COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF CLEAN WATER

TRIENNIAL REVIEW OF WATER QUALITY STANDARDS

RATIONALE FOR THE DEVELOPMENT OF AMBIENT WATER QUALITY CRITERIA FOR

AMMONIA

PROTECTION OF AQUATIC LIFE USE

Introduction

The United States Environmental Protection Agency (US EPA) has released its 2013 water quality criteria recommendations for protecting aquatic life from ammonia. These recommendations are intended as guidance to states, territories, and authorized tribes in developing water quality standards to protect aquatic life from exposure to ammonia. State-wide application of these nationally recommended water quality criteria would provide an appropriate level of protection for aquatic life from the effects of ammonia.

Sources of Ammonia in Freshwaters

Ammonia is used in agriculture both directly and as a precursor for other nitrogen-based fertilizers. Ammonia is also used in numerous industrial applications including metal finishing, pharmaceuticals, processing of crude oil, and corrosion protection. Ammonia can enter the aquatic environment via anthropogenic sources or discharges (e.g., municipal effluent, agricultural runoff), and via natural sources such as decomposition of organic waste matter, the discharge of ammonia by biota, and nitrogen fixation processes. Ammonia is converted relatively quickly to other forms of nitrogen in oxygenated waters. (USEPA, 2013)

Toxicity of Ammonia

When ammonia is present in water at high enough levels, it is difficult for aquatic organisms to sufficiently excrete the toxicant, leading to toxic buildup in internal tissues and blood, and potentially death. Environmental factors, such as pH and temperature, can affect ammonia toxicity to aquatic animals. (USEPA, 2013a)

Ammonia exists in aqueous solution as either the ammonium ion (NH_4^+) or un-ionized ammonia (NH_3). The ammonium ion is the more abundant form. The sum of these two forms of ammonia is called total ammonia nitrogen (or TAN). They exist in water according to the following equilibrium reaction:

$$\mathbf{NH_4^+ + OH^- \leftrightarrows NH_3 + H_2O}$$

As the pH increases, the ratio of un-ionized ammonia to ammonium ions increases. The increase in hydroxyl ions (OH^-) shifts the equilibrium and the result is a greater concentration of unionized ammonia. The unionized ammonia is more toxic than the ammonium ion. Therefore, higher pH levels are associated with greater toxicity of ammonia. This is true for both fish and invertebrates. Similarly, a rise in temperature increases the toxicity of ammonia for invertebrates, but vertebrate sensitivity to ammonia is independent of temperature. (USEPA, 2013)

PA's Early Ammonia Criteria

Pennsylvania's Water Quality Standards has incorporated water quality criteria for ammonia since the early 1970's. The criteria that was adopted in the early 1970's was bifurcated with the first level designed to be protective of cold water fishes (CWF) and was equal to 0.5 mg total ammonia nitrogen per liter. In the early 1970's the Pennsylvania Fish Commission recommended that any concentration greater than 0.5 mg/L adversely affects trout. This limit was based on that recommendation. The second level of the ammonia criteria was designed to be protective of trout stocking (TSF) and warm water fishes (WWF) and was set to 1.5 mg total ammonia nitrogen per liter. The 1.5 mg/L limit was based on work by M.M. Ellis (1937) which indicated that this concentration was not harmful to most varieties of fish. These criteria only applied to about one half of the streams in the state. (PADER, 1984)

PA's Current Criteria is based on EPA 1983

In 1984, Pennsylvania was beginning a new triennial review of its water quality standards. EPA had just released a draft report in 1983 called *Ambient Water Quality Criteria for Ammonia – 1983* (USEPA, 1983 draft). EPA implored Pennsylvania to consider promulgating ammonia criteria based on the findings presented in this report as part of its triennial review. Pennsylvania did adopt ammonia criteria as described in the draft report because of the following reasons. (1.) Data preceding publication of EPA's 1976 Water Quality Criteria (Red Book) supported criteria based on toxic levels of un-ionized ammonia. The 1984 dataset expanded on this basis, taking into account the effects of pH and temperature variation on the toxicity of ammonia. (2.) The federal draft recommendations (USEPA, 1983 draft) were based on EPA's ammonia toxicity models, which expressed allowable ammonia concentrations (total ammonia nitrogen concentrations) for specific pH and temperature conditions. (3.) Studies at the time indicated that un-ionized ammonia was the primary concern in aquatic toxicity, but total ammonia was also toxic to some degree and can impact on biochemical oxygen demand or BOD. Dissociation of ammonia in water is highly dependent on pH and temperature. The 1983 EPA model for allowable ammonia concentration included all of these considerations (PADER, 1984). Pennsylvania adopted ammonia criteria based on EPA's 1983 draft report, however, the recommendations in EPA's final document called *Ambient Water Quality Criteria for Ammonia – 1984* (USEPA, 1985) differed from their draft report, so Pennsylvania's current criteria differ from US EPA's final recommendation in the mid-1980's.

1999 Federal Revision

The federal recommendation was updated in 1999 to reflect the most recent available science. The 1999 recommended aquatic life criteria for ammonia were based on the most sensitive endpoints known at the time: the acute criterion was based on salmonid fish toxicity information, and the chronic criterion was based primarily on reproductive effects on the benthic invertebrate *Hyalella* or on survival and growth of bluegill sunfish early life stages (when present), depending on temperature and season (USEPA 2013). Pennsylvania did not adopt the 1999 recommendation because its criteria adopted in 1985 were considered to provide adequate protection for aquatic life from the effects of ammonia. Pennsylvania's current aquatic life criteria are still based on the USEPA 1983 draft report.

Pennsylvania's Current Ammonia Criteria: Aquatic Life Protection

Pennsylvania's current water quality criterion for protection of aquatic life from ammonia is found at Table 3 in Title 25 of the Pennsylvania Code; §93.7(a):

TABLE 3

Parameter	*Symbol*	*Criteria*	*Critical Use**
* * * * * *			
Ammonia Nitrogen	Am	The maximum total ammonia nitrogen concentration (in mg/L) at all times shall be the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) x ($\log^{-1}[pK_T\text{-}pH] + 1$), where: un-ionized ammonia nitrogen $= 0.12\ x\ f(T)/f(pH)$ $f(pH) = 1 + 10^{1.03(7.32-pH)}$ $f(T) = 1, T \geq 10$℃ $f(T) = \frac{1 + 10^{(9.73-pH)}}{1 + 10^{(pK_T-pH)}}, T < 10$℃ and $pK_T = 0.090 + \left[\frac{2730}{(T+273.2)}\right]$, the dissociation constant for ammonia in water. The average total ammonia nitrogen concentration over any 30 consecutive days shall be less than or equal to the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) X ($\log^{-1}[pK_T\text{-}pH] + 1$), where: un-ionized ammonia nitrogen $= 0.025\ x\ f(T)/f(pH)$ $f(pH) = 1, pH \geq 7.7$ $f(pH) = 10^{0.74(7.7-pH)}, pH < 7.7$ $f(T) = 1, \geq 10$℃ $f(T) = \frac{1 + 10^{(9.73-pH)}}{1 + 10^{(pK_T-pH)}}, T < 10$℃ The pH and temperature used to derive the appropriate ammonia criteria shall be determined by one of the following methods:	CWF, WWF, TSF, MF

		1) Instream measurements, representative of median pH and temperature – July through September. 2) Estimates of median pH and temperature – July through September – based upon available data or values determined by the Department. For purposes of calculating effluent limitations based on this value the accepted design stream flow shall be the actual or estimated lowest 30-consecutive-day average flow that occurs once in 10 years.	
* * * * * *			

USEPA's latest recommendation (USEPA 2013)

In 2003, EPA became aware of new toxicity studies indicating the relative sensitivity of freshwater mussels to ammonia and began to update the 1999 criteria to reflect this new information. In 2009, following external peer review, EPA published draft recommended ammonia criteria, for waters with and without mussels. Since the publication of the draft 2009 ammonia criteria, additional toxicity testing has validated information on the effects of ammonia on sensitive freshwater gill-breathing (non-pulmonate) snail species. The 2013 criteria incorporate scientific views received on the draft (2009) ammonia criteria and supersede EPA's previously recommended 1999 criteria. In April 2013, EPA finalized the updated ammonia criteria that are applicable nationally, taking into account the latest toxicity information for freshwater species, including unionid mussels and gill-breathing (non-pulmonate) snails. EPA is now imploring the PA DEP to consider adoption of the most recent federal recommendation for aquatic life protection from ammonia.

EPA analyzed the new data and determined that the pH and temperature relationships in the 1999 criteria are still supported by the most current research. In the development of the 2013 criteria equations, it was noted that temperature has little effect on the toxicity of total ammonia nitrogen to fish, therefore the effect concentrations for fish are only normalized for pH. For invertebrates, temperature and pH both affect the toxicity of TAN, so the TAN effect concentrations are normalized for both pH and temperature. The acute criterion magnitude is driven by freshwater unionid mussels at water temperatures greater than 15.7℃ at pH = 7. The TAN effects concentrations of salmonids and other fish drive the acute criterion magnitude at lower temperatures. The 2013 chronic criterion magnitude is determined primarily by the sensitivity of freshwater mollusks, particularly unionid mussels. (USEPA, 2013).

Freshwater unionid mussels are found in many states of the continental United States and many of these mussels are Federally-listed as endangered or threatened species. Non-pulmonate snails also have a very broad distribution across the United States. There are approximately 65 species of unionid mussels in Pennsylvania, including many that are rare or endangered. The seven most sensitive genera in the acute dataset are all in the family Unionidae and all of these genera except for *Venustaconcha* are found in Pennsylvania. The two most sensitive genera in the chronic dataset are also unionid mussels that are both found in Pennsylvania. The genus *Fluminicola* is ranked number 5 in chronic sensitivity. *Fluminicola* is a group of freshwater non-pulmonate (or prosobranch) snails in the family Hydrobiidae, and its members are commonly known as the pebblesnails. There are 6 families (including Hydrobiidae) and at least 16 genera of non-pulmonate snails in Pennsylvania (Evans, 2004).

EPA is recommending a single national acute criterion and a single national chronic criterion that will be protective of sensitive mollusks. EPA makes this recommendation because every state has at least one freshwater unionid mussel or bivalve mollusk, or non-pulmonate snail species, native or present in at least some of their waters. (USEPA 2013) It is appropriate for Pennsylvania to adopt these national criteria that were developed to be protective when sensitive mollusks are present because freshwater mussels are among the most sensitive genera in the dataset and many of these sensitive mussels reside in Pennsylvania. Additionally, Pennsylvania is host to at least 18 species of non-pulmonate (or prosobranch) snails.

EPA developed three equations to be used when mussels are present. The first equation is used to determine the acute criterion when mussels are present and salmonids are present. (USEPA 2013)

$$CMC = MIN\left(\left(\frac{0.275}{1+10^{7.204-pH}}+\frac{39.0}{1+10^{pH-7.204}}\right),\left(0.7249\times\left(\frac{0.0114}{1+10^{7.204-pH}}+\frac{1.6181}{1+10^{pH-7.204}}\right)\times\left(23.12\times10^{0.036\times(20-T)}\right)\right)\right)$$

The second acute equation is used when mussels are present and salmonids are absent (USEPA 2013).

$$CMC = 0.7249\times\frac{0.0114}{1+10^{7.204-pH}}+\frac{1.6181}{1+10^{pH-7.204}}\times MIN\left(51.93, 23.12\times10^{0.036\times(20-T)}\right)$$

The third equation is used to derive the chronic criterion when mussels are present. When mussels are present, the 2013 CCC magnitude is protective of fish early life stages regardless of temperature (USEPA 2013).

$$CCC = 0.8876\times\left(\frac{0.0278}{1+10^{7.688-pH}}+\frac{1.1994}{1+10^{pH-7.688}}\right)\times\left(2.126\times10^{0.028\times\left(20-MAX(T,7)\right)}\right)$$

The duration of the acute criterion is one hour. The duration of the chronic criterion is a 30-day rolling average with the additional restriction that the highest 4-day average within the 30 days be no greater than 2.5 times the chronic criterion magnitude. These values are not to exceed a frequency of more than once in 3 years on average. (USEPA 2013)

RECOMMENDATION

The Department recommends that the ammonia criteria should be updated to be reflective of the latest recommendation from the US EPA. The proposed criteria for the Commonwealth of Pennsylvania are borrowed directly from the 2013 federal recommendation, Aquatic life ambient water quality criteria for ammonia – freshwater 2013 (USEPA 2013). The Department has reviewed the current national aquatic life criteria for ammonia.

This latest recommendation from the US EPA considers the most recent scientific research regarding the effects of ammonia on aquatic life. The Department should replace its current water quality criteria for ammonia nitrogen (Am), having a critical Use of CWF, WWF, TSF, MF found in Table 3 at §93.7(a) with the following:

TABLE 3

Parameter	Symbol	Criteria	Critical Use*
		* * * * * *	
Ammonia Nitrogen	Am	In freshwater, the concentration of total ammonia nitrogen (TAN) shall not exceed (more than once in three years on average), the concentration calculated (in milligrams of TAN per liter) by the following: 1-hour average Criteria Maximum Concentration (CMC) acute criterion equation: $CMC = MIN\left(\left(\frac{0.275}{1+10^{7.204-pH}}+\frac{39.0}{1+10^{pH-7.204}}\right),\left(0.7249\times\left(\frac{0.0114}{1+10^{7.204-pH}}+\frac{1.6181}{1+10^{pH-7.204}}\right)\times\left(23.12\times10^{0.036\times(20-T)}\right)\right)\right)$ 30-day average Criteria Continuous Concentration (CCC) chronic criterion equation: $CCC = 0.8876\times\left(\frac{0.0278}{1+10^{7.688-pH}}+\frac{1.1994}{1+10^{pH-7.688}}\right)\times\left(2.126\times10^{0.028\times\left(20-MAX(T,7)\right)}\right)$ In addition, chronic concentration is not to exceed 2.5 times the CCC as a 4-day average within 30 days (e.g. 2.5 × 1.9 mg TAN/L at pH 7 and 20^{0}C or 4.8 mg TAN/L) more than once in 3 years on average. The pH and temperature used to derive the appropriate ammonia criteria shall be determined by instream measurements or best estimates, representative of the median pH and temperature of the receiving stream for the applicable time period and design conditions.	CWF, WWF, TSF, MF
		* * * * * *	

The nationally recommended criteria were developed to be protective of sensitive mollusks. The first equation above that is included with the proposed criteria will be the equation for the Criteria Maximum Concentration. EPA recommends using this equation to calculate the CMC when mussels are present and salmonids are present. The values generated for the acute criteria using this equation are more stringent below 17^{0}C than are the values generated using the CMC equation that EPA generated for situations where mussels are present and salmonids are absent. The Department proposes to use the more restrictive equation to determine the statewide CMC

for total ammonia nitrogen for several reasons. (1.) Sensitive salmonid fishes are common throughout Pennsylvania. (2.) This equation uses the set of conditions that generates the most stringent criteria, so our proposed CMC will most certainly be sufficiently protective. (3.) All of the proposed acute criteria values generated by the proposed equation (regardless of the ambient pH and temperature conditions) are less restrictive than the values for our current acute criteria calculated using the same pH and temperature, as depicted in Table One. Adopting this approach will not be detrimental to anyone who is currently a discharger because the acute standards will be less restrictive under all temperature and pH conditions. (4.) It is less complex (*and therefore simpler to understand and easier to implement with fewer errors*) to adopt a single statewide equation for the acute criteria (i.e. the more restrictive CMC equation for salmonids present and mussels present), rather than to adopt two separate equations which would otherwise be used in different situations to derive the CMC values.

COMPARISON OF PA'S CURRENT AND PROPOSED CRITERIA

Table One and Table Two are provided to illustrate the differences between Pennsylvania's current and proposed aquatic life criteria for ammonia. Table One compares the acute criteria and Table Two compares the chronic criteria. The varying hues of red and blue on both tables indicate the difference between the proposed criteria and Pennsylvania's current criteria. The darker or more intense shades of red and blue indicate where the proposed criteria are increasingly more or less restrictive than the current criteria, respectively.

All of the values for the proposed acute criteria will be less restrictive for all temperature and pH conditions, with the greatest departure from the current criteria at the lower pH values. The current chronic criteria is sometimes less restrictive than the proposed criteria and it will sometimes be more restrictive, depending on the temperature and pH conditions. There is a tendency for the proposed chronic criteria to be more restrictive than the current criteria at lower pH values.

TABLE ONE: ACUTE CRITERIA COMPARISON TABLES

Values on tables given in milligrams of Total Ammonia Nitrogen per liter (MG TAN / L)

Color Code = The difference between the federally recommended acute aquatic life criteria (EPA2013) and Pennsylvania's current acute aquatic life criteria (PA Current) is given in milligrams of total ammonia nitrogen per liter. (EPA2013 minus PA Current)

0 to 3	3 to 6	6 to 9	9 to 12	>12

PA Current vs EPA2013 with *Oncorhyncus mykiss* present

		Temperature															
	°C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
pH	°F	32	35.6	39.2	43	46.4	50	53.6	57.2	60.8	64.4	68	71.6	75.2	78.8	82.4	86
6	PA Current	26.98	26.98	26.98	26.98	26.98	26.97	23.09	19.80	17.02	14.66	12.65	10.94	9.48	8.23	7.16	6.24
	EPA2013	36.72	36.72	36.72	36.72	36.72	36.72	36.72	36.72	35.57	30.14	25.53	21.63	18.33	15.53	13.16	11.15
6.5	PA Current	25.51	25.51	25.51	25.51	25.51	25.50	21.83	18.73	16.10	13.87	11.97	10.35	8.97	7.79	6.78	5.91
	EPA2013	32.61	32.61	32.61	32.61	32.61	32.61	32.61	32.61	31.59	26.76	22.67	19.21	16.28	13.79	11.68	9.90
7	PA Current	20.59	20.59	20.59	20.59	20.59	20.58	17.62	15.12	13.00	11.20	9.67	8.37	7.26	6.31	5.49	4.79
	EPA2013	24.10	24.10	24.10	24.10	24.10	24.10	24.10	24.10	23.35	19.78	16.76	14.20	12.03	10.19	8.64	7.32
7.5	PA Current	12.40	12.40	12.40	12.40	12.40	12.40	10.62	9.12	7.85	6.77	5.85	5.07	4.41	3.83	3.34	2.92
	EPA2013	13.28	13.28	13.28	13.28	13.28	13.28	13.28	13.28	12.87	10.90	9.24	7.83	6.63	5.62	4.76	4.03
8	PA Current	5.47	5.47	5.47	5.47	5.47	5.47	4.70	4.04	3.49	3.02	2.62	2.28	1.99	1.74	1.53	1.34
	EPA2013	5.62	5.62	5.62	5.62	5.62	5.62	5.62	5.62	5.44	4.61	3.90	3.31	2.80	2.37	2.01	1.70
8.5	PA Current	2.03	2.03	2.03	2.03	2.03	2.03	1.76	1.52	1.32	1.16	1.01	0.89	0.79	0.70	0.62	0.56
	EPA2013	2.14	2.14	2.14	2.14	2.14	2.14	2.14	2.14	2.07	1.76	1.49	1.26	1.07	0.90	0.77	0.65
9	PA Current	0.75	0.75	0.75	0.75	0.75	0.75	0.66	0.58	0.52	0.46	0.41	0.37	0.34	0.31	0.29	0.26
	EPA2013	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.86	0.73	0.62	0.52	0.44	0.37	0.32	0.27

TABLE TWO: CHRONIC CRITERIA COMPARISON TABLE

Values on table given in milligrams of Total Ammonia Nitrogen per liter (MG TAN / L)

Color Code = The difference between the federally recommended chronic aquatic life criteria (EPA2013) and Pennsylvania's current chronic aquatic life criteria (PA Current) was calculated in milligrams of total ammonia nitrogen per liter. (EPA2013 minus PA Current) The value for the difference was assigned to a particular range and color coded as follows:

< -2.5	-1.25 to -2.5	-0.5 to -1.25	0 to -0.5
0 to 0.133	0.133 to 0.267	0.267 to 0.4	>0.4

		Temperature															
	°C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
pH	°F	32	35.6	39.2	43	46.4	50	53.6	57.2	60.8	64.4	68	71.6	75.2	78.8	82.4	86
6	PA Current	7.41	7.41	7.41	7.41	7.41	7.41	6.34	5.44	4.68	4.03	3.48	3.01	2.61	2.26	1.97	1.71
	EPA2013	5.13	5.13	5.13	5.13	4.81	4.23	3.72	3.27	2.87	2.52	2.22	1.95	1.71	1.51	1.32	1.16
6.5	PA Current	5.50	5.50	5.50	5.50	5.50	5.50	4.70	4.04	3.47	2.99	2.58	2.23	1.93	1.68	1.46	1.27
	EPA2013	4.92	4.92	4.92	4.92	4.61	4.06	3.57	3.13	2.75	2.42	2.13	1.87	1.64	1.45	1.27	1.12
7	PA Current	4.08	4.08	4.08	4.08	4.08	4.08	3.49	3.00	2.58	2.22	1.92	1.66	1.44	1.25	1.09	0.95
	EPA2013	4.36	4.36	4.36	4.36	4.09	3.60	3.16	2.78	2.44	2.15	1.89	1.66	1.46	1.28	1.13	0.99
7.5	PA Current	3.04	3.04	3.04	3.04	3.04	3.04	2.60	2.23	1.92	1.66	1.43	1.24	1.08	0.94	0.82	0.72
	EPA2013	3.22	3.22	3.22	3.22	3.02	2.66	2.33	2.05	1.80	1.59	1.39	1.22	1.08	0.95	0.83	0.73
8	PA Current	1.37	1.37	1.37	1.37	1.37	1.37	1.17	1.01	0.87	0.75	0.65	0.57	0.50	0.43	0.38	0.34
	EPA2013	1.80	1.80	1.80	1.80	1.68	1.48	1.30	1.14	1.01	0.88	0.78	0.68	0.60	0.53	0.46	0.41
8.5	PA Current	0.45	0.45	0.45	0.45	0.45	0.45	0.39	0.34	0.29	0.26	0.22	0.20	0.17	0.15	0.14	0.12
	EPA2013	0.80	0.80	0.80	0.80	0.75	0.66	0.58	0.51	0.45	0.40	0.35	0.31	0.27	0.24	0.21	0.18
9	PA Current	0.16	0.16	0.16	0.16	0.16	0.16	0.14	0.12	0.11	0.10	0.09	0.08	0.07	0.07	0.06	0.06
	EPA2013	0.36	0.36	0.36	0.36	0.34	0.30	0.26	0.23	0.20	0.18	0.16	0.14	0.12	0.11	0.09	0.08

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