Proposed Revision of the New Jersey Water Quality Standards for Cyanide in Saltwater

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INTRODUCTION

National Ambient Water Quality Criteria (AWQC) are established by the United States Environmental Protection Agency (EPA) following directives set forth in the Clean Water Act (CWA). The Act mandates the update of criteria as new information becomes available. The AWQC for cyanide have not been revised since they were issued by EPA in 1985. Over the last 22 years, many additional studies quantifying the adverse effects of cyanide on aquatic organisms have been published, and therefore deserve consideration for criteria derivation.

More recent toxicity tests with crabs in the genus *Cancer* are particularly relevant for updating the New Jersey water quality standards for cyanide in saltwater, because current values for both acute and chronic criteria (1.0 μg CN L^{-1}) are controlled by the high sensitivity of the rock crab, *C. irroratus*. The concentration of free cyanide that has been cited as causing 50 percent mortality (LC50) of *C. irroratus* larva in EPA's existing AWQC document is estimated to be 4.9 μg L^{-1} (Gentile 1980). The species mean acute value (SMAV) for this organism is six times lower than the SMAV of the next most sensitive taxon (*Acartia clausi* SMAV = 30 μg L^{-1}).

The cyanide AWQC document (US EPA 1985) provides estimates of acute-chronic ratios for only two saltwater species, and both taxa are relatively tolerant of cyanide. Acute-chronic ratios for species that can tolerate cyanide may not adequately represent ratios for sensitive taxa. In cases where the number of chronic tests is restricted, the criterion continuous concentration (CCC) is often computed by dividing the final acute value by the final acute-chronic ratio (Stephan et al. 1985). Consequently, a chronic criterion based on acute-chronic ratios for tolerant taxa may not accurately reflect the chronic toxicity of cyanide. Authors of the 1985 cyanide AWQC document circumvented this problem by setting the final chronic value equal to the criterion maximum concentration. They argued that the acute value for rock crab, which strongly influences the saltwater acute criterion, is controlled by larval toxicity, and thus is likely to be a good indicator of sensitivity to long-term cyanide exposure.

The objective of this document is to update the AWQC for cyanide by compiling results of laboratory toxicity tests that quantify the adverse effects of cyanide on saltwater species, and then to employ all acceptable values to recalculate the New Jersey acute and chronic criteria for cyanide in saltwater. Each toxicity value expresses the concentration of free cyanide (μg CN L^{-1}) associated with a particular endpoint (50% Lethal Concentration (LC50), 50% Effect Concentration (EC50), or Chronic Value).

METHODS

A thorough literature search was conducted on the toxicity of cyanide to saltwater organisms. Multiple databases (CAS, ECOTOX, ACQUIRE, BIOSIS, Environmental Sciences and Pollution Management) were searched to obtain reports and articles published since 1985. Relevant manuscripts were identified, by title and abstract, and their data selected according to recommendations described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al. 1985), hereafter referred to as the Guidelines. Acute and chronic toxicity values published since 1985 were incorporated into the appropriate cyanide AWQC tables, and used to recalculate the Criterion Maximum Concentration (CMC) and the CCC, following methods outlined in the Guidelines.

RESULTS

Acceptable acute values for saltwater species, including those from the cyanide AWQC document, as well as new and revised data are presented in Table 1. Table 1 includes eight genera; 10 species of invertebrates and three species of fish. Chronic values for saltwater organisms are presented in Table 2. We did not identify any new acceptable chronic data, therefore, our Table 2 is identical to the Saltwater Species section of Table 2 in the 1985 cyanide AWQC document. Table 3 contains species and genus mean acute values (GMAV), sorted in ascending order of sensitivity to cyanide (descending GMAV values).

The acute toxicity value for *Acartia clausi* (Gentile 1980) in Table 1, reported as 30 μg CN L^{-1} in the 1985 cyanide AWQC, has been revised to 17 μg CN L^{-1} in order to account for control mortality. The revision was recommended by Lussier and collaborators in a memorandum submitted to EPA (Lussier et al. 1985; Ecotox reference # 14599). Another significant change in

Table 1 is the addition of new toxicity values for *Cancer irroratus* and other species in this genus. Gensemer and collaborators (2006) reported two new values for *C. irorratus,* and Brix and collaborators (2000) published results of toxicity tests on *C. gracilis*, *C. magister*, *C. oregonensis*, and *C. productus*.

CRITERION MAXIMUM CONCENTRATION (CMC)

The four most sensitive genera listed in the 1985 criteria document were *Cancer*, *Acartia*, *Menidia,* and *Mysidopsis*. Their GMAVs and SMAVs from the 1985 document are provided below in Table 4.

Table 4. Acute toxicity data from the cyanide AWQC document (US EPA 1985).

SPECIES	SMAV (Fg/L)	GMAV (Fg/L)
Cancer irroratus	4.9	4.9
Acartia clausi	30	30
Menidia menidia	59	59
Mysidopsis bahia	113	
Mysidopsis bigelowi	124	118.4

The Final Acute Value (FAV) for cyanide in saltwater, calculated from the four lowest GMAVs listed above, was 2.03 μg CN L^{-1}. Thus, the CMC for cyanide in saltwater was set at CMC = FAV / 2 = 1.0.

The four genera we found to be the most sensitive to cyanide in our review are the same as those listed in the 1985 cyanide AWQC document, although *Mysidopsis bahia* and *M. bigelowi* are now classified as *Americamysis bahia* and *A. bigelowi* (Table 5). While the four most sensitive genera are the same as they were in the 1985 document, their SMAVs and GMAVs are different. As mentioned above, the original acute value for *Acartia clausi* (30 Fg CN L^{-1}, Gentile 1980) was revised to 17 Fg CN L^{-1} in order to account for mortality in the control treatment (Lussier et al. 1985). New toxicity values for *Cancer irroratus* (44.2 and 70.9 Fg CN L^{-1}) raised this species' mean acute value from 4.9 to 16.6 Fg CN L^{-1}. It is important to note that both studies (Gensemer et. al. 2006 and Johns and Gentile 1981) exposed larvae to cyanide using flow-through systems and measured concentrations of this pollutant. Even with the higher new values, *C. irroratus* still has the lowest SMAV of all of the saltwater species. As our objective is to develop a New Jersey-specific water quality standard for cyanide in saltwater, toxicity values for *Cancer* species that are not found along the Atlantic coast (*C. gracilis*, *C. magister*, *C. oregonensis*, and *C. productus*) were excluded from the analysis.

Table 5. Acute toxicity data from the present literature review.

SPECIES	SMAV (Fg/L)	GMAV (Fg/L)
Cancer irroratus	16.6	16.6
Acartia clausi	17.0	17.0
Menidia menidia	59.3	59.3
Americamysis bahia	113.0	
Americamysis bigelowi	124.0	118.4

The Final Acute Value (FAV), calculated with the four lowest GMAVs listed above (Table 5), is 5.334 µg CN L^{-1}. Thus, the recommended CMC for cyanide in NJ saltwater is CMC = FAV / 2 = 2.667, which we round to 2.7 µg CN L^{-1} following recommendations from the Guidelines.

CRITERION CONTINUOUS CONCENTRATION (CCC)

In the cyanide AWQC document (US EPA 1985), the criterion continuous concentration (CCC) in saltwater was set equal to the criterion maximum concentration (CMC) in saltwater. Only two chronic values and associated acute-chronic ratios (ACRs) were available for saltwater species, and both taxa were fairly insensitive to cyanide. The authors of the 1985 cyanide AWQC document argued that the acute value for the sensitive rock crab, which was based on the response of larva to cyanide exposure, was a better indicator of chronic sensitivity than an estimate based on the FAV/ACR ratio. Since our literature review has not added any new chronic values for saltwater species, we also recommend setting the CCC equal to the CMC. This decision follows the approach taken by authors of the 1985 cyanide AWQC document.

OTHER DATA

Cyanide toxicity data deemed to be unacceptable for deriving water quality criteria include Smith (1998) and Pablo and collaborators (1997a). Smith (1998) exposed *Skeletonema costatum*, a marine diatom, to multiple concentrations of potassium cyanide for 4, 8, or 17 h. Pablo et al. (1997a) examined effects of sodium cyanide on *Nitzschia closterium*, also a marine diatom, after 3 days of exposure (72 h). The duration of these exposure periods are inadequate; exposure periods ≥ 96 h are recommended by the Guidelines for toxicity tests with algae (Stephan et al. 1985).

UNUSED DATA

The following studies did not meet the Guidelines' requirements for incorporation of toxicity values into the calculation of water quality criteria: Chew and Ip (1992), Lasut (1999), and Pablo et al. (1996, 1997b, c). These toxicity tests were conducted with species that do not have naturally reproducing populations in North America. References for these manuscripts, as well as those listed in the section above ("Other Data") are listed in Appendix A.

NEW JERSEY WATER QUALITY STANDARDS

GLEC recommends the following text for revising the New Jersey Water Quality Standards for Cyanide in Saltwater: "Aquatic life in New Jersey saltwaters is likely to be protected against toxic effects of cyanide if the four-day average concentration of free cyanide does not exceed 2.7 Fg L^{-1} more than once every three years on average, and if the 24-hour average concentration does not exceed 2.7 Fg CN L^{-1} more than once every three years on average."

The recommended CMC and CCC will protect most saltwater species against toxic effects of cyanide. The revised criteria are lower than any acute or chronic value reported in the literature (Fig. 1), including those from algae (Table 4 in US EPA 1985). The three year minimum period between violations of the cyanide chronic criterion follows a general recommendation by the U.S. EPA. There is, however, variation among ecosystems in their ability to recover from perturbations such as excessively high cyanide concentrations. If longer periods are required for recuperation, or if shorter intervals are sufficient, then site-specific adjustments in return interval can be developed.

The use of criteria in designing waste treatment facilities requires the selection of an appropriate waste load allocation model. Dynamic models are preferred for the application of these criteria. Limited data or other factors may make their use impractical, in which case one should rely on a steady-state model. We recommend the interim use of 1Q5 or 1Q10 for CMC design flow, and 7Q5 or 7Q10 for the CCC design flow in steady-state models for unstressed and stressed systems, respectively. These matters are discussed in more detail in the USEPA Technical Support Document for Water Quality-Based Toxics Control (US EPA 1991).

Given the proposed acute and chronic criteria for cyanide (2.7 µg/L), and the permitted acute (16) and chronic (22.9) dilution factors allowed for PVSC's effluent, the new acute and chronic limits for cyanide in Passaic Valley discharges are projected as 43.2 and 61.8 µg CN/L, respectively.

Table 1 (continued)

Figure 1. Ranked summary of cyanide GMAVs.

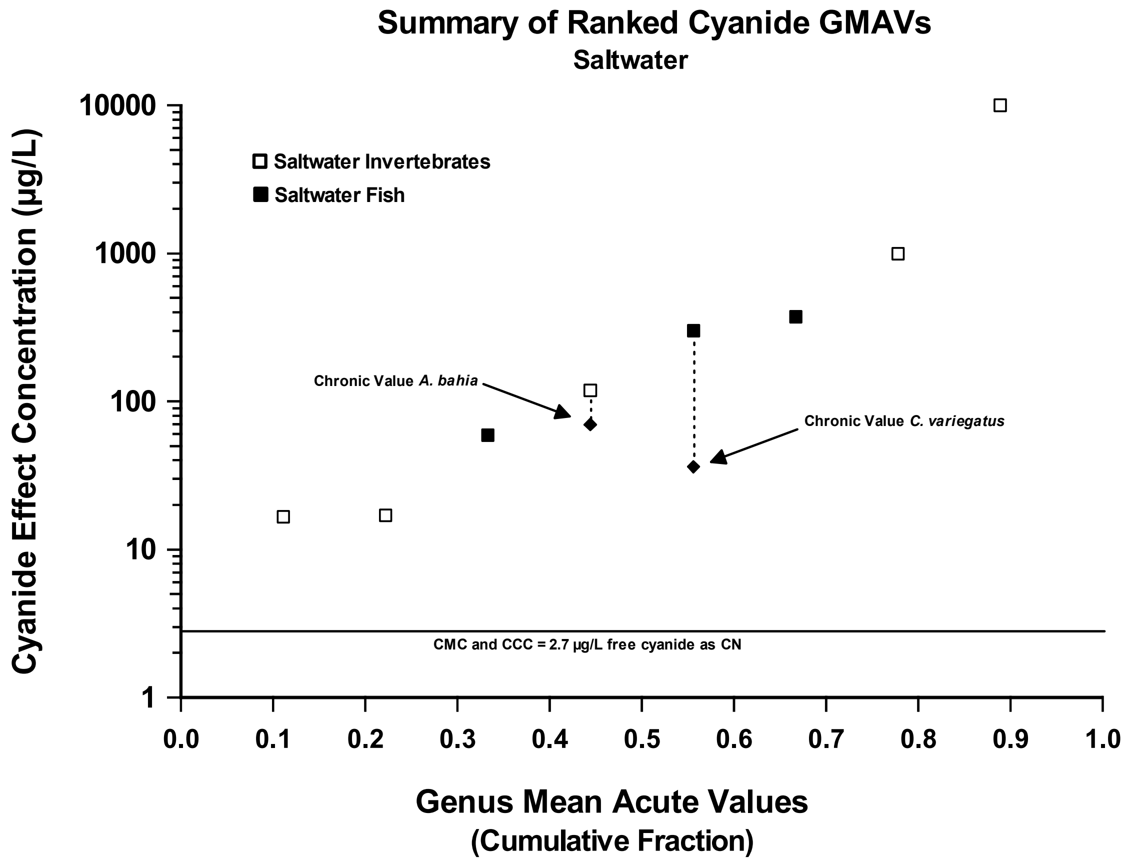

Table 1. Acute toxicity of cyanide to aquatic animals - Saltwater species (new or revised LC50/EC50 values are in bold).

Species	Method[A]	Salinity (g/kg) and (temp)	LC50/ EC50 (Fg/L)[B]	Species Mean Acute Value (Fg/L)	Reference
Calanoid copepod, *Acartia clausi*	S, U		**17.0**[C]	17.0	Lussier et al. 1985
Opossum shrimp, *Americamysis bahia*	S, U		93.0[D]		Gentile 1980
Opossum shrimp, *Americamysis bahia*	F, M		113.0	113.0	Lussier et al. manuscript
Shrimp, *Americamysis bigelowi*	S, U		124.0	124.0	Gentile 1980
Amphipod, *Ampelisca abdita*	S, U		1,220		Scott et al. manuscript
Amphipod, *Ampelisca abdita*	S, U		1,150		Scott et al. manuscript
Amphipod, *Ampelisca abdita*	S, U		704.0	995.9	Scott et al. manuscript
Graceful rock crab, *Cancer gracilis*	R, M	28 (10 °C)	**153.0**[D]		Brix et al. 2000
Graceful rock crab, *Cancer gracilis*	R, M	28 (10 °C)	**135.0**[D]	143.7[D]	Brix et al. 2000
Rock crab, *Cancer irroratus*	F, M		5.7		Johns and Gentile 1981
Rock crab, *Cancer irroratus*	F, M		4.2		Johns and Gentile 1981
Rock crab, *Cancer irroratus*	F, M	31.6 (15.6 °C)	**70.9**		Gensemer et al. 2006

Table 1 (continued)

Species	**Method**[A]	**Salinity (g/kg) and (temp)**	**LC50/ EC50 (µg/L)**[B]	**Species Mean Acute Value (µg/L)**	**Reference**
Rock crab, *Cancer irroratus*	F, M	30.7 (15.5 °C)	**44.2**	16.6	Gensemer et al. 2006
Dungeness or edible crab, *Cancer magister*	R, M	28 (10 °C)	**51.0**[D]		Brix et al. 2000
Dungeness or edible crab, *Cancer magister*	R, M	28 (10 °C)	**92.0**[D]	68.5[D]	Brix et al. 2000
Pigmy rock crab, *Cancer oregonensis*	R, M	28 (10 °C)	**111.0**[D]		Brix et al. 2000
Pigmy rock crab, *Cancer oregonensis*	R, M	28 (10 °C)	**154.0**[D]	130.7[D]	Brix et al. 2000
Red crab, *Cancer productus*	R, M	28 (10 °C)	**219.0**[D]		Brix et al. 2000
Red crab, *Cancer productus*	R, M	28 (10 °C)	**107.0**[D]	153.1[D]	Brix et al. 2000
Slipper limpet, *Crepidula fornicata*	S, U		>10,000	>10,000	Gardner and Nelson 1981
Sheepshead minnow, *Cyprinodon variegatus*	F, M		300.0	300.0	Schimmel et al. 1981
Atlantic silverside, *Menidia menidia*	F, U		59.3	59.3	Gardner and Berry 1981
Winter flounder, *Pseudopleuronectes americanus*	S, U		372.0	372.0	Cardin 1980

[A] S = static; R = renewal; F = flow-through; M = Measured; U = unmeasured.

[B] Results are expressed as concentrations of free cyanide (CN).

[C] Original value (30 µg/L, from Gentile 1980) in US EPA (1985) did not account for control mortality. The revision is based on a memorandum from Lussier and collaborators (Ecotox reference #14599).

[D] Value was not used to derive the cyanide criteria.

Table 2. Chronic toxicity of cyanide to aquatic animals – Saltwater species

Species	**Test**[A]	**Salinity (g/kg)**	**Limits (Fg/L)**[B]	**Chronic Value (Fg/L)**	**Reference**
Opossum shrimp, *Americamysis bahia*	LC		43-113	69.71	Lussier et al. manuscript
Sheepshead minnow, *Cyprinodon variegatus*	ELS		29-45	36.12	Schimmel et al. 1981

[A] LC = Life-cycle or partial life-cycle; ELS = Early life stage.

[B] Results are based on measured concentrations of free cyanide; limits are the reported No Observed Effect Concentration (NOEC) and Lowest Observed Effect Concentration (LOEC).

Table 3. Ranked genus mean acute values with species mean acute-chronic ratios for saltwater taxa exposed to cyanide.

Rank[A]	Genus Mean Acute Value (µg/L) [B]	Species	Species Mean Acute Value (Fg/L) [B, C]	Species Mean Acute-Chronic Ratio[D]
8	>10,000	Slipper limpet, *Crepidula fornicata*	>10,000	
7	995.9	Amphipod, *Ampelisca abdita*	995.9	
6	372.0	Winter flounder, *Pseudopleuronectes americanus*	372.0	
5	300.0	Sheepshead minnow, *Cyprinodon variegatus*	300.0	8.306
4	118.4	Shrimp, *Americamysis bigelowi*	124.0	
		Opossum shrimp, *Americamysis bahia*	113.0	1.621
3	59.3	Atlantic silverside, *Menidia menidia*	59.3	
2	17.0	Calanoid copepod, *Acartia clausi*	17.0	
1	16.6 [E]	Rock crab, *Cancer irroratus*	16.6	

[A] Ranked from most resistant to most sensitive based on Genus Mean Acute Value. Inclusion of "greater than" values does not necessarily imply a true ranking, but does allow for the use of all genera for which data are available, so that the Final Acute Value is not unrealistically low.

[B] Results are expressed as concentrations of free cyanide.

[C] From Table 1

[D] Chronic value from Table 2

[E] This GMAV is for *C. irroratus* only. SMAVs for west coast species were excluded because the proposed revision of the cyanide AWQC is for New Jersey.

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APPENDIX A

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