Vol. 10: 207–210, 1983 | MARINE ECOLOGY – PROGRESS SERIES Mar. Ecol. Prog. Ser. | Published January 3

SHORT NOTE

Estimation of the Allowable Upper Limit of Ammonia in Saline Waters*

Stephen Spotte[1] and Gary Adams[2]

[1] Sea Research Foundation, Inc., Mystic Marinelife Aquarium, Mystic, Connecticut 06355, USA

[2] Department of Mathematics and Physics, Thames Valley State Technical College, Norwich, Connecticut 06360, USA

ABSTRACT: A method is presented for estimating maximum allowable total ammonia nitrogen (NH_4-N) in saline waters (brackish water and seawater) when the allowable upper limit of free ammonia nitrogen (NH_3-N) is known. The experimental pK data of Khoo et al. (1977) were used to make a graph and tables showing the ratio of NH_4-N to NH_3-N as a function of pH, temperature, and salinity.

Ammonia** is toxic to aquatic organisms, and recommended upper limits are included with other 'redbook' data aimed at improving the environment (e.g. U.S. EPA, 1976). Because free ammonia (NH_3) is considered to be more toxic than ammonium ion (NH_4^+), allowable upper limits ordinarily are expressed as NH_3-N. However, only NH_4-N can be determined analytically (Koroleff, 1976). The concentrations of NH_3-N and NH_4^+-N are calculated values derived from thermodynamic considerations.

The equilibrium of ammonia in water, shown by

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+ \quad (1)$$

is affected by pH, temperature, and ionic strength, with pH exerting the greatest effect. In saline waters (brackish water and seawater), ionic strength is usually expressed operationally as salinity. Szumski et al. (1982) evaluated existing standards for free ammonia in natural freshwaters and concluded that criteria based on fixed allowable limits of NH_3-N are of limited use unless mediating chemical and physical factors are considered. The same is true of all natural waters. In this report we provide a graph and tables for estimating the allowable upper limit of NH_4-N in saline waters based on a predetermined standard for NH_3-N and as a function of pH, temperature, and salinity.

The ratio of NH_4-N to NH_3-N in water is expressed by 1 + antilog (pK – pH) where pK is minus the logarithm of the equilibrium constant of Equation 1. The pK is a function of temperature and salinity. The experimental data of Khoo et al. (1977) for the ionization of ammonium ion in seawater can be expressed by

$$pK = 0.09018 + 2727.92/(T + 273.1) + (0.1552 - 0.000314\ T)\ I \quad (2)$$

where T represents temperature (°C), S is salinity in parts per thousand (‰), and I is ionic (molal) strength as shown by

$$I = 19.973\ S/(1000 - 1.2005109\ S) \quad (3)$$

The ratios of NH_4-N to NH_3-N at different values of temperature, pH, and salinity are shown in Fig. 1 and Tables 1 through 6. To use the graph or tables the allowable upper limit of NH_3-N must first be established, either arbitrarily or experimentally, after which temperature, pH, and salinity are measured. Multiply the value of the ratio obtained from the graph or tables by the value of the allowable upper limit of NH_3-N to obtain maximum allowable NH_4-N. The ratio is dimensionless, and units can be either milligrams or moles of NH_4-N l^{-1}.

The pK values of Whitfield (1974) derived theoretically are remarkably close to those of Khoo et al. (1977) obtained experimentally. Typical errors based on uncertainties in the pK data of Khoo and his coworkers (one standard deviation) are 1.7 %. The data expressed here are in close agreement with tabular values presented by Bower and Bidwell (1978), who based their work on Whitfield's theoretical pK data.

* Contribution No. 39, Sea Research Foundation, Inc.

** As used here, 'ammonia' is synonymous with total ammonia (measured as total ammonia nitrogen, or NH_4-N), which is the sum of NH_3 and NH_4^+. Concentrations of all 3 ordinarily are expressed as nitrogen (NH_3-N, NH_4^+-N, NH_4-N)

0171-8630/83/0010/0207/$ 02.00

Table 1. Ratio of total NH_4-N to NH_3-N at pH 7.8 and varying temperature and salinity

pH = 7.8	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	133.4	138.2	143.3	148.6	154.1	159.9	166.0
6	123.1	127.5	132.2	137.0	142.2	147.5	153.1
7	113.7	117.7	122.0	126.5	131.2	136.1	141.3
8	105.0	108.8	112.7	116.8	121.2	125.7	130.5
9	97.1	100.5	104.2	108.0	112.0	116.1	120.5
10	89.8	93.0	96.3	99.9	103.5	107.4	111.4
11	83.1	86.1	89.2	92.4	95.8	99.3	103.1
12	77.0	79.7	82.6	85.5	88.7	92.0	95.4
13	71.3	73.9	76.5	79.2	82.1	85.2	88.3
14	66.1	68.5	70.9	73.5	76.1	78.9	81.9
15	61.4	63.5	65.8	68.1	70.6	73.2	75.9
16	57.0	59.0	61.1	63.2	65.5	67.9	70.4
17	52.9	54.8	56.7	58.7	60.8	63.1	65.4
18	49.2	50.9	52.7	54.6	56.5	58.6	60.7
19	45.8	47.4	49.0	50.7	52.6	54.5	56.4
20	42.6	44.1	45.6	47.2	48.9	50.7	52.5
21	39.7	41.0	42.5	43.9	45.5	47.1	48.9
22	37.0	38.2	39.5	40.9	42.4	43.9	45.5
23	34.5	35.6	36.9	38.1	39.5	40.9	42.4
24	32.2	33.2	34.4	35.6	36.8	38.1	39.5
25	30.0	31.0	32.1	33.2	34.4	35.6	36.8
26	28.0	29.0	30.0	31.0	32.1	33.2	34.4
27	26.2	27.1	28.0	29.0	30.0	31.0	32.1
28	24.5	25.3	26.2	27.1	28.0	29.0	30.0
29	22.9	23.7	24.5	25.3	26.2	27.1	28.1
30	21.5	22.2	22.9	23.7	24.5	25.4	26.2
31	20.1	20.8	21.5	22.2	23.0	23.7	24.6
32	18.9	19.5	20.1	20.8	21.5	22.2	23.0
33	17.7	18.3	18.9	19.5	20.2	20.9	21.6
34	16.6	17.2	17.7	18.3	18.9	19.6	20.2
35	15.6	16.1	16.6	17.2	17.8	18.4	19.0

Table 2. Ratio of total NH_4-N to NH_3-N at pH 7.9 and varying temperature and salinity

pH = 7.9	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	106.2	110.0	114.0	118.2	122.6	127.2	132.1
6	98.0	101.5	105.2	109.1	113.1	117.4	121.8
7	90.5	93.7	97.1	100.7	104.4	108.3	112.4
8	83.6	86.6	89.7	93.0	96.4	100.1	103.8
9	77.3	80.1	83.0	86.0	89.1	92.5	95.9
10	71.5	74.1	76.7	79.5	82.4	85.5	88.7
11	66.2	68.6	71.0	73.6	76.3	79.1	82.1
12	61.3	63.5	65.8	68.2	70.6	73.2	76.0
13	56.9	58.9	61.0	63.2	65.5	67.9	70.4
14	52.7	54.6	56.5	58.6	60.7	62.9	65.2
15	49.0	50.7	52.5	54.3	56.3	58.4	60.5
16	45.5	47.1	48.7	50.4	52.3	54.2	56.2
17	42.3	43.7	45.3	46.9	48.5	50.3	52.1
18	39.3	40.6	42.1	43.6	45.1	46.7	48.4
19	36.6	37.8	39.1	40.5	42.0	43.5	45.0
20	34.0	35.2	36.4	37.7	39.0	40.4	41.9
21	31.7	32.8	33.9	35.1	36.4	37.6	39.0
22	29.6	30.6	31.6	32.7	33.9	35.1	36.3
23	27.6	28.5	29.5	30.5	31.6	32.7	33.9
24	25.7	26.6	27.5	28.5	29.5	30.5	31.6
25	24.0	24.9	25.7	26.6	27.5	28.5	29.5
26	22.5	23.2	24.0	24.8	25.7	26.6	27.5
27	21.0	21.7	22.4	23.2	24.0	24.8	25.7
28	19.7	20.3	21.0	21.7	22.5	23.2	24.0
29	18.4	19.0	19.7	20.3	21.0	21.7	22.5
30	17.3	17.8	18.4	19.0	19.7	20.4	21.1
31	16.2	16.7	17.3	17.8	18.4	19.1	19.7
32	15.2	15.7	16.2	16.7	17.3	17.9	18.5
33	14.3	14.7	15.2	15.7	16.2	16.8	17.3
34	13.4	13.8	14.3	14.8	15.2	15.7	16.3
35	12.6	13.0	13.4	13.9	14.3	14.8	15.3

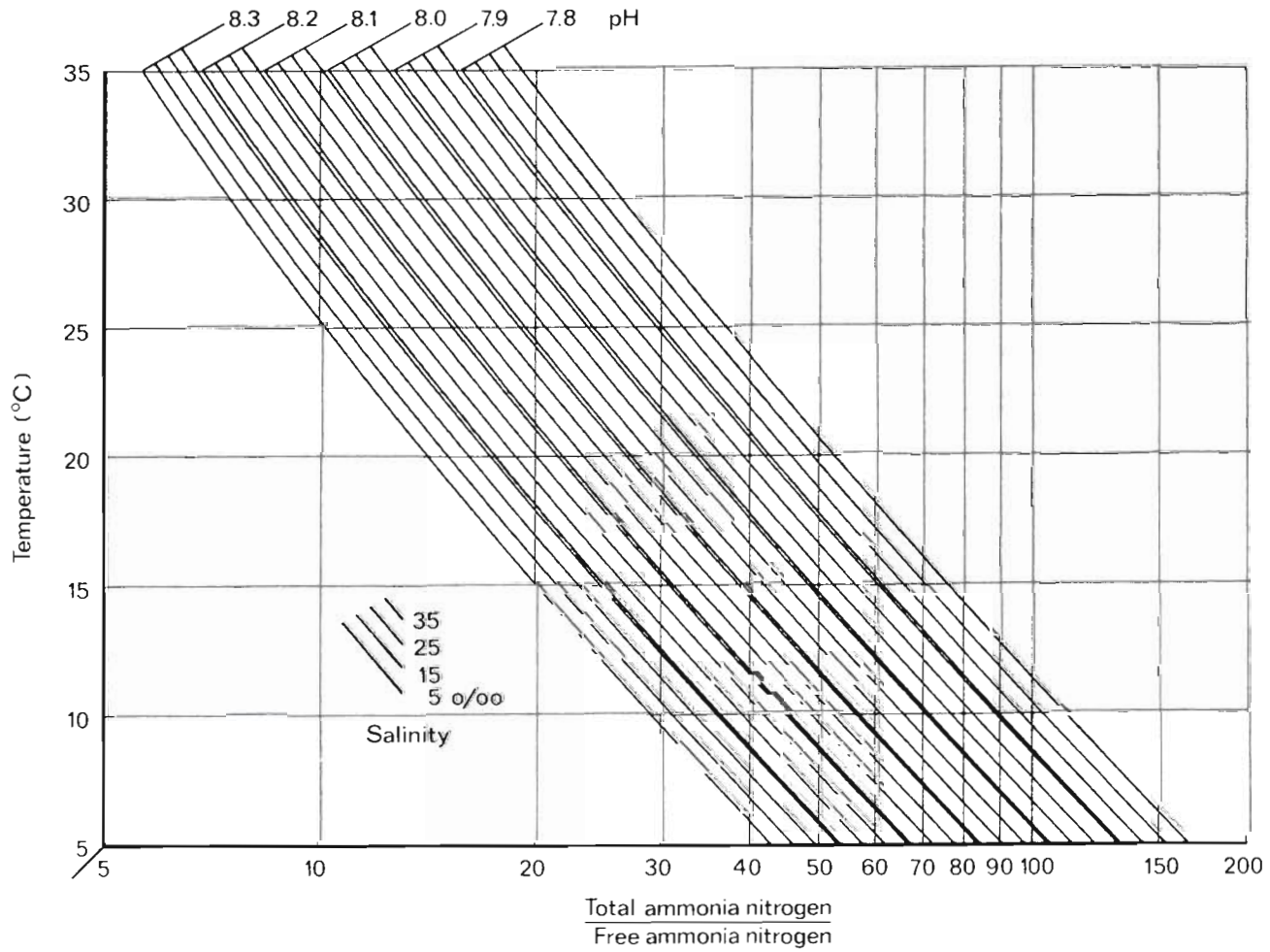

Fig. 1. Ratio of total NH_4-N to NH_3-N in saline waters at different values of pH, temperature, and salinity

Table 3. Ratio of total NH_4-N to NH_3-N at pH 8.0 and varying temperature and salinity

pH = 8.0	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	84.5	87.6	90.8	94.1	97.6	101.3	105.1
6	78.0	80.8	83.8	86.8	90.1	93.4	97.0
7	72.1	74.7	77.4	80.2	83.1	86.3	89.5
8	66.6	69.0	71.5	74.1	76.8	79.7	82.7
9	61.6	63.8	66.1	68.5	71.0	73.7	76.4
10	57.0	59.0	61.2	63.4	65.7	68.1	70.7
11	52.8	54.7	56.6	58.7	60.8	63.0	65.4
12	48.9	50.7	52.5	54.3	56.3	58.4	60.6
13	45.4	47.0	48.6	50.4	52.2	54.1	56.1
14	42.1	43.6	45.1	46.7	48.4	50.2	52.0
15	39.1	40.5	41.9	43.4	44.9	46.6	48.3
16	36.3	37.6	38.9	40.3	41.7	43.2	44.8
17	33.8	34.9	36.2	37.4	38.8	40.2	41.6
18	31.4	32.5	33.6	34.8	36.0	37.3	38.7
19	29.2	30.2	31.3	32.4	33.5	34.7	36.0
20	27.2	28.2	29.1	30.2	31.2	32.3	33.5
21	25.4	26.3	27.2	28.1	29.1	30.1	31.2
22	23.7	24.5	25.3	26.2	27.1	28.1	29.1
23	22.1	22.9	23.6	24.4	25.3	26.2	27.1
24	20.7	21.3	22.1	22.8	23.6	24.4	25.3
25	19.3	19.9	20.6	21.3	22.0	22.8	23.6
26	18.1	18.7	19.3	19.9	20.6	21.3	22.1
27	16.9	17.5	18.0	18.6	19.3	19.9	20.6
28	15.8	16.4	16.9	17.5	18.0	18.7	19.3
29	14.8	15.3	15.8	16.3	16.9	17.5	18.1
30	13.9	14.4	14.8	15.3	15.8	16.4	16.9
31	13.1	13.5	13.9	14.4	14.9	15.4	15.9
32	12.3	12.7	13.1	13.5	13.9	14.4	14.9
33	11.5	11.9	12.3	12.7	13.1	13.5	14.0
34	10.9	11.2	11.6	11.9	12.3	12.7	13.1
35	10.2	10.5	10.9	11.2	11.6	12.0	12.3

Table 4. Ratio of total NH_4-N to NH_3-N at pH 8.1 and varying temperature and salinity

pH = 8.1	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	67.4	69.8	72.3	75.0	77.7	80.7	83.7
6	62.2	64.4	66.7	69.2	71.7	74.4	77.2
7	57.5	59.5	61.7	63.9	66.3	68.7	71.3
8	53.1	55.0	57.0	59.1	61.2	63.5	65.9
9	49.1	50.9	52.7	54.6	56.6	58.7	60.9
10	45.5	47.1	48.8	50.5	52.4	54.3	56.3
11	42.2	43.6	45.2	46.8	48.5	50.3	52.2
12	39.1	40.4	41.9	43.4	44.9	46.6	48.3
13	36.2	37.5	38.8	40.2	41.7	43.2	44.8
14	33.7	34.8	36.0	37.3	38.7	40.1	41.5
15	31.3	32.3	33.5	34.7	35.9	37.2	38.5
16	29.1	30.1	31.1	32.2	33.3	34.5	35.8
17	27.0	28.0	28.9	29.9	31.0	32.1	33.3
18	25.2	26.0	26.9	27.9	28.8	29.9	30.9
19	23.4	24.2	25.1	25.9	26.8	27.8	28.8
20	21.8	22.6	23.4	24.2	25.0	25.9	26.8
21	20.4	21.1	21.8	22.5	23.3	24.1	25.0
22	19.0	19.7	20.3	21.0	21.7	22.5	23.3
23	17.8	18.4	19.0	19.6	20.3	21.0	21.7
24	16.6	17.2	17.7	18.3	19.0	19.6	20.3
25	15.5	16.1	16.6	17.1	17.7	18.3	19.0
26	14.6	15.0	15.5	16.0	16.6	17.1	17.7
27	13.6	14.1	14.5	15.0	15.5	16.0	16.6
28	12.8	13.2	13.6	14.1	14.5	15.0	15.5
29	12.0	12.4	12.8	13.2	13.6	14.1	14.6
30	11.3	11.6	12.0	12.4	12.8	13.2	13.7
31	10.6	10.9	11.3	11.6	12.0	12.4	12.8
32	10.0	10.3	10.6	10.9	11.3	11.6	12.0
33	9.4	9.7	10.0	10.3	10.6	11.0	11.3
34	8.8	9.1	9.4	9.7	10.0	10.3	10.6
35	8.3	8.6	8.8	9.1	9.4	9.7	10.0

Table 5. Ratio of total NH_4-N to NH_3-N at pH 8.2 and varying temperature and salinity

pH = 8.2	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	53.7	55.6	57.6	59.7	62.0	64.3	66.7
6	49.6	51.4	53.2	55.2	57.2	59.3	61.6
7	45.8	47.5	49.2	51.0	52.8	54.8	56.8
8	42.4	43.9	45.5	47.1	48.8	50.6	52.5
9	39.2	40.6	42.1	43.6	45.2	46.8	48.6
10	36.3	37.6	39.0	40.4	41.8	43.4	45.0
11	33.7	34.9	36.1	37.4	38.7	40.1	41.6
12	31.2	32.3	33.5	34.7	35.9	37.2	38.6
13	29.0	30.0	31.1	32.2	33.3	34.5	35.8
14	26.9	27.9	28.8	29.8	30.9	32.0	33.2
15	25.0	25.9	26.8	27.7	28.7	29.7	30.8
16	23.3	24.1	24.9	25.8	26.7	27.6	28.6
17	21.7	22.4	23.2	24.0	24.8	25.7	26.6
18	20.2	20.9	21.6	22.3	23.1	23.9	24.8
19	18.8	19.5	20.1	20.8	21.5	22.3	23.1
20	17.6	18.1	18.8	19.4	20.1	20.8	21.5
21	16.4	16.9	17.5	18.1	18.7	19.4	20.0
22	15.3	15.8	16.3	16.9	17.5	18.1	18.7
23	14.3	14.8	15.3	15.8	16.3	16.9	17.5
24	13.4	13.8	14.3	14.8	15.3	15.8	16.3
25	12.6	13.0	13.4	13.8	14.3	14.8	15.3
26	11.8	12.1	12.5	12.9	13.4	13.8	14.3
27	11.0	11.4	11.7	12.1	12.5	12.9	13.4
28	10.4	10.7	11.0	11.4	11.8	12.1	12.5
29	9.7	10.0	10.4	10.7	11.0	11.4	11.8
30	9.2	9.4	9.7	10.0	10.4	10.7	11.1
31	8.6	8.9	9.2	9.4	9.7	10.1	10.4
32	8.1	8.4	8.6	8.9	9.2	9.5	9.8
33	7.7	7.9	8.1	8.4	8.6	8.9	9.2
34	7.2	7.4	7.7	7.9	8.1	8.4	8.7
35	6.8	7.0	7.2	7.4	7.7	7.9	8.2

Table 6. Ratio of total NH_4-N to NH_3-N at pH 8.3 and varying temperature and salinity

pH = 8.3	Salinity (‰)						
T (°C)	5	10	15	20	25	30	35
5	42.9	44.4	46.0	47.7	49.4	51.3	53.2
6	39.6	41.0	42.5	44.0	45.6	47.3	49.1
7	36.6	37.9	39.3	40.7	42.2	43.7	45.4
8	33.9	35.1	36.3	37.6	39.0	40.4	41.9
9	31.4	32.5	33.6	34.8	36.1	37.4	38.8
10	29.1	30.1	31.1	32.3	33.4	34.6	35.9
11	27.0	27.9	28.9	29.9	31.0	32.1	33.3
12	25.0	25.9	26.8	27.7	28.7	29.8	30.9
13	23.2	24.0	24.9	25.7	26.7	27.6	28.6
14	21.6	22.3	23.1	23.9	24.8	25.6	26.6
15	20.1	20.8	21.5	22.2	23.0	23.8	24.7
16	18.7	19.3	20.0	20.7	21.4	22.2	23.0
17	17.4	18.0	18.6	19.3	19.9	20.6	21.4
18	16.2	16.8	17.3	17.9	18.6	19.2	19.9
19	15.2	15.7	16.2	16.7	17.3	17.9	18.5
20	14.2	14.6	15.1	15.6	16.1	16.7	17.3
21	13.2	13.7	14.1	14.6	15.1	15.6	16.1
22	12.4	12.8	13.2	13.6	14.1	14.6	15.1
23	11.6	12.0	12.3	12.7	13.2	13.6	14.1
24	10.9	11.2	11.6	11.9	12.3	12.7	13.2
25	10.2	10.5	10.8	11.2	11.5	11.9	12.3
26	9.6	9.8	10.2	10.5	10.8	11.2	11.6
27	9.0	9.2	9.5	9.8	10.2	10.5	10.8
28	8.4	8.7	9.0	9.2	9.5	9.8	10.2
29	7.9	8.2	8.4	8.7	9.0	9.3	9.6
30	7.5	7.7	7.9	8.2	8.4	8.7	9.0
31	7.1	7.3	7.5	7.7	7.9	8.2	8.5
32	6.7	6.8	7.1	7.3	7.5	7.7	8.0
33	6.3	6.5	6.7	6.9	7.1	7.3	7.5
34	5.9	6.1	6.3	6.5	6.7	6.9	7.1
35	5.6	5.8	5.9	6.1	6.3	6.5	6.7

Acknowledgement. We thank Carol E. Bower for her review of the manuscript.

LITERATURE CITED

Bower, C. E., Bidwell, J. P. (1978). Ionization of ammonia in seawater: effects of temperature, pH, and salinity. J. Fish. Res. Bd Can. 35: 1012–1016

Khoo, K. H., Culberson, C. H., Bates, R. G. (1977). Thermodynamics of the dissociation of ammonium ion in seawater from 5 to 40°C. J. Soln. Chem. 6: 281–290

Koroleff, F. (1976). Determination of ammonia. In: Grasshoff, K. (ed.) Methods of seawater analysis. Verlag Chemie, Weinheim, pp. 126–133

Szumski, D. S., Barton, D. A., Putnam, H. D., Polta, R. C. (1982). Evaluation of EPA un-ionized ammonia criteria. J. Water Pollut. Contr. Fed. 54: 281–291

U.S. Environmental Protection Agency. (1976). Quality criteria for water. Rpt. No. EPA-440/9-76-023, U.S. EPA, Washington, DC, pp. 16–24

Whitfield, M. (1974). The hydrolysis of ammonia ions in sea water – a theoretical study. J. mar. biol. Ass. U. K. 54: 565–580

Accepted for printing on September 17, 1982