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Nitroguanidine Freshwater Ambient Water Quality Criteria

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Abstract

Nitroguanidine has been used in triple base and high energy propellant military applications for several decades. The propellant has recently been used in the insensitive munition IMX-101 which reduces unintentional detonation. The compound can enter the aquatic environment during production, use, and disposal and has been shown to be toxic to aquatic animals. The present study established the U.S. Environmental Protection Agency numerical freshwater ambient water quality criteria for the compound. The Criterion Maximum Concentration (CMC), which indicates that aquatic life should not be affected if the one-hour average concentration of nitroguanidine does not exceed the value more than once every three years, is 633 mg/L. The Criterion Continuous Concentration (CCC), which indicates that aquatic life should not be affected if the four-day average concentration of nitroguanidine does not exceed the value more than once every three years, is 372 mg/L. In general, nitroguanidine is less toxic than other common military propellant related compounds. However, if nitroguanidine is exposed to sunlight or the compound is exposed to UV radiation during wastewater treatment, the photolyzed degradation products can be 100- to 1,000-fold more toxic. A better understanding of the rates of photolysis in both oligotrophic and eutrophic surface waters and UV-treated wastewater is necessary to adequately assess the toxicological risk of the photolyzed byproducts to aquatic animals.

Keywords: Nitroguanidine; Aquatic Toxicity; Criterion Maximum Concentration (CMC); Criterion Continuous Concentration (CCC); Photolysis

Introduction

Nitroguanidine (CAS 556-88-7) is a gun propellant that has been used in military operations for several decades. It is used primarily in triple base (along with nitroglycerin and nitrocellulose) and high energy (along with nitroglycerin, nitrocellulose, and hexahydro-1,3,5-trinitro-1,3,5-triazine) propellant applications. More recently nitroguanidine (NQ) has been used in the insensitive munition IMX-101 (2,4-dinitroanisole, 3-nitro-1,2,4-triazol-5-one, and NQ) which is one of several insensitive munitions replacing conventional munitions to reduce unintentional detonation. Nitroguanidine has been shown to enter aquatic environments during the production, use, and disposal of both conventional munitions and the insensitive IMX-101 munition [1-4].

U.S. Environmental Protection Agency (EPA) numerical ambient water quality criteria for the compound have not been determined [5]. Because of the continued manufacture and use of NQ in the military and other commercial uses [6], nitroguanidine numerical national water criteria for freshwater organisms were developed in this paper. Numerical national water criteria for saltwater organisms were not considered because of insufficient NQ toxicity data for saltwater organisms.

Materials and Methods

Toxicity data that met the requirements given in the EPA guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms were used in the evaluation [7]. Sufficient acute toxicity data for invertebrates and fish (Table 1) were available to determine a Final Acute Value (FAV). The FAV is established using the Genus Mean Acute Value (GMAV) for one or more toxicity values for each species. In the cases where two or more toxicity values are available for a species, the geometric mean of the values is calculated to form the GMAV for the species. The GMAV values are used to calculate the FAV using the equations given Table 2. The FAV is used to establish the Criterion Maximum Concentration (CMC) which is one-half of the FAV.

Species	Exposure Duration (Hours)	Genus Mean Acute Values (mg/L)	Reference(s)
Midge *(Paratanytarsus dissimillis)*	48	3,395[a]	[12]
Fathead Minnow *(Pimephales promelas)*	96	3,002[a,c]	[12,13]
Oligochaete *(Lumbriculus variegatus)*	48	2,868[a]	[12]
Amphipod *(Hyalella azteca)*	48	2,730[a]	[12]
Amphipod *(Gammarus minus)*	48	2,720[a]	[12]
Channel Catfish *(Ictalurus punctatus)*	96	2,636[a]	[12]
Bluegill *(Lepomis macrochirus)*	96	2,634[a]	[12]
Hydra *(Hydra littoralis)*	48	2,061[b]	[13]
Cladoceran *(Ceriodaphnia dubia)*	48	1,780[b,d]	[4,13]
Cladoceran *(Daphnia magna)*	48	1,705[a,e]	[9,12]
Rainbow Trout *(Oncorhynchus mykiss)*	48	1,578[a,f]	[12,13]
Zebrafish *(Danio rerio)*	96	1,323[b]	[20]

[a] NOEC at solubility limit

[b] LC50

[c] Geometric mean of 2,714 mg/L [12] and 3,320 mg/L [13]

[d] Geometric mean of 1,174 mg/L [4] and 2,696 mg/L [13]

[e] Geometric mean of >1,024 mg/L [9] and 2,838 at solubility limit [12]

[f] Geometric mean of 1,520 mg/L [12] and1,638 mg/L [13]

Table 1: Acute Toxicity of Nitroguanidine to Freshwater Organisms

Rank (R)	Gmav[a]	Ln Gmav[b]	$(\text{Ln GMAV})^2$	$P = R/(N + 1)^C$	$\sqrt{P}$
4	1,780	7.484	56.010	0.308	0.555
3	1,705	7.441	58.232	0.231	0.481
2	1,578	7.364	54.228	0.154	0.392
1	1,323	7.188	51.667	0.077	0.277
Sum		29.477	220.137	0.769	1.705

[a] Four lowest genus mean acute values (mg/L) taken from Table 1

[b] Natural log of GMAV

[c] P is comparative probability for each GMAC; N = 12 GMAVs

$$S^2 = \frac{\Sigma\left[(\mathit{ln}\ \text{GMAV})^2\right] - \left[(\Sigma \mathit{ln}\ \text{GMAV})^2\right] / 4}{\Sigma(\text{P}) - \left[(\Sigma\sqrt{\text{P}})^2\right] / 4} = 1.1986$$

$S = 1.0949$

$L = [\Sigma(\ln \text{GMAV}) - S(\Sigma\sqrt{P})] / 4 = 6.8978$

$A = S(\sqrt{0.05}) + L = 7.1426$

Final Acute Value = $e^{7.1426}$ = 1,265 mg/L

Criterion Maximum Concentration (CMC) = 1,265 mg/L / 2 = 633 mg/L

Table 2: Ranking and FAV Calculations of Acute Toxicity Studies

The Criterion Continuous Concentration (CCC) is equal to the lowest of a Final Chronic Value, Final Plant Value, and Final Residue Value when all three values are available [7]. Fish and invertebrate data were available to calculate a Final Chronic Value (Table 3). One study with the green alga *(Selenastrum capricornutum)* was available to approximate a Final Plant Value. No Final Residue Value was established because little if any bioaccumulation of NQ by aquatic organisms should occur because the octanol-water partition coefficient ($\log k_{ow}$) is -0.89 [8]. The Final Chronic Value (FCV) was established by dividing the Final Acute Value (FAV) by the Final Acute-Chronic Ratio (FACR).

Species	Exposure Duration	Genus Mean Chronic Values (mg/L)	Acute-Chronic Ratio[a]	Reference(s)
Green Alga *(Selenastrum capricornutum)*	120-hour EC50	2,146[b]	N/A	[12]

Species	Exposure Duration	Genus Mean Chronic Values (mg/L)	Acute-Chronic Ratio[a]	Reference(s)
Rainbow Trout *(Oncorhynchus mykiss)*	35- & 40-day ELS	1,137[c]	2.00[d]	[12,13]
Fathead Minnow *(Pimephales promelas)*	28-day ELS	1,050	2.86	[13]
Cladoceran *(Ceriodaphnia dubia)*	7 days	260	6.85	[13]
Geometric Mean			3.3965	

[a] Acute-chronic ratios calculated from genus mean acute values in Table 1 and genus mean chronic values in Table 3

[b] 120-h EC50 based on dry weight standing crop; value not used in the final CCC calculation

[c] Geometric mean of 850 mg/L [12] and 1,520 mg/L [13]

[d] The calculated rainbow trout acute-chronic ratio is 1.39; however, the EPA guidelines [7] state that a value of 2 should be used when an acute-chronic ratio is <2 because acclimation may have occurred during the chronic test

Final Acute-Chronic Ratio (FACR) = 3.3965
Final Chronic Value = 1,265 mg/L / FACR = 372 mg/L
Criterion Continuous Concentration (CCC) = 372 mg/L

Table 3: Chronic Toxicity of Nitroguanidine to Freshwater Organisms

All data used in the criteria analyses were taken from bioassays conducted with published toxicity tests methods. Nitroguanidine concentrations were measured in all toxicity tests with the exception of one acute study [9]. The EPA guidelines state that toxicity results of static and renewal acute tests based on initial nominal concentrations are acceptable if measured concentrations are not available. In addition, only toxicity tests that had solution renewals every 24 hours or continuous flow were used because it has been shown NQ undergoes photolysis in aqueous solutions. Toxicity values reported as "greater than" values and values that were at or near the solubility of NQ in the test systems were used [7].

Results and Discussion

Acute toxicity data for NQ were found for 12 species which met the criteria of at least eight different families specified in the EPA guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms [7]. Two values were available for each of the two cladocerans *Ceriodaphnia dubia* and *Daphnia magna*, rainbow trout *(Oncorhynchus mykiss)*, and fathead minnow *(Pimephales promelas)*. The geometric mean of each of the two values was calculated to provide the Genus Mean Acute Value for each species. The genus mean acute value for the 12 species is given in Table 1. The values are listed from the least toxic to the most toxic which facilitated the calculation of the Final Acute Value that uses the four lowest Genus Mean Acute Values (Table 2).

Four of 16 acute toxicity values were either 48- or 96-hour LC50s (concentrations that kill 50% of the population) while 11 of 16 were no observed effect concentrations (NOEC) obtained at or near the solubility limits of NQ which range from 2,600 to 4,400 mg/L between 20 °C and 25 °C [10,11]. The geometric Genus Mean Acute Value for *D. magna* is composed of one >1,024 mg/L value [9] and 2,838 mg/L at solubility [12].

The acute NQ toxicity ranged from a high of 3,395 mg/L for a larval midge *(Paratanytarsus dissimillis)* to a low of 1,323 mg/L for the larval zebrafish *(Danio rerio)*. The Final Acute Value based on the four lowest Genus Mean Acute Values of the organism listed in Table 1 is 1,265 mg/L as calculated by the equations shown in Table 2. The Criterion Maximum Concentration, which is equal to one-half of the FAV, is 633 mg/L.

Chronic NQ toxicity data were available for three species which met the EPA criteria of at least one fish, one invertebrate, and one organism which was an acutely sensitive species (Table 3). A 35-day early life stage (ELS) test value of 1,520 mg/L [13] and a 40-day ELS test of 850 mg/L [12] were available for the rainbow trout *(O. mykiss)*. The geometric mean of the two values was calculated to provide a Genus Mean Chronic Value of 1,137 mg/L (Table 3). A chronic value of 1,050 mg/L was obtained for the fathead minnow *(P. promelas)* in a 28-day ELS test [13] and a NOEC of 260 mg/L was established in a 7-day cladoceran *(C. dubia)* neonate production test [13].

A 10-day LC50 of 894 mg/L was found for the amphipod *Hyalella azteca* [14]; however, the LC50 did not met the EPA guidelines for establishing a Final Chronic Value [7].

The Genus Mean Acute Values in Table 1 and Genus Mean Chronic Values in Table 3 for the rainbow trout, fathead minnow, and cladoceran *(C. dubia)* were used to determine to the Acute-Chronic Ratio for each species (Table 3). The Final Acute-Chronic Ratio (FACR), which is the geometric mean of the acute-chronic ratios, was used to determine the Final Chronic Value. The Final Chronic Value of 372 mg/L was established by dividing the Final Acute Value by the FACR [7].

A 120-h EC50 (effective concentration that affects 50% of the population) of 2,146 mg/L (based on dry weight standing crop) for the green alga *(S. capricornutum)* was available to approximate a Final Plant Value [12]. No data were available to establish a Final Residue Value. The Criterion Continuous Concentration (CCC) is the lowest of the Final Chronic Value, Final Plant Value, and Final Residue Value. Thus, the Final Chronic Value of 373 mg/L was used to establish the CCC.

A number of studies indicate that NQ is less toxic to freshwater organisms relative to several other common military propellant related energetic compounds. For example, the 48-hour LC50s for nitroglycerin range from 17 to 55 mg/L for several invertebrates [13,15] including four that are given in Table 1. Nitroglycerin 96-hour LC50s have been shown to range from 1 to >18 mg/L for the four fish listed in Table 1 [15]. The 48-hour LC50s of diethyleneglycol dinitrate (DEGDN) for the cladoceran *D. magna*, midge larva, mayfly larva, and amphipod range from 90 to 355 mg/L [16] while the range for NQ is >1,024 for *D. magna* [9] to 3,395 mg/L for the midge *(P. dissimillis)* [12]. The 96-hour LC50s for DEGDN for bluegill, channel catfish, rainbow trout, and fathead minnow range between 258 and 491 mg/L [16] in contrast to a range of 1,578 to 3,002 mg/L for NQ (Table 1).

It has been shown that NQ is degraded by ultraviolet (UV) radiation around 264 nm [11,17,18]. Haag, *et al.* [11] estimated that the fate of NQ in oligotrophic streams and lakes is dominated by photolysis with surface half-lives at 40 °N that range from 0.6 days in the summer to 2.3 days in winter. In colored eutrophic surface waters where photolysis is inhibited, they estimated that the half-life would be several days. It has been shown that photolysis of NQ produces large amounts of guanidine, nitrate, and nitrite, and smaller amounts of cyanamide, cyanoguanidine, urea, and ammonium [19].

The UV-induced degradation products have been shown to be more toxic than the parent compound. van der Schalie photolyzed various NQ concentrations using laboratory UV light until the NQ concentrations reached non-detectable levels (<0.1 mg/L) [12]. The nominal concentrations for the photolyzed NQ tests were given as mg/L NQ based on dilutions from the measured (un-photolyzed) stock solution values. A stock solution of 198 mg/L photolyzed for 5.5 hours produced a 48-hour LC50 for the cladoceran *D. magna* of 25 mg/L versus >2,838 mg/L parent compound. A stock solution of 613 mg/L photolyzed for 7 hours produced a 96-hour LC50 of 35 mg/L for the fathead minnow *P. promelas* in contrast to a 96-hour LC50 of 2,714 mg/L parent compound. The 120-hour EC50 (based on dry weight standing crop) for the green alga *S. capricornutum* was 32 mg/L photolyzed solution when a stock solution of 316 mg/L was photolyzed for 6.5 hours; the parent NQ 120-hour EC50 was 2,146 mg/L.

Two acute photolyzed NQ tests using the cladoceran *(C. dubia)* were conducted by Kennedy, *et al.* [4]. Tests 1 and 2 started with initial stock NQ solutions of 1,619 and 108 mg/L, respectively. The solutions were exposed in a photoreactor for 4 hours which correlated to 48 hours of sunlight exposure in Vicksburg, Mississippi (32.3637 latitude; -90.8913 longitudes). Photo-induced 48-hour LC50s of 16.1 and 0.8 mg/L occurred in tests 1 and 2, respectively. The 48-hour LC50 for the parent compound was 1,174 mg/L. As concluded by the authors, photo-irradiation increased toxicity of NQ by 100- to 1,000-fold depending on the starting concentration. Similarly, Gust, *et al.* [20] exposed larval zebrafish *(D. rerio)* to a starting NQ solution of 3,000 mg/L exposed in a photoreactor for 4 hours which correlated to 48 hours of sunlight exposure in Vicksburg, Mississippi. The 96-hour LC50 of the zebra fish exposed to the UV-treated solution was 77 mg/L in contrast to 1,323 mg/L for the parent compound.

The chronic toxicity of photolyzed NQ to the cladoceran *C. dubia* was evaluated by Burton, *et al.* [13]. A 100 mg/L initial stock solution of NQ was exposed to direct sunlight in Shady Side, Maryland (38.8418 latitude; -76.5122 longitudes) in mid-September for a total of 80 hours until the parent compound reached non-detectable levels. The stock solution was covered each evening with black plastic so the actual hours of sunlight could be calculated. Light intensity was not estimated by the use of a chemical actinometer. The 7-day lowest observed effect concentration (LOEC) and NOEC for reproduction were 3.6 and 2.2 mg/L, respectively. In contrast, the 7-day LOEC and NOEC for the cladoceran (reproduction) exposed to the parent compound were 440 and 260 mg/L, respectively. Photolyzed NQ was approximately two orders of magnitude more toxic to the cladoceran under the same test conditions.

Conclusion

The freshwater NQ ambient water quality criteria CMC and CCC show that the compound is less toxic than other common military propellant related compounds. However, if NQ is exposed to sunlight during production, use, and/or disposal or the compound is exposed to UV radiation during wastewater treatment, the photolyzed degradation products can be 100- to 1,000-fold more toxic. A better understanding of the rates of photolysis in both surface waters and UV-treated wastewater is necessary to adequately assess the toxicological risk to aquatic animals. Systematic studies such as those by Kennedy, *et al.* [4] and Gust, *et al.* [20] of NQ exposed to UV radiation in a photoreactor with known light durations that can be correlated to set times of sunlight at specified latitude are necessary. Since the initial concentration of NQ before UV irradiation influences by-product production and subsequent toxicity one could argue that additional studies should start with similar NQ concentrations. The CCC could be used as a standard initial concentration. A difficult, but important step, will ultimately be extrapolating from laboratory UV photolysis systems and toxicity exposures to potential toxicity that may occur in photolyzed wastewater and surface waters.

References

1. Patterson JN, Shapira I, Brown J, Duckert W, Polson J (1976) State-of-the-art: Military explosives and propellants production industry. Volume III. Wastewater characterization. U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, OH, EPA-600/2-76-213c.

2. Kenyon KF (1983) A data base assessment of environmental fate aspects of nitroguanidine. Defense Tech Information Center, Alexandria, VA, AD A125591.

3. Sunflower Army Ammunition Plant (2016) Installation action plan. Sunflower Army Ammunition Plant, DeSoto, KS.

4. Kennedy AJ, Poda AR, Melby NL, Moores LC, Jordan SM, et al. (2017) Aquatic toxicity of photo-degraded insensitive munition 101 (MX-101) constituents. Environ Toxcol Chem 36: 2050-057.

5. United States Environmental Protection Agency (2019) National recommended water quality criteria – Aquatic life criteria table. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

6. Market Research (2019) Global nitroguanidine (CAS 556-88-7) consumption market research by company, type & application 2013-2025. Market Research, Las Vegas, NV.

7. Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, et al. (1985) Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. National Technical Information Service, U.S. Department of Commerce, Springfield, VA, PB85-227049.

8. Hansch C, Leo A, Hoekman D (1995) Exploring QSAR - Hydrophobic, electronic, and steric constants. American Chemical Society, Washington, DC.

9. Dave G, Nilsson E, Wernersson AS (2000) Sediment and water phase toxicity and UV-activation of six chemicals used in military explosives. Aquat Ecosystem Hlth Manage 3: 291-9.

10. U.S. Army (1974) Encyclopedia of explosives and related items. PATR 2700. Vol. 6. Picatinny Arsenal, Dover, NJ, G154-8.

11. Haag WR, Spanggord R, Mills T, Podoll RT, Chow TW, et al. (1990) Aquatic environmental fate of nitroguanidine. Environ Toxicol Chem 9: 1359-67.

12. van der Schalie WH (1985) The toxicity of nitroguanidine and photolyzed nitroguanidine to freshwater aquatic organisms. Defense Tech. Information Center, Alexandria, VA, AD A153045.

13. Burton DT, Turley SD, Peters GT (1993) Toxicity of nitroguanidine, nitroglycerin, hexahydro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) to selected freshwater aquatic organisms. Defense Tech. Information Center, Alexandria, VA, AD A267467.

14. Lotufo GR, Stanley JK, Chappell P, Melby NL, Wilbanks MS, et al. (2018) Subchronic, chronic, lethal and sublethal toxicity of insensitive munitions mixture formulations relative to individual constituents in Hyalella azteca. Chemosphere 210: 795-804.

15. Bentley RE, Dean JW, Ells SJ, Hollister TA, LeBlanc GA, et al. (1977) Laboratory toxicity of nitroglycerine to aquatic organisms. Defense Tech. Information Center, Alexandria, VA, AD A061739.

16. Fisher DJ, Burton DT, Paulson RL (1989) Comparative acute toxicity of diethyleneglycol dinitrate to freshwater aquatic organisms. Environ Toxicol Chem 8:545-50.

17. Bissett FH, Levasseur LA (1976) Analytical methods for nitroguanidine and characterization of its degradation products. Defense Tech. Information Center, Alexandria, VA, AD A034455.

18. Noss CI, Chyrek RW (1984) Nitroguanidine wastewater pollution control, technology: Phase III. Treatment with ultraviolet radiation, ozone, and hydrogen peroxide. Defense Tech. Information Center, Alexandria, VA, AD A139389.

19. Becher JB, Beal SA, Taylor S, Dontsova K, Wilcox DE (2019) Photo-transformation of aqueous nitroguanidine and 3-nitro-1,2,4-triazol-5-one. Emerging munitions compounds. Chemosphere 228: 418-26.

20. Gust KA, Stanley JK, Wilbanks MS, Mayo ML, Chappell P, et al. (2017) The increased toxicity of UV-degraded nitroguanidine and IMX-101 to zebrafish larvae: Evidence implicating oxidative stress. Aquat Tocicol 190: 228-45.