WAIORA PROCEDURE FOR CALCULATING STREAM TOTAL AMMONIA DOWNSTREAM OF INFLOWS

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DEFINITIONS AND EXPLANATIONS

Much confusion can arise in the usage of the term "ammonia". The following definitions are presented to clarify its use in WAIORA:

- *Total ammonia* is the mixture of ammonia (NH_3) and ammonium (NH_4^+). Neither species ever exists on its own in environmental samples. “Total ammonia” is the USA terminology. It is sometimes also called "ammoniacal-nitrogen" in New Zealand, in which case it is clear that it is being reported "as N", not "as NH_3". WAIORA uses "total ammonia" exclusively.

- *Ammonia* is "free ammonia" or "un-ionised ammonia" or "non-ionised ammonia". It is sometimes used interchangeably with "total ammonia".

Note that in the influential water quality criteria published by USEPA (1986) ammonia and total ammonia were reported in mg(NH_3)/L, whereas others commonly report it as mg(N)/L, or even µg(N)/L (in which cases conversions need to be applied).[1] But in recent revisions (USEPA 1998, 1999) it is now reported "as N".

Toxicity to aquatic organisms concerns mostly ammonia, rather than ammonium, but laboratory tests measure total ammonia. The proportion of the total ammonia that is free (non-ionised) is a function of the water pH and temperature, such that the higher these variables are the more toxic a sample becomes. Therefore stream pH and temperature are important variables in assessing stream toxicity.

USEPA (1998) updated the previous 1984/1986 "criteria" using new toxicity data (generally making the criteria less strict). Major changes included:

- dropping temperature dependence in the computation of the CMC (Criteria Maximum Concentration) and CCC (Criteria Continuous Concentration);

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[1] e.g., converting mg(NH_3)/L to µg(N)/L the factor is 14006.7/(14.0067 + 3x1.00797) = 822.44.

- using a 30-day average for the CCC and replacing the previous 4-day average with the requirement that the highest 4-day average within the 30-day period not exceed 2xCCC;

- expressing total ammonia "as N", not "as NH3".

USEPA (1999) kept the same CMC limits but:

- re-included temperature in the calculation of the CCC;

- re-defined the 4-day average limit as 2.5xCCC.

ANZECC (2000) included Australasian data to devise four chronic trigger values for total ammonia (as N) at pH 8 for four levels of protection (Table 3.4.1 of Vol. 1: 320, 900, 1430 and 2300 ppb for %age protection of species set at 99%, 95%, 90%, 80% respectively). They followed USEPA (1998) by not indexing triggers to temperature. A means of converting total ammonia to measured pH (and temperature) is given in Vol. 2 (sec. 8.3.7.3, p. 156). One presumes this is a long-term average, as these are chronic limits--there are no acute limits in the ANZECC guidelines. WAIORA takes pH as the same 30-day average used in the USEPA CCC computation.

A potted history of the development of ammonia criteria, by USEPA and by ANZECC, is given in the Appendix.

MATHEMATICAL BACKGROUND

Assume that we have a stream segment with a number (n) of inflows containing ammonia. Assume too that once discharged into the stream the total ammonia follows a first-order decay (this is the most appropriate and robust assumption, Cooper 1986). The general situation is as depicted below, where C is total ammonia concentration and Q is stream flow. Either variable without a subscript refers to their value at the downstream end of the segment. The flow is constant between inflows, but concentrations reduce.

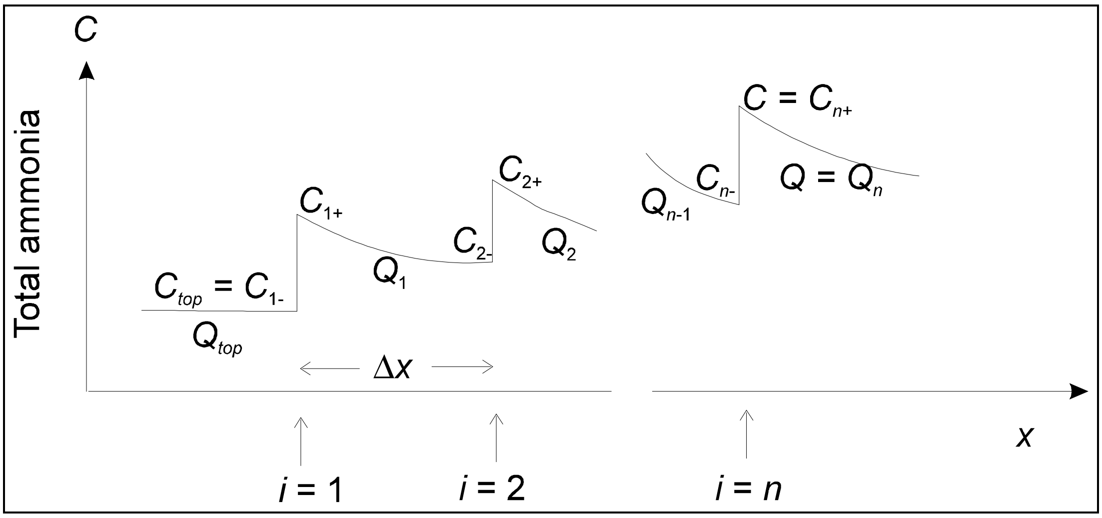

Figure 1: General case for mass balance.

First order decay means that for any uniform reach of length Δx (i.e., with constant cross-section-average velocity U) the total ammonia concentration at the downstream end is related to that at the upstream end by:

$$C_{i-} = \alpha C_{(i-1)+} : \quad \alpha = e^{-k\Delta x/U} \qquad (1)$$

where k is the stream total ammonia removal rate coefficient with units of reciprocal travel-time, and $\Delta x/U$ is the reach travel-time. We may call α the "total ammonia decay number".

Typical values of the three variables in α may be taken as:

- $k = 2$ day^{-1} (Cooper 1986, McBride *et al.* 1991);
- $\Delta x = 200 – 1000$ m;
- $U = 0.05 – 1.0$ m/s.

from which, noting that there are 86,400 seconds in a day, we can calculate that the range of the decay number is:

$\alpha_{\max}$ = exp[–(2/86400)x200/1.0] ≈ 0.99 (a swift stream with densely packed inflows)

$\alpha_{\min}$ = exp[–(2/86400)x1000/0.05] ≈ 0.63 (a slow stream with sparse inflows)

General mass balance

We wish to develop an equation for the total ammonia concentration at the downstream end of a segment containing n inflows. We use mass balances of total ammonia and water to do this.

Assuming immediate and complete mixing of inflows, we can write the instantaneous mass balance of total ammonia just downstream of the first inflow (i.e., $i = 1$ on Figure 1) as:

$$Q_1 C_{1+} = Q_{top} C_{top} + Q_{in,1} C_{in,1} \tag{2}$$

At the second inflow we have:

$$Q_2 C_{2+} = Q_1 C_{2-} + Q_{in,2} C_{in,2} \tag{3}$$

and using (1) this is:

$$Q_2 C_{2+} = Q_1 \alpha_1 C_{1+} + Q_{in,2} C_{in,2} \tag{4}$$

where α_1 is the total ammonia decay number for the uniform reach downstream of the first inflow. Substituting (2) we have:

$$Q_2 C_{2+} = \alpha_1 (Q_{top} C_{top} + Q_{in,1} C_{in,1}) + Q_{in,2} C_{in,2} \tag{5}$$

For the third inflow we have:

$$Q_3 C_{3+} = Q_2 C_{3-} + Q_{in,3} C_{in,3} \tag{6}$$

and again using (1) this is :

$$Q_3 C_{3+} = Q_2 \alpha_2 C_{2+} + Q_{in,3} C_{in,3} \tag{7}$$

so that, using (5):

$$Q_3 C_{3+} = (\alpha_2 \alpha_1)(Q_{top} C_{top} + Q_{in,1} C_{in,1}) + \alpha_2 Q_{in,2} C_{in,2} + Q_{in,3} C_{in,3} \tag{8}$$

By induction we obtain the general equation for the n^{th} inflow as:

$$QC = (\alpha_{n-1} \times \ldots \times \alpha_1)(Q_{top} C_{top} + Q_{in,1} C_{in,1}) + (\alpha_{n-1} \times \ldots \times \alpha_2) Q_{in,2} C_{in,2} + \ldots + Q_{in,n} C_{in,n} \tag{9}$$

(recall that Q and C are the water flow and total ammonium concentration at the downstream end of the segment of n inflows). This general situation is not amenable to simple solution, because there are so many variables. So we make some gross simplifications:

(a) α_i = constant = α

(b) $Q_{in,i}$= constant = Q_{in}

(c) $C_{in,i}$= constant = C_{in}

Note that (a) does not mean that all of the components of the total ammonia decay number (i.e., k, Δx and U) must be the same for all reaches; it merely requires that $k\Delta x/U$ be constant.

Using these assumptions (9) becomes:

$$QC = (1 + \alpha + \alpha^2 + \ldots + \alpha^{n-1}) Q_{in} C_{in} + \alpha^{n-1} Q_{top} C_{top} \tag{10}$$

To obtain an equation for Q we use the water mass balance, i.e.,

$$Q = Q_{top} + nQ_{in} \tag{11}$$

Substituting (11) into (10) and using the standard summation formula for the geometric series in parentheses in (noting that □ < 1, as required), we obtain the formula for downstream total ammonia concentration:

$$C = \frac{\left(\dfrac{1-\alpha^{n}}{1-\alpha}\right) Q_{in} C_{in} + \alpha^{n-1} Q_{top} C_{top}}{Q_{top} + nQ_{in}} \tag{12}$$

This solution can be made dimensionless by defining the "flow ratio" (q) and the total ammonia ratio (c) as:

$$q = \frac{Q_{in}}{Q_{top}} \tag{13}$$

and:

$$c = \frac{C}{C_{in}} \tag{14}$$

so, after dividing through by C_{in}, (12) becomes:

$$c = \frac{\left(\dfrac{1-\alpha^{n}}{1-\alpha}\right) q + \alpha^{n-1} c_{top}}{1 + nq} \tag{15}$$

Note that c is a function of four parameters, i.e., $c = c(\alpha, n, q, c_{top})$, so that presentation stored in two-dimensional nomograph form is not feasible. Therefore we use direct dimensional solutions of (12) using a stored code **Amgraph**. The code contains a subroutine (**Ammcrit**) that reproduces the ammonia and total ammonia toxicity limits in USEPA (1999 and ANZECC 2000—and, as noted in its comments, corrects the typographical errors in that Agency's explanations of the algorithm used to generate the tables).

ASSUMPTIONS

- Inflows are immediately and completely mixed over the stream cross-section.
- In-stream decline of total ammonia is first order with respect to downstream distance.
- The rates of flow of all discharges are approximately equal.
- The total ammonia concentrations of all discharges are approximately equal.
- The maximum one-hour stream pH and temperature (required for calculation of the one-hour maximum total ammonia toxicity limit) equals the daily maximum stream Ph and temperature.
- The maximum four-day stream pH and temperature (required for calculation of the four-day maximum total ammonia toxicity limit, as promulgated by USEPA) equals the daily-average stream pH and temperature.

DATA REQUIRED

Total ammonia concentration calculation:

- the number of inflows (*n*);
- the minimum & maximum stream flow at the top of the segment (Q_{top}, in litres per second), upstream of the abstraction;
- the rate of water discharge from any individual inflow (Q_{in}, in litres per second);
- the average spacing between inflows (Δx, in metres);
- the cross-section average stream velocity (U, in metres per second);
- the total ammonia concentration of any inflow (C_{in}, in milligrams of N per litre);
- the total ammonia concentration at the top of the segment (C_{top}, in micrograms of N per litre).

Total ammonia toxicity limits:

- The maximum one-hour stream pH and temperature.
- The maximum four-day stream pH and temperature.

EXAMPLE

Take a stream segment with these data:

- number of inflows $n = 10$;
- range of stream flows at the top of the segment $Q_{top} = 50 – 500$ L/s;
- rate of water discharge from any individual inflow $Q_{in} = 1.0$ L/s;
- average spacing between inflows $\Delta x = 400$ m;
- cross-section average stream velocity $U = 0.3$ m/s;
- total ammonia concentration in each inflow $C_{in} = 10$ mg(N)/L;
- total ammonia concentration at the top of the segment $C_{top} = 20$ µg(N)/L;
- daily maximum stream pH = 8.8;
- daily maximum stream temperature pH = 24.0^{o}C;
- daily-average stream pH = 7.2;
- daily-average stream temperature pH = 22.0^{o}C.

Running the code we get the following graph (Figure 2).

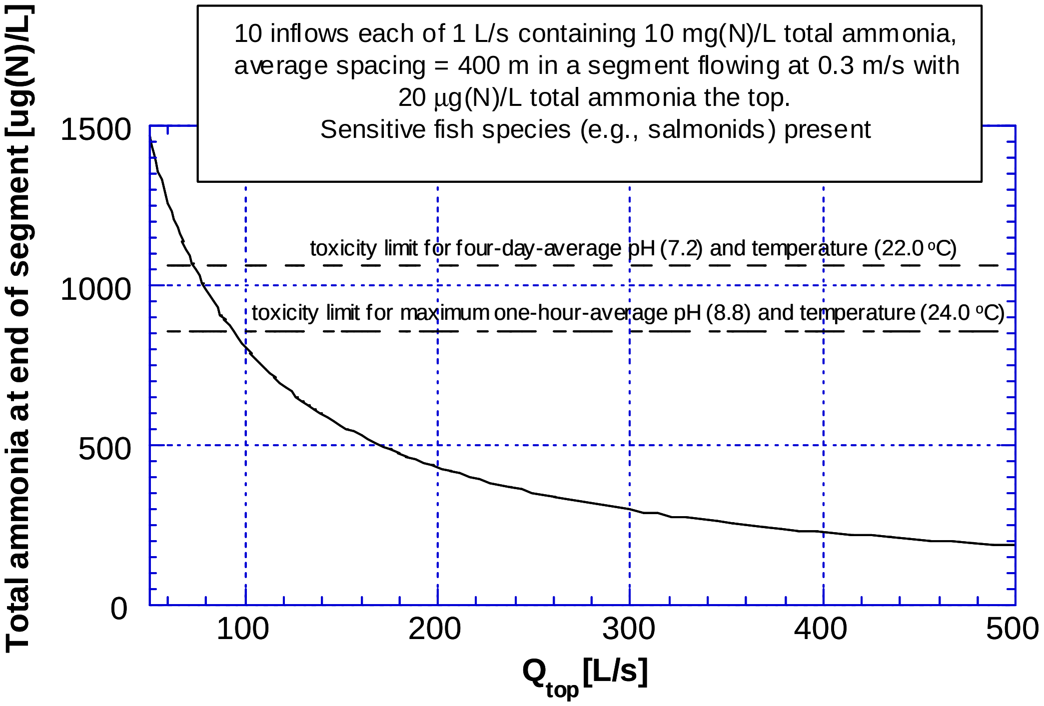

Figure 2: Change in total ammonia concentration with discharge. The toxicity data shown on this graph are from USEPA (1986). WAIORA v.2.0 uses USEPA (1999) and ANZECC (2000).

This result shows how the total ammonia at the downstream end of the segment rises with decreasing flow. It shows that for these data the limit of the one-hour-average total ammonia toxicity limit is more constraining than the limit of the four-day average (this is not always the case).

REFERENCES

ANZECC (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Volumes 1 & 2.

Cooper, A.B. (1986). Developing management guidelines for river nitrogenous oxygen demand. *Journal of the Water Pollution Control Federation 58(8)*: 845–852.

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USEPA (1986). Water Quality Criteria. EPA 440/5-86-001. Office of Water Regulations and Standards. Washington, D.C.

USEPA (1998). 1998 Update of Ammonia Water Quality Criteria for Ammonia. EPA-822-R-98-008.

USEPA (1999). 1999 Update of Ammonia Water Quality Criteria for Ammonia. EPA-822-R-99-014.

APPENDIX: A POTTED HISTORY OF FRESHWATER AMMONIA CRITERIA

In 1986 USEPA produced the "Yellow Book": “Water Quality Criteria 1986 (EPA 440/5-86-001). It contains acute and chronic criteria for total ammonia (as NH_3) as a function of pH and temperature, for “Salmonids or Other Sensitive Coldwater Species Present” and for “Salmonids or Other Sensitive Coldwater Species Absent”. The chronic criterion for “Salmonids or Other Sensitive Coldwater Species Present” at pH = 8 and $T = 20^{o}$C is 0.93 mg(NH_3)/L = 0.77 mg(N)/L.

In 1992 ANZECC issued their first guidelines document (“Australian Water Quality Guidelines for Fresh and Marine Waters”), essentially repeating the part of the USEPA (1986) table from which the above figure was drawn.[2]

In 1998 USEPA released an updated ammonia criteria document: “1998 Update of Ambient Water Quality Criteria for Ammonia” (EPA 822-R-98-008). This incorporated new data, making the guidelines less strict, removes temperature dependence from both acute and chronic criteria, and uses total ammonia as N (not as NH_3). The chronic criterion for “salmonids present” at pH = 8 is 1.27 mg(N)/L.

In 1999 USEPA revised those criteria again: “1999 Update of Ambient Water Quality Criteria for Ammonia” (EPA-822-R-99-014), reintroducing temperature into the calculation of the chronic criterion (but not to the acute criterion). This relaxed the criteria even more. The chronic criterion for pH = 8 and $T = 20^{o}$C is 1.71 mg(N)/L.

In 2000 ANZECC & ARMCANZ issued new guidelines.[3,4] They contain only chronic values (in Table 3.4.1 of ANZECC & ARMCANZ 2000a), but for four levels of protection: “trigger values” are given for “level of protection (% species)” of 99%, 95%, 90%, 80%. These limits are total ammonia = 0.32, 0.9, 1.43 and 2.3 mg(N)/L respectively.[5] These are defined at pH = 8 and are independent of temperature (they are based on the approach in USEPA 1998). To obtain the proportion of free and ionized ammonia at any pH and temperature one must go Table 8.3.6 in ANZECC & ARMCANZ (2000b) and also to Table 8.3.7 to relate the trigger values to other pH values. Finally, these trigger values are to be compared to the median of data (sec. 7.4.4.9 of ANZECC & ARMCANZ 2000a, page 7.4-7).

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[2] But it is incorrect in saying that the figures in that table correspond to undissociated ammonia = 0.2–0.3 mg(NH_3)/L.

[3] ANZECC & ARMCANZ (2000a). Australian and New Zealand guidelines for fresh and marine water quality 2000. *Paper No. 4, Volume 1*. Australian and New Zealand Environment and Conservation Council, Agricultural and Resource Management Council of Australia and New Zealand.

[4] ANZECC & ARMCANZ (2000b). Australian and New Zealand guidelines for fresh and marine water quality 2000. *Paper No. 4, Volume 2*. Australian and New Zealand Environment and Conservation Council, Agricultural and Resource Management Council of Australia and New Zealand.

[5] At least I infer that it is mg(N)/L and not mg(NH_3)/L: the relevant footnote (D) to that table says “Ammonia as TOTAL ammonia as [NH_3-N]….”!