CONCEPTUAL MODEL OF AQUATIC PLANT DECAY AND AMMONIA TOXICITY FOR SHALLOW LAKES

By Leslie A. Farnsworth-Lee1 and Lawrence A. Baker,2 Member, ASCE

ABSTRACT: A conceptual process model was developed to examine the potential for late summer ammonia toxicity in shallow lakes. Processes represented in the model were macrophyte decay; growth, death, and sedimentation of phytoplankton; nitriﬁcation and death of zooplankton; nitrifying; volatilization; and chemical equilibrium (carbonate and ammonium systems). Peak NH3 concentrations occur at the peak of the phytoplankton bloom that develops about 2 weeks after macrophyte decay starts, when the pH is elevated. Ammonia peaks are highly transient, lasting <1 day. It is hypothesized that late summer ammonia toxicity following macrophyte senescence may be a common but generally unrecognized phenomenon in shallow lakes.

INTRODUCTION

Late summer fish kills are fairly common in shallow lakes. Low dissolved oxygen levels, elevated temperatures, algal toxins, and ammonia toxicity can cause fish kills, although the cause of a particular fish kill generally is not known. For example, late summer fish kills are common in the shallow, eutrophic reservoirs scattered throughout the White Mountains of central Arizona (Jones and Ziebell 1982).

These lakes are shallow and often have dense growths of macrophytes (aquatic plants) in their littoral zones. In late summer, macrophytes senesce and decay, releasing nutrients to the water column (Nichols and Keeney 1973; Smith 1978; Landers 1982). The potential ammonia concentration resulting from decomposition of a plant bed with a density of 500 g m–2 and nitrogen content of 5% in 1 m of water would be 25 mg N L–1. This concentration would never be observed because (1) some of the N in macrophyte biomass is resistant to decomposition; (2) ammonium released during decay is removed from the water column by phytoplankton assimilation, nitrification, and other processes; and (3) only un-ionized ammonia (NH3) is toxic (Quality 1976), and this species may be a small fraction of the “total ammonium” (CNH4 = NH4+ + NH3). The distribution between ammonium (NH4+) and NH3 is controlled by pH, with NH3 predominating at pH levels >9.3 (Fig. 1). Ammonia toxicity therefore requires not only elevated levels of total ammonium, but also elevated pH levels.

In situ bioassay experiments with hatchery trout in the White Mountain lakes showed that 20–100% mortality occurred within 24 h when concentrations of un-ionized ammonia (NH3) were in the range of 92–141 µg NH3-N L–1 (Fisher and Ziebell 1980). This is comparable with the lowest lethal concentration known to cause mortality in salmonids, 165 µg NH3-N L–1 (Quality 1976). It is assumed that threshold toxicity occurs at 100 µg NH3-N L–1.

In this paper a conceptual process model is developed to explore the following question: under what environmental conditions could late summer macrophyte decay lead to toxic levels of NH3? The model represents both nitrogen and carbon transformations associated with macrophyte decomposition and the subsequent algal bloom triggered by the release of nutrients from the macrophytes. Model development included writing the FORTRAN code and conducting a partial calibration and sensitivity analysis for model coefficients. The model was used to examine the effect of environmental conditions (macrophyte density, lake depth, and wind speed) on peak NH3 concentrations following macrophyte senescence and to analyze the effect of macrophyte harvesting and water-level control on late postsenescent ammonia levels. Model results suggest that late summer ammonia toxicity following macrophyte senescence may be more common than generally recognized.

CONCEPTUAL DEVELOPMENT

The model is based on the late summer behavior of Eurasian milfoil (Myriophyllum spicatum L.) because it is one of the most widespread aquatic plants in North America and one of the most intensively studied. Processes represented in the model are shown in Fig. 2. Myriophyllum fragments in late summer following attainment of peak biomass (Adams and McCracken 1974; Grace and Wetzel 1978) as do many other aquatic plants (Schulthorpe 1967). Decay of Myriophyllum starts several weeks after initial fragmentation and then proceeds quickly (Landers 1982). Decomposition in the model of this study therefore starts at the end of a lag period that follows fragmentation. A significant portion of the macrophyte biomass resists decomposition (the “refractory fraction” R). Nutrients in the refractory fraction become part of the sediment and never enter the water column. Jewell (1971) reported that the refractory fraction for several macrophyte species ranged from 11 to 50%, with a mean of 24%. As the biodegradable fraction of macrophytes decays by first-order kinetics, ammonia and carbon dioxide are given off to the surrounding water in proportion to their stoichiometry in the macrophytes. Subsequent biological processes are modeled in a fairly conventional manner, generally following Thomann and Meuller (1987). Ammonia is converted to nitrate through nitrification by a first-order process. It is assumed that phytoplankton growth is controlled by nitrogen, which generally is the limiting nutrient in Arizona’s lakes, or by light limitation. Loss of phytoplankton occurs by decomposition, zooplankton grazing, and settling from the water column. Zooplankton grow in response to the availability of food (phytoplankton) and are lost from the system by death and settling. Decomposition of phytoplankton and zooplankton release CO2 and NH3 to the water column. Settling of phytoplankton permanently removes nutrients from the water column. Eqs. (1)–(6) show how the biological processes were incorporated into an ammonium mass balance. Phytoplankton biomass was modeled as follows:

\[
d(\text{chla}/dt) = G_s(\text{chla}) - D_p(\text{chla}) - v/h \cdot \text{chla}
\]

where \(G_s\) = phytoplankton growth rate (day–1); \(D_p\) = death rate, (day–1); \(v\) = net settling rate. © ASCE, ISSN 0733-9372/00/0003-0199–0207/$12.00 + $.50 per page. Paper No. 14940.
where \( f \) was modeled after Thomann and Mueller (1987) where \( N = \text{half-saturation constant} \) equal efficiency. In the model, this is done by using the same Nitrate and ammonium were assumed to be taken up with rate (day\(^{-1}\)); \( G_p \) was modeled as a function of the maximum growth rate \( G_{\text{max}} \) (day\(^{-1}\)), with limiting terms for nitrogen \((G(N)\) and light \(G(L)\) (dimensionless ratios)

\[
G_p = G_{\text{max}}G(N)G(L)
\]

where \( N = C_{TNH_4} + [\text{NO}_3^-] \), both in \( \mu g\) N L\(^{-1}\). Light limitation was modeled after Thomann and Mueller (1987)

\[
G(I) = \frac{2.718f[\exp(-\alpha_I) - \exp(-\alpha_s)]}{K_h}
\]

where \( f = \text{photoperiod (days)} \); \( K_r = \text{extinction coefficient} \); \( \alpha_I = I/I_s \cdot \exp(-K_rH) \); \( \alpha_s = I/I_s \); \( I_s = \text{saturating light intensity (ly day}^{-1} \); and \( I_s = \text{average light intensity (ly day}^{-1})/I_s f \), where \( I_f = \text{total daily radiation} \).

Zooplankton growth was represented as a balance between growth and death, as modeled by the following:

\[
dZ/dt = Z[Z_{zzc}(\text{chla})(a_{ps}) - D_z]
\]

where \( Z = \text{zooplankton standing crop (} \mu g\ C\ L^{-1}) \); \( Z_{zzc} = \text{zooplankton grazing rate (day}^{-1}) \); chla = chlorophyll concentration \((\mu g\ L^{-1})\); \( a_{ps} = \mu g\ C/\mu g\ \text{chla} \); and \( D_z = \text{zooplankton death rate (day}^{-1}) \). Total ammonium in the water column was then computed by mass balance

\[
dC_{TNH_4}/dt = \frac{(K_m)(M)(\alpha_s)}{V} + (D_p - G_p)(\text{chla})(a_{ps}) + (D_p)(Z)(a_p) + [(Z_{zzc})(\text{chla})(a_{ps})Z] - (G_p)(Z)a_p - (K_{\text{NDS}})(C_{TNH_4}) - \frac{(C_p - C_m)(\nu)}{h}
\]

where \( K_m = \text{decay rate of macrophytes (day}^{-1}) \); \( M = \text{mass of biodegradable macrophyte remaining at time} t (\mu g) \); \( \alpha_s = \text{stoichiometric ratio of macrophyte N:dry weight (DW)} \); \( K_{\text{NDS}} = \text{nitration rate constant (day}^{-1}) \); \( a_{ps} = \text{stoichiometric conversion of chla to carbon} \); \( a_p \) and \( a_{ps} = \text{stoichiometric conversions for phytoplankton and zooplankton (} \mu g\ N/\mu g\ DW) \), \( C_p = \text{concentration of free ammonia in the atmosphere,} \mu g\ N L^{-1}\); \( C_w = \text{concentration of free ammonia in water,} \mu g\ N L^{-1}\); \( V = \text{transfer velocity across the air-water interface (} \text{m day}^{-1}) \); \( \nu = \text{lake volume (L)} \); and the other terms have been defined previously.

The model also includes algorithms for computing pH. \([\text{NH}_4]\) from total ammonium \((C_{TNH_4} = [\text{NH}_4] + [\text{NH}_3] \) and gas \((\text{NH}_3; \text{CO}_2) \text{ volatilization. Ammonium dissociation is computed from the equilibrium expression}

\[
K_{\text{NDS}} = \frac{[\text{NH}_4](H^+) - [\text{NH}_3]}{[\text{NH}_4]}
\]

Note that when the pH = 9.3, \([\text{NH}_3] = [\text{NH}_4]. At pH values >9.3, \text{NH}_4 \text{ predominates, whereas at pH values <9.3, NH}_3 \text{ predominates (Fig. 1).}

A mass balance for dissolved inorganic carbon (DIC = \( C_{\text{DICO}_3} = H_2CO_3^+ + HCO_3^- + CO_3^{2-} \)) produces an equation similar to that for nitrogen

\[
d\text{DIC}/dt = \frac{(K_m)(M)(\alpha_s)}{V} + (D_p - G_p)(\text{chla})(a_{ps}) + (D_p)(Z)(a_p) + [(Z_{zzc})(ap_s)(\text{chla})(Z) - (G_p)(Z)a_p - (C_p - C_m)(\nu)/h}
\]

where \( \alpha_c = \text{ratio of carbon:dry weight in macrophytes} (\mu g\ C/\mu g\ chla) \); \( a_{ps} = \text{ratio of carbon:chlorophyll a (} \mu g\ C/\mu g\ chla) \); \( a_p = \text{ratio of carbon:dry weight for zooplankton (} \mu g\ C/\mu g\ zoop) \); and other terms have been defined previously.

Water column pH at each time interval was computed from DIC (variable) and alkalinity (assumed constant), resulting in a fourth-order polynomial, which was solved by the secant method

\[
[H^+] = [H^+]_0^0 + [H^+]_0^0 (K_i + ALK) + [H^+]_0^0 (K_i ALK - C_{\text{DICO}_3}K_i) - K_n + K_n K_i = [H^+]_0^0 (K_i K_i + K_n K_n) + K_n K_n = 0
\]
Fig. 3 shows the relationship between pH and DIC for a lake with an alkalinity ~2 meq L⁻¹. When the lake is at equilibrium with atmospheric CO₂, the pH is 8.7. When CO₂ is added to the water (e.g., respiration > photosynthesis), the DIC increases and pH decreases. When there is net consumption of CO₂ (e.g., photosynthesis > respiration), DIC declines and pH increases.

The model provides for gains or losses of CO₂ and NH₃ by gas transfer across the lake surface by the following:

\[
dC/dt = \frac{(C_s - C_v)v_v}{h}
\]

where \( C_v \) = concentration of gas (CO₂ or NH₃) in the overlying atmosphere; and \( C_{sv} \) = equilibrium concentration of gas dissolved in water. The molar concentration of \( C_v \) was determined using Henry’s law (Snoeyink and Jenkins 1980)

\[
C_v = K_{H_s}p_g
\]

where \( K_{H_s} \) = Henry’s law constant for gas \( g \) (mol L⁻¹ atm⁻¹); and \( p_g \) = partial pressure of gas \( g \) in the overlying atmosphere. It is assumed that an atmospheric partial pressure of 10⁻³ atm for CO₂ (Snoeyink and Jenkins 1980) and 0 for NH₃ (e.g., there is no NH₃ in the atmosphere). The transfer or piston velocity \( v_v \) in (11) was derived from thin-film theory of mass transport. Diffusion through these two layers requires both vapor-phase and water-phase diffusions, as described by the following equation (Schwartzbenbach et al. 1993):

\[
\frac{1}{v_v} = \frac{1}{v_{sw}} + \frac{1}{v_wK_p}
\]

where \( v_v \) = transfer velocity across the water-air film (cm s⁻¹); \( v_{sw} \) = transfer velocity across the air-water film (cm s⁻¹); and \( K_p \) = dimensionless form of Henry’s law constant. These piston velocities are related to windspeed. The following equations [from Schwartzbenbach et al. (1993)] were used to compute transfer velocities for oxygen (across the water-air film) and water vapor (across the water-air film):

\[
v_o(O_2) \sim 4 \times 10^{-4}u_{10} + 4 \times 10^{-4} \text{ (cm s}^{-1})
\]

\[
v_w(H_2O) \sim 0.2w_{10} + 0.3 \text{ (cm s}^{-1})
\]

where \( u_{10} \) = wind speed measured 10 m above the water surface (m s⁻¹); \( v_o(O_2) \) = piston velocity for water-film transfer of oxygen (cm s⁻¹); and \( v_w(H_2O) \) = piston velocity for air-film transfer of water (cm s⁻¹).

Transfer velocities for the gases of interest (NH₃; CO₂) were computed as follows (Schwartzbenbach et al. 1993):

\[
v_a(compound) = v_w(H_2O)[D_w(compound)/D_w(H_2O)]^\beta
\]

where \( \alpha = 0.67, \beta = 0.57, \) and \( D_a \) and \( D_w \) = diffusivity in air or water (cm² s⁻¹), respectively. Diffusivities for NH₃ and CO₂ were computed from the diffusivities of oxygen in water (water phase) and water vapor in air (air phase) on the basis of their molecular weights

\[
\frac{D_a}{D_w} \sim (MW_a)^{1/2} / (MW_o)^{1/2}
\]

where \( D_a \) and \( D_w \) = diffusivities of compounds A and B for air or water (cm² s⁻¹); and \( MW_a \) and \( MW_o \) = molecular weight of compounds A and B (g mol⁻¹) (Hemond and Fechner 1994).

The complete model included 19 fixed inputs and 13 model coefficients. The model was written in FORTRAN 77 interfaced with EXCEL spreadsheets and graphs to inspect data. User-defined fixed inputs included mean depth, surface area, alkalinity, photoperiod, initial macrophyte biomass, wind-speed, and initial values for \( C_{TPNH₃} \), nitrate, chlorophyll a, zooplankton, and pH. Stoichiometric coefficients for the biological components and chemical equilibrium constants were derived from the literature.

Because peak NH₃ concentrations were the primary interest of this study, an abbreviated model output was used to determine peak [NH₃] and timing of this peak. A nitrogen mass balance was developed to verify that the model was properly conserving nitrogen and to determine which nitrogen pools were quantitatively important. Pools included in the nitrogen mass balance were “new” atmospheric nitrogen (degassed ammonia), water column ammonia and nitrate, macrophyte N, phytoplankton N, zooplankton N, and “new” sediment N. Details of model formulation can be found in Farnsworth-Lee (1996).

CALIBRATION AND MASS BALANCE CHECK

Stoichiometric coefficients and initial estimates of process coefficients were taken from the literature (Rates 1985) (Table 1). These were modified through calibration using data from a macrophyte enclosure study conducted by Landers (1982) with additional data from Dixon Landers (personal communication 1995). Landers’ enclosures were placed in the littoral zone of Lake Monroe, Ind., at approximately the time of maximum macrophyte (primarily Myriophyllum) biomass. He monitored the enclosures for the remainder of the summer and into the autumn, a total of 119 days. After 21 days of healthy growth, the plants began to fragment. By day 51 (late August), “advanced decay” was evident. Signs of “postdecay” were observed by day 63 (early September), and by day 96 (mid-October) no plants or floating material were visible. All of the enclosures and several nearby open-water sites were sampled at least once a week. Chemical analyses included phosphorus, nitrate, ammonium, and chlorophyll a. Ammonium and nitrate concentrations peaked during the advanced decay period, and chlorophyll a peaked in the postdecay period.

To obtain a reasonable match between model predictions

<table>
<thead>
<tr>
<th>TABLE 1. Stoichiometric Coefficients Used in Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
</tr>
<tr>
<td>(1)</td>
</tr>
<tr>
<td>( a_{i} ) (µg N/µg DW)</td>
</tr>
<tr>
<td>( a_{c} ) (µg C/µg DW)</td>
</tr>
<tr>
<td>( a_{i} ) (mg C/µg chla)</td>
</tr>
<tr>
<td>( a_{zn} ) (µg N/µg chla)</td>
</tr>
<tr>
<td>( a_{zn} ) (µg N/µg zoop)</td>
</tr>
<tr>
<td>( a_{zn} ) (µg C/µg DW)</td>
</tr>
</tbody>
</table>

Note: DW = dry weight; N = nitrogen; C = carbon. Source: USEPA (Rates 1985).
and measured values, it was necessary to “start” the decay process in the model at day 51 of Landers’ experiment, 30 days after observed fragmentation and the beginning of what Landers (1982) called the advanced decay phase. By calibrating the model to fit Landers’ data, a good fit was obtained for the ammonia and nitrate curves in this study (Fig. 4), while keeping all model coefficients within the range of published values (Table 2). A good fit between modeled and observed chlorophyll could not be obtained. One reasonable explanation for the fact that the model presented here could readily be calibrated to predict ammonium and nitrate, but not chlorophyll, is that the phytoplankton in Lake Monroe was phosphorus-limited rather than nitrogen-limited. Thus, calibration was very useful in adjusting the starting time, the macrophyte decay constant, the refractory fraction, and the nitrification constant but was not as useful in fitting constants related to phytoplankton growth.

It was verified that the model conserved nitrogen. A mass balance showed that nitrogen was properly conserved through all model runs (Fig. 5). The mass balance also shows that at any given time throughout the 40-day model run, the largest N pool was in biomass (macrophytes, phytoplankton, and zooplankton). Total ammonium in the water column was never more than ~10% of total N in the system. By the end of the model run, nitrate was around 15% of the total N in the system. Sedimentation was the only appreciable N sink; volatilization of NH3 was negligible (~1% of initial macrophyte N).

### SENSITIVITY ANALYSIS

A simple sensitivity analysis was performed by altering model coefficients, one by one, to one-half and twice their original values. The model was run to predict peak $C_{T, NH4}$, chlorophyll a, and zooplankton. Results (Table 3) show that predicted $C_{T, NH4}$ and chlorophyll a were very sensitive to values used for the refractory fraction $R_f$, the macrophyte decay rate $K_f$, and the maximum phytoplankton growth rate $G_{max}$. In addition, modeled peak chlorophyll concentrations were very sensitive to light intensity parameters $I_s$ and $I_a$ and the net settling rate. The timing and magnitude of peak $C_{T, NH4}$ and chlorophyll concentrations were not very sensitive to zooplankton parameters because zooplankton populations did not become large until phytoplankton became abundant.

### MODEL SCENARIOS

#### Initial Conditions

The model was developed to represent small lakes and ponds. A mean depth of 2 m and macrophyte coverage of 70% was initially used. Data from Grace and Wetzel (1978) yielded an average Myriophyllum density of 500 g m$^{-2}$ for plant beds in a variety of lakes. For 70% coverage, this is 350 g m$^{-2}$ for a lake-wide average. Wind speed was initially set to 5 m s$^{-1}$ (about 10 m h$^{-1}$). Low concentrations were used to initialize phytoplankton biomass (1 $\mu$g L$^{-1}$), zooplankton biomass (1 $\mu$g L$^{-1}$), and $C_{T, NH4}$ (20 $\mu$g N L$^{-1}$). The alkalinity was set at ~2 meq L$^{-1}$.

#### Initial Model Runs

Fig. 6 illustrates a typical model run. Release of nutrients from the decaying macrophytes stimulates a phytoplankton bloom [Fig. 6(a)], which peaks around day 12. Zooplankton grow rapidly in the presence of food (phytoplankton), reaching a peak population a few days after the phytoplankton peak. The phytoplankton bloom declines because of light limitation and zooplankton grazing. Decomposition produces CO2, which causes the DIC to increase and the pH to decline [Fig. 6(b), also see Fig. 2]. The highest DIC concentration and lowest pH (7.5) occur at around day 5. As the phytoplankton population...
The effect of initial macrophyte density on pH and un-ionized ammonia levels was examined. Initial macrophyte density in the model varied from 100 to 600 g m$^{-2}$, and all other variables were held constant. Peak concentrations of $C_{T,NH_4}$ increased in direct proportion to initial macrophyte density [Fig. 7(a)]. This result is intuitive: the greater the initial macrophyte density, the greater the amount of ammonium released. Because the magnitude of the postsenescent phytoplankton bloom depends upon nitrogen supply, the phytoplankton bloom also increased in direct proportion to initial macrophyte density (not shown).

The effect of initial macrophyte density on pH and un-ionized ammonia is more complex. Peak pH values are highest at intermediate initial macrophyte densities and decline at high and low densities. The peak pH value is 8.6 at intermediate initial macrophyte densities (day 35). The pH declines because at these times pH is depressed as the result of high CO$_2$ levels.
higher or lower initial macrophyte densities [Fig. 7(b)]. Un-ionized ammonia concentrations follow the same trend [Fig. 7(c)]. These observations can be explained as follows. As noted above, the magnitude of the phytoplankton bloom depends upon the supply of total ammonium, which in turn depends upon initial macrophyte density. With very low macrophyte densities, there is little ammonium release, and the subsequent phytoplankton bloom is small. CO₂ production (by decomposition) and uptake (by phytoplankton) are nearly in balance, resulting in a pH of ≈8.7. At the highest initial macrophyte densities, there is more production of CO₂ from decomposition but also more CO₂ consumption from phytoplankton uptake, but the two processes are again in balance, resulting in a pH near 8.7 [Fig. 7(b)]. At intermediate initial macrophyte densities, CO₂ consumption by the phytoplankton is greater than production of CO₂ by decomposition; thus peak DIC concentrations are lower, and the peak pH is higher than at either lower or higher initial macrophyte densities [Fig. 7(b)]. An initial macrophyte density of 300 g m⁻² resulted in the highest peak pH [9.3; Fig. 7(b)].

Highest concentrations of un-ionized ammonia also occur at intermediate macrophyte densities. At initial macrophyte densities <300 g m⁻², both peak $C_{\text{TNH}_4}$ and pH were lower, resulting in low peak NH₃ concentrations (<50 μg N L⁻¹ for densities <200 g m⁻²). As macrophyte densities increase, un-ionized NH₃ concentrations increase, to a peak of 122 μg N L⁻¹ at a macrophyte density of 400 g m⁻². The peak NH₃ concentration occurred at this density because the high pH [9.3; Fig. 7(b)], favoring the un-ionized species. Peak NH₃ concentrations decline as macrophyte densities increase above 400 g m⁻², even though peak $C_{\text{TNH}_4}$ is higher [Fig. 7(a)] because the pH declines [Fig. 7(b)]—the result of greater net CO₂ production. This reduces the proportion of $C_{\text{TNH}_4}$ in the un-ionized form.

**Lake Depth**

Model runs with varying average lake depth show that peak concentrations of NH₃ decline with increasing lake depth (Fig. 8). This is primarily a dilution effect. These model runs show that the potential for ammonia toxicity resulting from macrophyte decomposition exists only in very shallow lakes (~2 m). At depths below ~1.2 m the model becomes unstable because the phytoplankton growth rate/mean depth term becomes less than the settling velocity, resulting in modeled phytoplankton concentrations <0. This hysteresis effect is not important at a depth ≥1.5 m.

**Effect of Wind Speed**

Increasing wind speed increases the transfer velocity for both CO₂ and NH₃ by decreasing the thickness of the air-water boundary layer. One would therefore postulate that wind speed affects both pH and NH₃ concentrations. Model runs with varying wind speed show that both peak [NH₃] and peak pH increase with increasing wind speed (Figs. 9 and 10). These results are counterintuitive. One might expect that degassing of NH₃ would increase with wind speed, causing NH₃ concentrations to decrease. Similarly, the pCO₂ of the water column should come closer to equilibrium with the atmosphere as the wind speed increases.

The explanation for these results requires an understanding of the temporal sequence of events. At the start of the model run, the lake water has a pH of ~8. Before day 12, macrophyte decomposition produces CO₂ faster than phytoplankton growth consumes CO₂, resulting in oversaturation of CO₂. The extent of CO₂ oversaturation is greatest with no wind and declines as wind speed increases. This result is expected: degassing of CO₂ to the atmosphere increases with increasing wind speed, preventing CO₂ buildup.

During the postensocent phytoplankton bloom, the model...
predicts that CO₂ is removed from the water column by photosynthesis faster than it is produced by decomposition. CO₂ consumption during the fast-growing phytoplankton bloom is faster than the atmospheric exchange rate throughout the range of modeled wind speeds. However, with no wind the buildup of CO₂ in the water column at the beginning of the phytoplankton bloom is higher than it is with high wind, for the reasons noted above. With no wind (or low wind), the water column therefore remains oversaturated with CO₂, even at the peak of the phytoplankton bloom. In the absence of wind, the minimum pH during the model run is 7.3 (at day 8); consumption of CO₂ during the phytoplankton bloom raises the pH to 8.2 by day 14. With high wind, pCO₂ in the water column is closer to atmospheric equilibrium at the beginning of the phytoplankton bloom. Rapid consumption of CO₂ during the phytoplankton bloom therefore results in undersaturation of CO₂ and correspondingly high pH levels.

Prior to the phytoplankton bloom, most CNT is in the un-ionized form; thus, volatilization losses are minimal with or without wind. The maximum pH during the phytoplankton bloom increases with wind speed, and the higher pH favors the un-ionized NH₃ species. Thus, wind speed affects peak [NH₃] through its effect on the volatilization of CO₂ and, consequently, pH. The effect of wind speed on volatilization of NH₃ is insignificant.

DISCUSSION

The modeled scenarios show that toxic NH₃ concentrations (>100 μg N L⁻¹) could result from macrophyte senescence in many shallow (<2–3 m) lakes. These include many small agricultural storage reservoirs, man-made lakes in residential and urban areas, prairie pothole lakes, and wetland ponds.

Sequence of Events Leading to Ammonia Toxicity

Ammonia toxicity occurs for the following reason: nutrients are released by the decomposing macrophytes, which leads to a phytoplankton bloom about 2 weeks later. Phytoplankton consume CO₂, raising the pH. Highest pH values were always observed at the peak of the phytoplankton bloom. The rise in pH shifts the NH₄⁺-NH₃ equilibrium toward NH₃. Peak concentrations of un-ionized NH₃ always occur at the peak of the phytoplankton bloom, when the pH is highest. In most model runs, this was about 2 weeks after the onset of macrophyte decomposition.

A lakeside observer would observe the following. First, the macrophyte bed would fragment. For Myriophyllum, this fragmentation is easily visible: one week the bed is there, and the next week it is not. The plant fragments apparently live for about a month before decomposition starts. Water clarity may be high during this period. About 6 weeks after observed fragmentation, the resulting phytoplankton bloom would be readily visible (chlorophyll concentrations in many runs were >100 μg L⁻¹). Dead fish might be observed at this time, or perhaps a day or two later. It is unlikely that the observer, even a knowledgeable fisheries biologist, would make the connection between the fish kill at this time and macrophyte senescence 6 weeks earlier.

It is hypothesized that postsenescent ammonia toxicity is common in shallow lakes, but the temporal separation between macrophyte fragmentation and ammonia toxicity obscures diagnosis of the problem. Identification of ammonia toxicity is made more difficult by toxic conditions that are highly transient, with toxic conditions often lasting <1 day. A water sample collected a day or two after an ammonia-induced fish kill would probably not reveal toxic conditions. Furthermore, special considerations would have to be employed in water analysis to determine ammonia toxicity. In particular, analysis of pH would have to be done in situ or with samples that had been collected in gastight containers used in “closed-cell” pH measurements. Samples collected and analyzed in a normal fashion may not reveal elevated pH because adsorption of CO₂ in undersaturated samples (e.g., during measurements made with an open beaker in the lab) would cause the measured pH to be lower than in situ values. Subsequent calculations [8] would result in lower levels of un-ionized ammonia that really existed in the lake environment.

Factors Contributing to Postsenescent Ammonia Toxicity

Model runs show that ammonia toxicity is likely to occur only in very shallow lakes (~2 m). At greater depths, dilution would reduce the potential for toxicity. The potential for toxicity appears to be greatest for intermediate macrophyte densities. At lower initial densities, the phytoplankton bloom is not sufficient to raise the pH high enough to cause ammonia toxicity. At very high densities, production of CO₂ from decomposition may be sufficiently high to offset CO₂ depletion during the large phytoplankton bloom. For typical model runs, peak NH₃ concentrations occurred with initial lake-wide macrophyte densities around 350–450 g m⁻².

Continuous wind exacerbated ammonia toxicity. The worst-case scenario would be windy conditions during early decomposition, followed by a period of no wind during the phytoplankton bloom. The wind would remove CO₂ produced during early decomposition, bringing the water to near-equilibrium conditions at the start of the phytoplankton bloom. Under windless conditions, atmospheric replenishment of CO₂ consumed by phytoplankton would be diminished, resulting in highly undersaturated conditions. Under these conditions, pH values >9.5 would be expected.

Management Implications

The model suggests that water-level control and judicious macrophyte harvesting would be reasonable lake management options to reduce the likelihood of fish kills. Water-level control could be achieved at the time of initial design (for new urban lakes), by sediment removal, or by water-level control. For small agricultural reservoirs, such as those in the White Mountains of Arizona, water conservation measures (e.g., lining irrigation canals) could maintain higher late summer water depths and reduce potential ammonia toxicity. The model presented here showed that postsenescent ammonia toxicity would probably not occur in lakes with average depths >>2 m. Macrophyte harvesting would likely reduce the potential for postsenescent ammonia toxicity, although minimal harvesting of very dense plant beds could theoretically make the situation worse (Fig. 7).
Further Research

The conceptual model presented here yields an important hypothesis: macrophyte decomposition in shallow lakes may lead to ammonia toxicity. If true, the phenomenon has significant implications with respect to the management of shallow lakes. Direct observational studies are needed to verify this hypothesis. This model could also be improved in several ways by (1) including phosphorus limitation; (2) including the effects of calcium carbonate precipitation in the DIC-pH model; and (3) modifying the phytoplankton removal term.

CONCLUSIONS

Previous field and laboratory experiments have demonstrated the importance of macrophyte senescence in releasing nutrients and stimulating phytoplankton blooms. Based on results from the conceptual mathematical model presented here, it is hypothesized that fish kills that often occur in late summer or early fall may be caused by macrophyte senescence. The sequence of events is (1) macrophytes fragment; (2) decomposition starts in a few weeks, releasing nutrients; (3) nutrients stimulate a phytoplankton bloom; (4) photosynthesis consumes CO2; (5) pH increases, favoring the predominance of un-ionized NH3; and (6) fish die from ammonia toxicity. Model results show that postsenescent ammonia toxicity is most likely to occur in very shallow mean lakes (mean depth < 2 m) with extensive macrophyte beds.

It is hypothesized that ammonia toxicity caused by macrophyte senescence is fairly common. However, because ammonia toxicity is temporally separated from macrophyte fragmentation, most water samples are not collected in a manner that would reveal ammonia toxicity, and toxic conditions are highly transient, the problem is not widely recognized. Because this process has significant management implications for small lakes, detailed field studies are needed to verify this hypothesis.

ACKNOWLEDGMENTS

The writers would like to thank Dixon Landers for sharing much of the raw data from his experiment and for his insights on the issue of nutrient regeneration during macrophyte senescence. This study was funded in part by a Clean Lakes Program grant through the Arizona Department of Environmental Quality. The writers would like to thank Tom Trent, the project officer, Stuart Parks, who assisted with sampling at Rainbow Lake, and Susan Fitch (ADECQ) who provided technical support.

APPENDIX I. REFERENCES


APPENDIX II. NOTATION

The following symbols are used in this paper:

\[ a_a = \text{ratio of C:chlorophyll a for phytoplankton (mg C/µg chla);} \]

\[ a_{ac} = \text{ratio of C:chl a for phytoplankton (µg C/µg chla);} \]

\[ a_{an} = \text{ratio of N:DW for phytoplankton (µg N/µg chla);} \]

\[ a_{az} = \text{ratio of C:DW for zooplankton (µg C/µg zoop);} \]

\[ a_{azn} = \text{ratio of N:dry weight for zooplankton (µg N/µg DW);} \]

\[ C_e = \text{equilibrium concentration of gas in air (mol L}^{-1};} \]

\[ C_{DIC} = \text{dissolved organic carbon} = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_2 (\text{mol L}^{-1} \text{ or µg L}^{-1});} \]

\[ C_{NH_3} = \text{total ammonium concentration} = [\text{NH}_3] + [\text{NH}_4^+] (\text{mol L}^{-1} \text{ or µg L}^{-1});} \]

\[ C_{chla} = \text{concentration of dissolved gas in water (mol L}^{-1} \text{ or µg L}^{-1});} \]

\[ \text{chla} = \text{phytoplankton chlorophyll a (µg L}^{-1});} \]

\[ D_s = \text{diffusivity in water (cm}^2 \text{s}^{-1});} \]

\[ D_p = \text{phytoplankton death rate (day}^{-1});} \]

\[ D_e = \text{diffusivity in water (cm}^2 \text{s}^{-1});} \]

\[ D_z = \text{zooplankton death rate (day}^{-1});} \]

\[ f = \text{photoperiod (day)}; \]

\[ G(L) = \text{light limitation term (0–1.0; unitless);} \]

\[ G_{max} = \text{maximum growth rate of phytoplankton at 20°C (day}^{-1});} \]

\[ G(N) = \text{nutrient limitation term (0–1.0; unitless);} \]

\[ G_a = \text{actual growth rate of phytoplankton (day}^{-1});} \]

\[ G_z = \text{zooplankton growth rate (day}^{-1});} \]

\[ h = \text{lake depth (m)}; \]

\[ I_s = \text{actual light intensity (ly day}^{-1}); \]

\[ I_F = \text{saturation light intensity (ly day}^{-1}); \]

\[ K_e = \text{extinction coefficient (unitless);} \]

\[ K_H = \text{Henry’s law constant (mol atm}^{-1} \text{ L}^{-1});} \]

\[ K_I = \text{dimensionless form of Henry’s law constant (unitless);} \]

\[ K_n = \text{decay rate of macrophyte (day}^{-1});} \]

\[ K_{NO3} = \text{nitrification rate constant (day}^{-1});} \]

\[ K_a = \text{half-saturation concentration (µg N L}^{-1});} \]

\[ K_i = \text{first dissociation constant for carbonate system (unitless);} \]

\[ K_z = \text{second dissociation constant for carbonate system (unitless);} \]

\[ M = \text{biodegradable macrophyte biomass (µg)}; \]
$MW_A, MW_B$ = molecular weight of compound A and B (g mol$^{-1}$);

$M_0$ = initial macrophyte biomass (kg);

$p_g$ = partial pressure of gas $g$ (atm);

$u_{10}$ = wind speed measured 10 m above the water surface (m s$^{-1}$);

$V$ = lake volume (L);

$v_s$ = phytoplankton settling velocity (m day$^{-1}$);

$\alpha$ = empirical constant for diffusion correction equation (=0.67);

$\alpha_c$ = ratio of C:dry weight for macrophytes ($\mu$g C/$\mu$g DW);

$\alpha_n$ = ratio of macrophyte N:dry weight ($\mu$g N/$\mu$g DW);

$\beta$ = empirical constant for diffusion correction term (=0.57); and

$\eta$ = zooplankton assimilation efficiency (unitless).