WAIORA TOTAL AMMONIA MODEL VALIDATIONS

G. McBride and R. Wilcock

NIWA, Hamilton

INTRODUCTION

As part of a study to test the total ammonia prediction part of the WAIORA decision support system, ammonia addition experiments were conducted in two rivers in the Auckland region. Results were then used to calibrate and test the decay coefficients used in the WAIORA v.2.0 ammonia model.

METHODS

Study sites

Experiments were conducted on the Kumeu and Waiwera Rivers (Table 1). These two streams provided contrasting conditions in terms of size and were both substantially smaller than the site where the decay rates for the WAIORA model were initially derived (Ararimu Stream in the Kaipara catchment). Thus, decay rates were compared for a small stream and a large stream, both dominated by macrophytes, at two different flows.

The selected reach on Kumeu River had no visible inflows and extended 360 m downstream from a tributary below the Highway 16 Bridge (Table 1). We chose a 300 m reach of the upper Waiwera River (catchment area = 14 km^2) between two small tributaries (see Table 1). The reach had no visible inflows and at low flow had an appreciable cover of macrophytes with attached filamentous algae. This site contrasted with Kumeu River in size (approx. 28 and 88 L s^{-1} for Waiwera compared with 63 and 380 L s^{-1} for Kumeu on the two dates that the experiment was conducted), geology (sandstones and siltones for Waiwera and alluvium for Kumeu) and intensity of land use (with Waiwera having 54% pasture, 16% forest and 30% shrub, compared with 78% pasture, 11% forest, 5% horticulture and 5% shrub for Kumeu).

Table 1: Summary of characteristics of the WAIORA validation sites. Median and maximum temperatures, dissolved oxygen and NH_4-N values are for morning and afternoon spot temperatures made in ARC's Long-term Baseline Water Quality Monitoring Programme.

	Kumeu	Waiwera
Map reference NZMS260	Q10 497 905	R10 574 161
Predominant land use	Mixed	Mixed
Catchment area (km^2)	48	33
Approx. width (m)	5	6
Q_5 ($L\ s^{-1}$)	26	40
Substrate	Macrophytes with sand-silt	Macrophytes with sand/silt (upper); Bedrock with algae (lower)
Average time of sampling	14:00	12:45
Temperature (°C; median/ maximum)	15.5 / 22.5	15.0 / 24.5
DO (%sat.; median / minimum)	82.4 / 44.2	93.0 / 44.0
DO ($g\ m^{-3}$; median / minimum)	8.3 / 4.3	9.4 / 4.0
NH_4-N[1] ($g\ m^{-3}$; median/ maximum)	0.05 / 0.22	0.03 / 0.26

[1] Total ammoniacal nitrogen

Ammonia releases

Continuous releases of NH_4-N and Br^- were carried out in each stream on two different dates. Experiments conducted in March were at a time of extended baseflow, whereas those conducted in April occurred during a recession period after recent high flows. The autumn freshes did not greatly deplete stream macrophytes so that for each stream we had two measurements of ammonia loss at different flows and travel times, but with broadly similar plant biomasses. Estimated macrophyte cover was 75-80% for the first experiment, and 50% at both sites for the second experiment (Table 2). In the second experiment, flows were six times higher than the first experiment at Kumeu and three times higher at Waiwera (Table 2).

The method adopted was essentially that used in "Residual Flow and Water Quality Studies for the Ararimu (Campbell Road) Water Supply Scheme" (McBride *et al.* 1991). In each experiment we released a solution containing known concentrations of ammonium-N (as ammonium sulphate, $(NH_4)_2SO_4$) and potassium bromide (KBr, a conservative tracer to allow for changes in concentration due to dilution by inflows or groundwater accrual). A small quantity of rhodamine WT dye was added to each salt solution as a visual indicator for sampling stream water. Peak concentrations ranged from 2.4 g m^{-3} (Waiwera at low flow) to 0.4 g m^{-3} (Kumeu at high flow). Maximum stream concentrations approximated the short-term (acute, or 1-h) exposure criteria for sensitive freshwater species at pH 8.5 (USEPA 1999). This represents a worst-case scenario and is 10 x higher than maximum values in the ARC's stream monitoring programme (Table 1).

Solutions were added continuously with FMI pumps (model QB2, Fluid Metering Inc., Syosset, NY) that were calibrated in the laboratory to dispense solutions at 200 ± 1 mL min^{-1} (except for the April 18 Kumeu experiment, where the rate was 210 mL min^{-1}). Details of the ammonium releases are given in Table 2.

Water samples were collected at 3 sites on each stream reach using Isco automatic samplers. Kumeu sampling sites were 72, 210 and 360 m downstream from the point of release, whereas the upper Waiwera sites were 85, 200 and 300 m downstream. Samples were stored on ice overnight and then transported to the NIWA laboratory, where they were filtered and frozen prior to analysis. Total (un-ionised and ionised) ammonia (NH_4-N) was determined by indophenol blue colorimetry, and bromide (Br^-) by ICP-MS (Hill Laboratories Ltd).

Flows at the sites at the time of ammonia addition were measured using conventional stream gauging methods. Flows for the Kumeu River were obtained from ARC.

Table 2: Input concentrations and flow rates of NH_4-N and Br^- solutions, stream flows and plant cover in study reaches.

	Kumeu	Waiwera	Kumeu	Waiwera
Date	13 March 2001	14 March 2001	18 April 2001	19 April 2001
NH_4-N (g m^{-3})	28200	18100	49100	16700
Br^- (g m^{-3})	3920	2061	4830	1930
Input rate (mL min^{-1})	200	200	210	200
Pumping period (h)	4	4	4	4
Sampling period (h)	11	7	7	3
Stream flow (L s^{-1})	63	28	380	88
% plant cover	75	80	50	50
Dominant plant species in stream channel	*Potamogeton crispus, Egeria densa*	*Egeria densa, Nitella hookeri*, filamentous algae	*Potamogeton crispus, Egeria densa*	*Egeria densa, Nitella hookeri*, filamentous algae (reduced cover)

RESULTS

Ammonia decay rates (*k*)

Concentrations of NH_4-N and Br^- reached plateau values at each site, with the bromide showing little change in each stream reach (Figures 1 and 2). Concentration-time curves at sites closest to the top of each reach were not as smooth as were curves for sites further downstream, yet all sites were well beyond the minimum distance for complete later mixing to have occurred (Chapra 1997). The results indicate that the reaches did not have significant inflows (of ammonia) that might have confounded the results.

First-order rate constants for NH_4-N were estimated as follows:

- plateau concentrations [NH_4-N] and [Br^-] were averaged for each site;
- times of travel for each site were estimated by fitting a curve to the fronts of each bromide concentration-time profile and estimating the time taken to reach half the maximum (plateau) concentration (J.C. Rutherford, NIWA, pers. comm.). This is based on the superposition principle whereby a continuous release of a tracer can be simulated from the responses of several slug injections. The time of travel coincides with the centroid of the first slug (Kilpatrick *et al.* 1989);
- the first-order rate constant, k (d^{-1}), was calculated from the slope of the linear regression of $\ln\frac{[NH_4-N]}{[Br^-]}$ against travel time, ΔT (min), so that (k = – slope x 60 x 24). Uncertainties were calculated from standard deviations of slopes.

As a check on these linear regressions, the intercept values were used to estimate the approximate ratio of NH_4-N-to-Br^- concentrations at the top of each stream reach, assuming instantaneous complete mixing and no losses. Thus, mass (or concentration) ratio = exp(intercept). These are compared with masses of NH_4-N and Br^- weighed in the laboratory prior to each experiment (Table 3).

Plateau concentrations of NH_4-N and Br^- and calculated values of k are shown in Table 3. The k values are in the middle of the range of published data for ammonia uptake measurement in streams (Table 4). The WAIORA default value for k is 2 d^{-1} and is based on measurements made in the Ararimu Stream (Table 4), which is acknowledged to be "at the lower end of stream data reported by Cooper (1986)" (McBride *et al.* 1991, 1998).

At summer low flows the stream values of the total ammonia removal rate coefficient (k) are somewhat greater than the default value (2 d^{-1}) in WAIORA. Published values vary considerably and it is not straightforward to recommend a single value for all stream types. The values found here (3–5 d^{-1}) at low flow (and velocity) and high plant biomass are similar to measurements made in other New Zealand streams (Table 4).

Table 3: Summary of results for ammonia (NH_4-N) uptake experiments showing slopes (R^2) and k values for each release. Initial ratios of NH_4-N/Br concentrations were calculated from the linear regression intercepts and are compared with ratios measured by weighing salts in the laboratory prior to each release experiment.

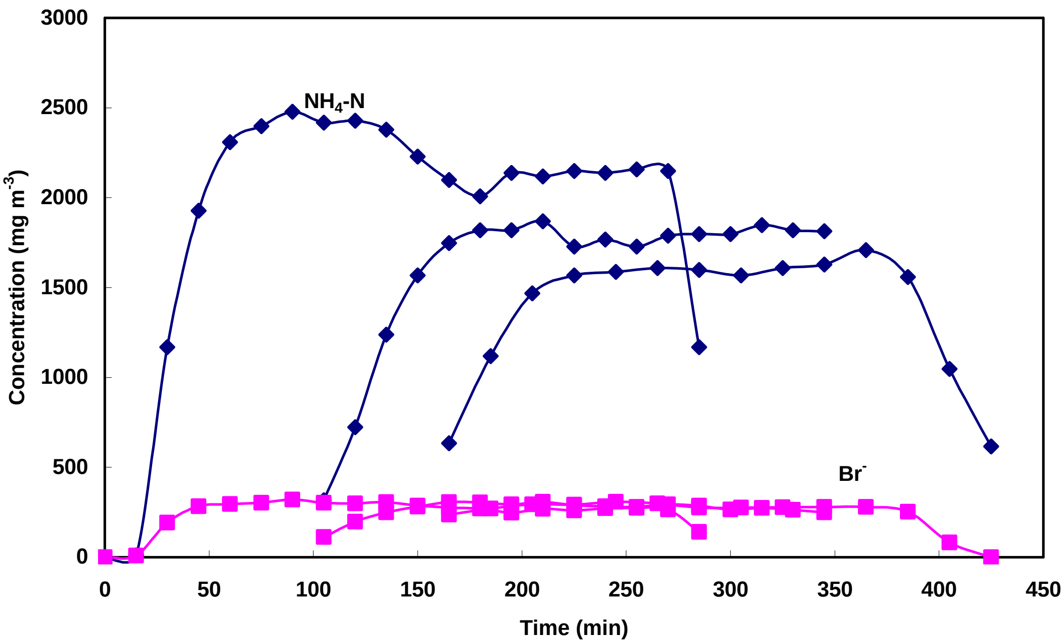
	Kumeu		Waiwera	
	13 March 2001	**18 April 2001**	**14 March 2001**	**19 April 2001**
Stream flow (L s^{-1})	63	380	28	88
Average velocity (m s^{-1})	0.0280	0.0953	0.0305	0.0799
Slope (min^{-1})	-0.00213 (0.97)	-0.00101 (0.20)	-0.00335 (0.99)	-0.00140 (0.64)
k (d^{-1})	3.07 ± 0.58	1.5 ± 1.5	4.82± 0.51	2.0 ± 1.6
Initial ratio of NH_4-N/Br (calculated)	6.7	8.5	8.7	7.5
Initial ratio of NH_4-N/Br (measured)	6.6	9.4	8.8	8.2

Table 4: Values of the first-order decay coefficient (k) for NH_4-N in New Zealand streams.

Stream	***k* (d^{-1})**	**Flow (L s^{-1})**	**Reference**
Ararimu	2.2	362	McBride *et al.* 1991
Toenepi	1.4-5.9	1.6-6.9	Unpublished NIWA data
Waiotapu	1.5-4.0	2380*	Cooper 1986
Waiohewa	5.5-6.4	300	Cooper 1986
Kumeu	1.5-3.1	63-380	This study
Waiwera	2.0-4.8	28-88	This study

* estimated as the long-term average low-flow at Reporoa

Waiwera River 14 March 2001



Kumeu River 13 March 2001

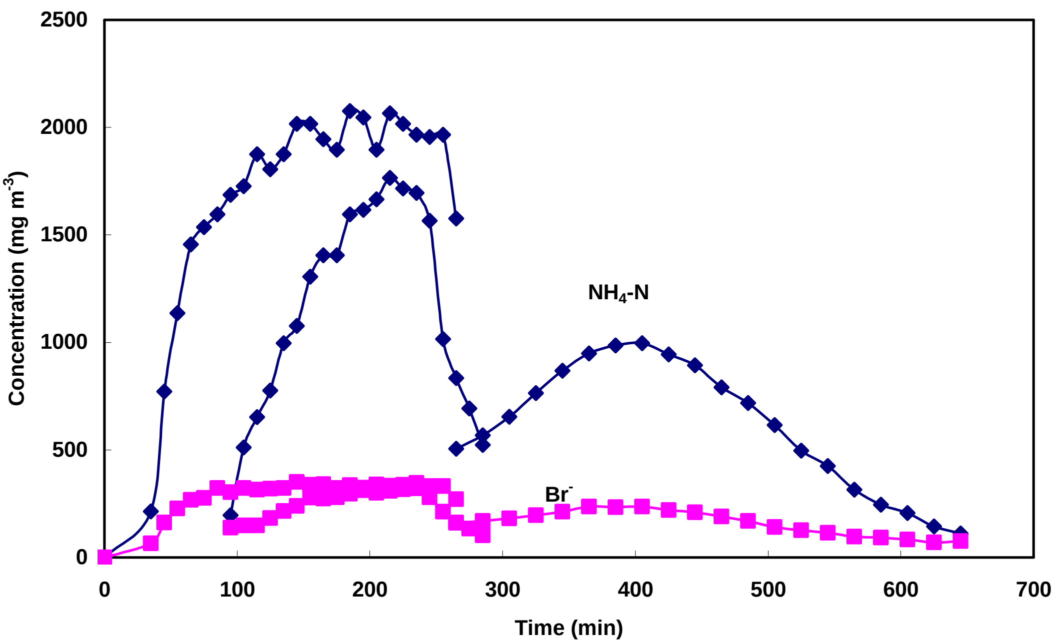
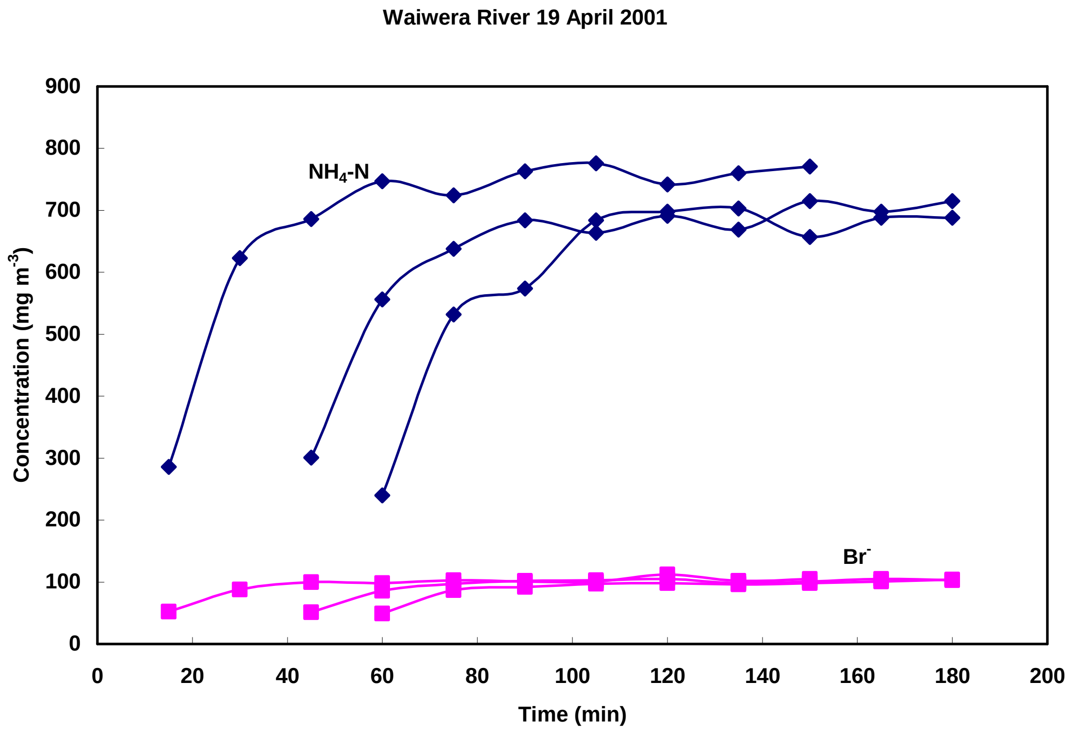


Figure 1: Profiles of NH_4-N and Br^- for Waiwera River and Kumeu River under low-flow conditions in March.



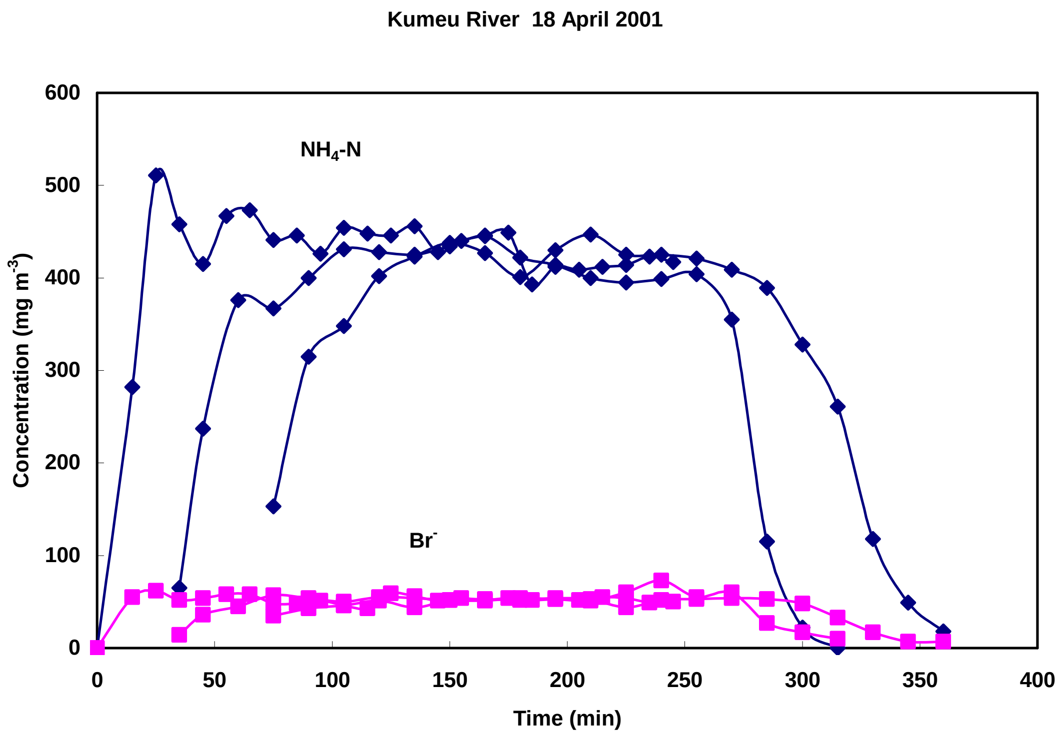


Figure 2: Profiles of NH_4-N and Br^- for Waiwera River and Kumeu River under higher-flow conditions in April.

Effects of changes in flow

At high flows *k* values were lower at the two sites where measurements were made (Table 3). Recent studies of headwater streams show that ammonia is removed from stream water primarily through assimilation by photosynthetic (unicellular algae, filamentous algae and bryophytes) and heterotrophic (bacteria and fungi) organisms and by sorption to sediments, and secondarily by nitrification (Peterson *et al.* 2001). At higher flows some of these processes may be inhibited by shear, or slowed because of lower stream temperatures. Also, the surface area-to-volume ratio is reduced so that ammonia molecules do not come into contact as often with surfaces and attached organisms. Measurements of ammonia uptake made in the Ararimu Stream yielded a k value of 2.2 d^{-1} at a flow rate of 362 L s^{-1} (McBride *et al.* 1991).

Sensitivity analysis

Details of an analysis of the sensitivity of the WAIORA total ammonia model to its removal rate coefficient (*k*) are presented in Appendix 1 for a hypothetical reach of 5 km with five ammonia inflows (Figure 3[1])

The sensitivity analysis indicated that for swift flowing systems little sensitivity to *k* is apparent. Even for sluggish systems the *k*-sensitivity over its usual range (2–4 day^{-1}) is not very pronounced. Thus, variations in *k* are not likely to have a significant impact on estimates of total ammonia concentrations in streams using the existing WAIORA model. Nevertheless, based on the relations found in the ammonia release experiment the WAIORA v.2.0 model has been refined by changing the embedded *k* values as follows:

1. $k = 2\ d^{-1}$ where mean velocity >0.08 m/s;

2. where velocity ≤0.08 m/s, *k* is calculated from the mean water velocity (*V* m/s) using the formula $k = 5 - 36.8 \times V$ d^{-1}.

[1] Calculations and graphing were done using Kaleidagraph™. Note that a unit conversion factor is needed in the calculation of α, because the exponent in its definition ($k\Delta x/U$) must be dimensionless. That is, with k in units day^{-1}, Δx in km and U in m s^{-1}, we have a factor 1/86.4. This is obtained noting that there are 86,400 seconds in a day and 1000 metres in a kilometre. Then we have $\alpha = e^{-(k/86{,}400)(1{,}000\Delta x)/U} = e^{-k\Delta x/(86.4U)}$. Note that $\Delta x = L/(n-1)$, where L is the reach length (L= 5 km in the calculations herein).

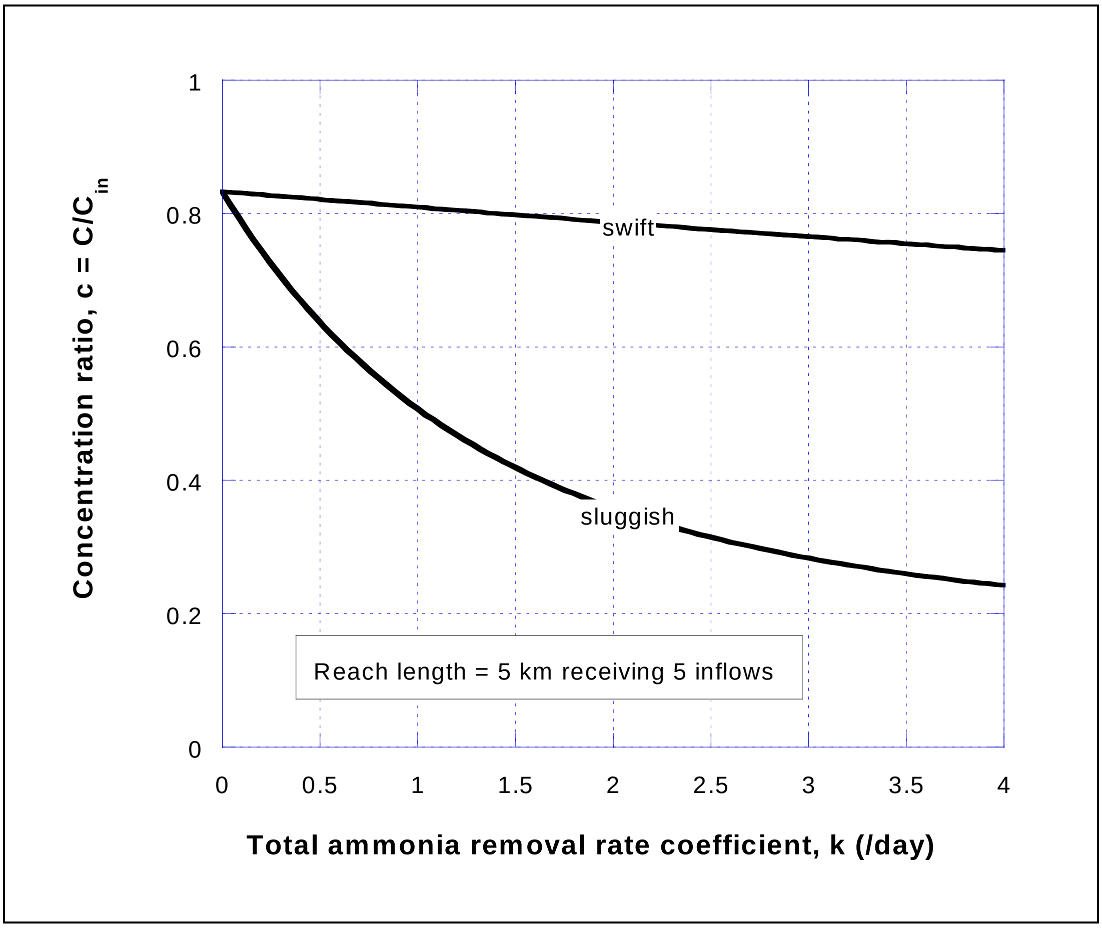


Figure 3: Sensitivity graph for k in a sluggish reach (U = 0.05 m s^{-1}) and in swift reach (U = 1.0 m s^{-1}).

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APPENDIX 1

Sensitivity analysis of WAIORA total ammonia model assessed by varying the ammonia removal rate coefficient

OBJECTIVE

To quantify the sensitivity of the WAIORA total ammonia model to its removal rate coefficient over a fixed river reach.

APPROACH

The model in McBride *et al.* (1998) is simplified to obtain a graph of total ammonia concentration ratios versus values of the "total ammonia removal rate coefficient" (k) over its range of reasonable values (up to 4 day^{-1})[2] for a reach of length 5 km. The reach will receive five inflows.

DETAILS

The model described in McBride *et al.* (1998) results in the following equation for dimensionless total ammonia concentration at the downstream end of a river reach receiving multiple, regularly-spaced, identical inflows:

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

where:

$c = C/C_{in}$ is the ratio of total ammonia concentration at the downstream end of the reach that contains n evenly-spaced inflows, and c_{top} is that ratio for the upstream end of that segment;

$\alpha = e^{-k\Delta x/U}$ is the "total ammonia decay number", with Δx being the distance between each equally-spaced inflow and U is the reach average water velocity;

$q = Q_{in}/Q_{top}$ is the ratio of the discharge of each inflow to the stream flow at the top end of the reach.

Equation A-1 contains four variables on its right-hand-side (α, n, q and c_{top}), making it impossible to demonstrate its overall behaviour on simple graphs. However, by making two simplifying assumptions we can reduce this number of variables by two, as follows:

[2] k is a first-order coefficient, meaning that at any point along the reach the longitudinal rate of removal of total ammonia is proportion to the total ammonia concentration at that point; k is then the proportionality constant.

There is no total ammonia at the upstream end of the segment, so that C_{top} = 0 and hence c_{top} = 0.

The discharge of each inflow equals the stream flow at the upstream end of the reach, so that $Q_{in} = Q_{top}$ and hence $q = 1$.

These assumptions are not expected to greatly influence the overall pattern of results to be obtained.

The simplified equation is now:

$$c = \frac{1-\alpha^n}{(1-\alpha)(1+n)} \qquad \text{(A-2)}$$

in which the right-hand-side is a function of only two variables (n and α). Note that this formula does not hold in the conservative case (i.e., where $k = 0$); in that case, using equation (10) in McBride *et al*. (1998), we can derive the following equation:

$$c = \frac{n}{1+n} \text{ for } k = 0 \qquad \text{(A-3)}$$[3]

All we need do now is to select appropriate values of n and α to produce the required graphs.

For n (the number of equally-spaced inflows to the segment) we choose $n = 5$ to represent a relatively large number.[4] We also choose a sluggish and a swift reach, using $U = 0.05$ and 1.0 m s^{-1}, respectively. This arrangement gives us the graph shown in Figure A-1.[5]

INTERPRETATION

For swift flowing systems the little sensitivity to k is apparent. Even for sluggish systems the k-sensitivity over its usual range (2–4 day^{-1}) is not very pronounced.

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[3] In this case $\alpha = e^0 = 1$.

[4] There must be a minimum of 2 inflows for this procedure to work; with fewer the between-inflow distance (Δx) is meaningless.

[5] Calculations and graphing were done using Kaleidagraph™. Note that a unit conversion factor is needed in the calculation of α, because the exponent in its definition ($k\Delta x/U$) must be dimensionless. That is, with k in units day^{-1}, Δx in km and U in m s^{-1}, we have a factor 1/86.4. This is obtained noting that there are 86,400 seconds in a day and 1000 metres in a kilometre. Then we have $\alpha = e^{-(k/86{,}400)(1{,}000\Delta x)/U} = e^{-k\Delta x/(86.4U)}$. Note that $\Delta x = L/(n-1)$, where L is the reach length (L= 5 km in the calculations herein).

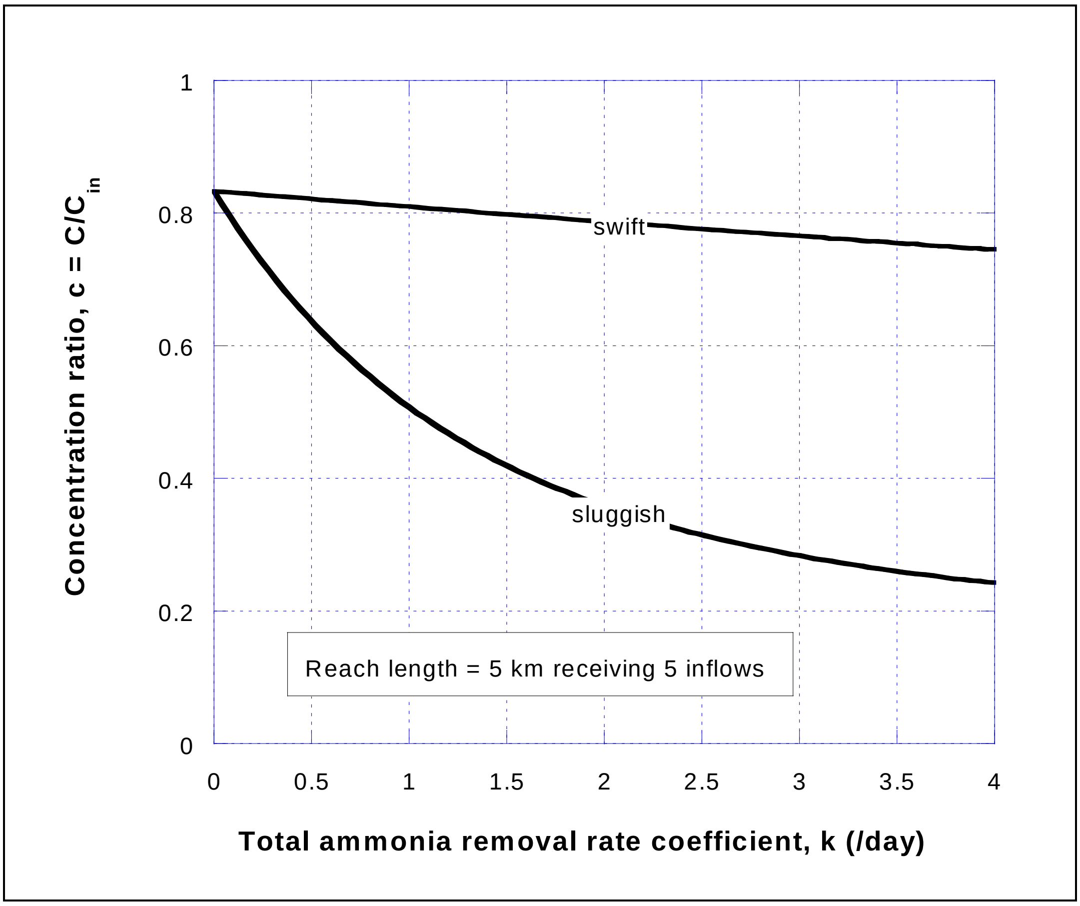

Figure A-1: Sensitivity graph for k in a sluggish reach (U = 0.05 m s^{-1}) and in swift reach (U = 1.0 m s^{-1}).