Springfield, Illinois on September 6, 2002, with sufficient postage affixed as indicated above.

Nancy JD Lamport

SUBSCRIBED AND SWORN TO BEFORE ME

this day of September 6, 2002.

Brenda Boehner
Notary Public

OFFICIAL SEAL
BRENDA BOEHNER
NOTARY PUBLIC, STATE OF ILLINOIS
MY COMMISSION EXPIRES 11-14-2005

THIS FILING PRINTED ON RECYCLED PAPER

8

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