ISSUE:

The purpose of this policy is to provide Water Bureau (WB), Surface Water Assessment Section (SWAS), guidance necessary to calculate ammonia toxicity water quality-based effluent limits (WQBELs) for National Pollutant Discharge Elimination System (NPDES) permits. Appropriate sources of data used in making the calculations are also identified.

AUTHORITY:

Part 31 Rules, Water Resources Protection, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended.

DEFINITIONS:

- Un-ionized ammonia – the fraction of total ammonia nitrogen existing as the NH_3 molecule. This excludes the fraction of total ammonia nitrogen existing as the ammonium ion, NH_4^+.

INTRODUCTION:

Un-ionized ammonia is toxic to aquatic life above certain concentrations. Final acute values (FAVs) and final chronic values (FCVs) for un-ionized ammonia have been developed for warm and coldwater-designated surface waters of the state under R323.1057 of the Part 4 Water Quality Standards (WQS), Toxic Substances. These are contained in Table 1.

Table 1 – Un-ionized ammonia FAVs and FCVs for warm and coldwater streams

	Warmwater		Coldwater	
	FAV	FCV	FAV	FCV
Un-ionized ammonia (mg/l)	0.420	0.053	0.320	0.029

The SWAS routinely evaluates the need for ammonia WQBELs for NPDES permits based on the un-ionized ammonia FCVs. These WQBELs are expressed in terms of total ammonia and are recommended as 30-day average concentrations. In cases where a discharge may have very high levels of total ammonia, daily maximum ammonia WQBELs based on the un-ionized ammonia FAVs may be included in an NPDES permit.

The degree of ammonia ionization is dependent on water temperature and pH. To calculate the fraction of total ammonia that exists as un-ionized ammonia (*f*), SWAS uses the methodology described by Emerson et. al., 1975.

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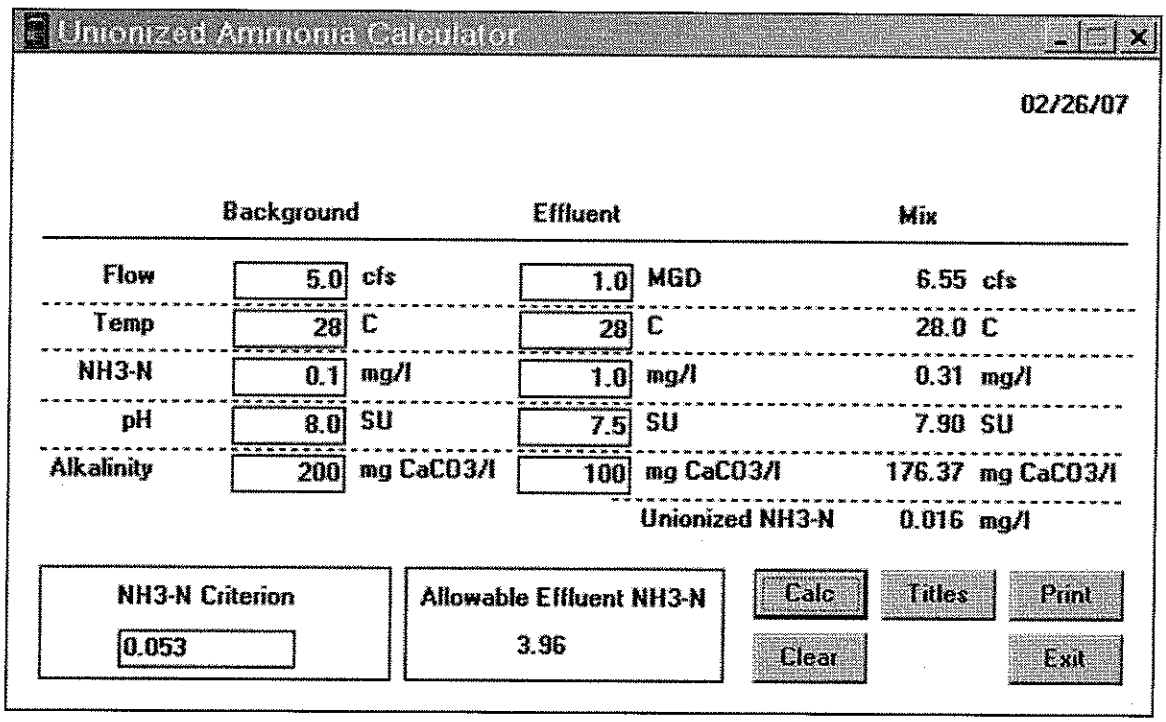
$$f\ \left(10^{pKa - pH} + 1\right)$$

where $pKa \quad 0.09018 + \frac{2729.92}{T}$

T is temperature in degrees Kelvin (° K), and pH is expressed in standard units (S.U.).

WQBEL CALCULATION PROCEDURE:

Ammonia WQBELs are calculated so that *f* does not exceed the un-ionized ammonia FAV or FCV in a receiving water as the result of a point source discharge. The complete set of equations used in the calculation of *f* are contained in Appendix A. These equations can be used in a spreadsheet to calculate *f*, or *f* can be determined using the SWAS's Visual Basic un-ionized ammonia fraction calculator which uses the same mathematics. A screen shot of the un-ionized ammonia calculator is shown below. Values for flow, temperature, total ammonia concentration, pH, and alkalinity are required for both the background flow (if any) and effluent. Note that background flow is in units of cubic feet per second (cfs), while effluent flow is in millions of gallons per day. The relevant un-ionized ammonia criterion (in this case the warmwater FCV of 0.053 milligrams per liter (mg/l) un-ionized ammonia) is also entered. The user then clicks the "Calc" button to generate an allowable concentration of total ammonia that can be discharged to meet the criterion. Here, the calculator indicates that a 30-day average WQBEL of 3.96 mg/l is required.



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Thirty-day average ammonia WQBELs based on the un-ionized ammonia FCV are recommended only when their value is less than the corresponding daily maximum total ammonia WQBEL based on dissolved oxygen (D.O.) concerns. If daily maximum total ammonia WQBELs are generated based on the un-ionized ammonia FAV, the more restrictive of the daily maximum ammonia WQBELs based on ammonia toxicity and on D.O. should be recommended. Similar to D.O.-based WQBELs, toxicity-based ammonia WQBELs are recommended for each of up to four seasons (R323.1090(3), Applicability of water quality standards, Part 4 WQS).

Background water quality (ammonia nitrogen concentration, pH, and alkalinity) should be based on sampling data from local Storage and Retrieval System stations or from other WB sampling, if available. If no relevant data exist, background water quality can be assumed as per the Great Lakes and Environmental Assessment Section (GLEAS) Procedure 80, Guidance on Water Quality-Based Effluent Limits Recommendations for Oxygen Demanding Substances (MDEQ, 1995). Default values for pH and ammonia concentration are 8.0 S.U. and 0.1 mg/l, respectively. Alkalinity is assumed to be 200 mg/l as $CaCO_3$. Seasonal design temperatures are contained in Effluent Limit Coordination Procedure 15 (MDEQ, 1980).

In the case of new-use treated sanitary wastewater discharges, effluent pH is assumed to be 7.5 S.U. and effluent alkalinity is assumed to be 100 mg/l as $CaCO_3$. If the discharge under consideration is from an existing facility, whether treated sanitary or industrial, effluent pH should be estimated from discharge monitoring reports (DMRs). Generally, the most recently available 12-months worth of daily DMR pH data are averaged for use in the un-ionized ammonia calculator. These daily data are available from WB's NPDES Management System (NMS) database and can readily be exported to an Excel spreadsheet.

Literature Cited

Emerson, K., R.C. Russo, R.E. Lund, and R.V. Thurston. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. J. Fish. Res. Board Can. 32:2379-2383.

MDEQ. 1995. Great Lakes and Environmental Assessment Section. Procedures Manual, Vol. II. Procedure 80: Guidance on WQBEL Recommendations for Oxygen Demanding Substances. WB, MDEQ.

MDEQ. 1980. Effluent Limit Coordination Procedure No. 15: Design Background Temperature for Inland Streams. GLEAS, SWQD.

Trinklein, F. 1990. Modern Physics. Holt Rinehart Winston. Austin, Texas.

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METHOD OF DISTRIBUTION:

Electronic, WB shared network drive

Responsibility		**Action**
SWAS Modeler	1.	Obtain necessary background receiving water data
	2.	Obtain necessary effluent data
	3.	Develop 30 day average and/or daily maximum ammonia toxicity WQBELs as per this procedure.

Approved: Diana Klemans
Diana Klemans, Chief
Surface Water Assessment Section
Water Bureau

Date: October 29, 2007

Last reviewed by: _____
Name
Title

Date: (effective date)

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Appendix A - Ammonia Toxicity Calculations

Aqueous ammonia ionization equilibrium equation

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Mix Flow

$$Q_m = Q_b + Q_e$$

where Q_m is the mix flow (cfs)
Q_b is the background receiving water flow (cfs)
Q_e is the effluent flow (cfs)

Mix Temperature

$$T_m = \frac{(Q_b T_b) + (Q_e T_e)}{Q_m}$$

where T_m is the mixed stream temperature (°C)
T_b is the background temperature (°C)
T_e is the effluent temperature (°C)

Mix Alkalinity

$$[Alk_m] = \frac{(Q_b [Alk_b]) + (Q_e [Alk_e])}{Q_m}$$

where $[Alk_m]$ is the molar concentration of mix stream alkalinity (moles/L as $CaCO_3$)
$[Alk_b]$ is the molar concentration of background water alkalinity (moles/L as $CaCO_3$)
$[Alk_e]$ is the molar concentration of background water alkalinity (moles/L as $CaCO_3$)

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Mix pH

$$pH = -\mathrm{Log}[H^+] \rightarrow 10^{-pH} = [H^+]$$

$$[Alk] = C(\alpha_1 + \alpha_2) + [OH^-] - [H^+]$$

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$\alpha_1 = \frac{1}{1 + ([H^+]/K_1) + (K_2/[H^+])}$$

$$\alpha_2 = \frac{1}{1 + ([H^+]/K_2) + (K_1/[H^+])}$$

$$\mathrm{Log}\, K_w = \frac{-4470.99}{T + 273.15} + 6.0875 - 0.01706T$$

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$$C_m = \frac{(Q_b C_b) + (Q_e C_e)}{Q_m}$$

$$0 = [H^+]^4 + (K_1 + [Alk_m])[H^+]^3 + (K_1 K_2 + K_1[Alk_m] - C_m K_1 - K_w)[H^+]^2 + K_1(K_2[Alk_m] - 2C_m K_2 - K_w)[H^+] - K_1 K_2 K_w$$

where $[H^+]$ is the molar concentration of hydrogen ion (moles/L)
C is the total carbonate carbon (moles/L)
$\alpha 1$ is the ionization fraction of the carbonate ion
$\alpha 2$ is the ionization fraction of the bicarbonate ion
K_w is the solubility product of water) = 1.0×10^{-14}
K_1 is the first solubility product of carbonic acid
K_2 is the second solubility product of carbonic acid
C_m is the total mix carbonate carbon (moles/L)
C_b is the background carbonate carbon (moles/L)
C_e is the effluent carbonate carbon (moles/L)
Further detailed pH calculations and values of above constants may be found in an inorganic water chemistry text such as Snoeyink, 1980.

Mix Total Ammonia

$$NH_{3+4_m} = \frac{(Q_b NH_{3+4_b}) + Q_e NH_{3+4_e}}{Q_m}$$

where NH_{3+4m} is the mix concentration of total ammonia (mg/l)
NH_{3+4b} is the background concentration of total ammonia (mg/l)
NH_{3+4e} is the effluent total ammonia concentration (mg/l)

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Mix Un-ionized Ammonia

$$NH_{3_m} = \frac{NH_{3+4_m}}{1+10^{(0.09018+\frac{2729.92}{T+273.15}-pH_m)}}$$

where pHm is the mix pH (S.U.)

Source:

Hobrla, R. 1982. Ammonia toxicity calculations. GLEAS, SWQD.

Literature Cited

Snoeyink, V. and Jenkins, D. Water Chemistry. John Wiley & Sons, Inc. New York. 1980.

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