

Ammonia and Toxicity Criteria in Polluted Onondaga Lake, New York

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ABSTRACT: Temporal patterns of total ammonia (T-NH₃) in the upper layers of an ammonia-polluted, saline, hypereutrophic urban lake, Onondaga Lake, New York, and its status with respect to ammonia toxicity criteria are documented and evaluated for the spring to fall interval over 10 years (1989 to 1998). Implications of revisions ($n = 5$) in the criteria (1985 to 1999) and the omission of ionic strength effects in the most recent revisions for this saline system are considered. The implications of diurnal variations in pH for application of both chronic and acute criteria are illustrated based on 14 days of hourly pH data. Concentrations of T-NH₃ in the upper layers of this lake were extremely high because of discharges received from a 3.5 m³/s (80 mgd) wastewater treatment plant; the average concentration during the April to June interval for the 10 years was 2.3 mg/L. Substantial interannual and seasonal variations were observed in the T-NH₃ pool of the lake. April concentrations were largely regulated by the dilution provided by antecedent (i.e., December to March) tributary flow.

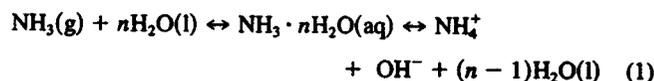
Revisions of the chronic criteria have been progressively less stringent for low ionic strength conditions. However, under the saline conditions of this lake, the most recent (1998 and 1999) revisions can be more stringent than the earlier criteria. The 1984 chronic criterion (published in 1985) was exceeded by a wide margin annually (average factor of 2.2 for April to June) and for durations greater than 75 days. Widely different diurnal patterns in pH and the occurrence of an exceedance of the 1998 acute criterion during a pH maximum are documented. These diurnal variations are an important factor in the design of programs to assess status and in application of criteria for productive systems. *Water Environ. Res.*, 72, 731 (2000).

KEYWORDS: ammonia, criteria, diurnal, eutrophication, lakes, pH, toxicity.

Introduction

Ammonia is an important component of the nitrogen (N) cycle of freshwater bodies (Wetzel, 1983). This constituent is of water quality concern where large loads (e.g., domestic wastewater effluents) are received because (1) it is the preferred form of N for supporting algae growth (Harris, 1986, and Wetzel, 1983), (2) it can promote oxygen depletion through the nitrification process (Gelda et al., 2000a, and Hall, 1986), and (3) it is toxic to aquatic life at low concentrations (U.S. EPA, 1985 and 1998). The toxicity issue is a particularly timely one because of changes in national criteria that have occurred over the past 15 years (Heber and Ballentine, 1992, and U.S. EPA, 1985, 1996, 1998, and 1999) to protect aquatic life in surface water.

Typically used analytical methods determine the concentration of total ammonia (T-NH₃), which is the sum of the ionized (NH₄⁺) and un-ionized (NH₃) forms. In aqueous solutions, un-ionized, or free, ammonia (NH₃) exists in equilibrium with the ammonium ion (NH₄⁺) (Thurston et al., 1981b).



The fraction of T-NH₃ that exists as NH₃ (f) is described by the following equation (Messer et al., 1984):

$$f = 1/(10^{pk_a - \text{pH} - s} + 1) \quad (2)$$

Where

pk_a = negative logarithm of the acid dissociation constant for NH₄⁺ (NH₄⁺ ↔ NH₃ + H⁺), and

s = salinity correction term that accommodates solution activity.

The value of pk_a is a function of temperature (Emerson et al., 1975), and s is a function of ionic strength (Messer et al., 1984). This speciation relationship is important to ammonia toxicity because NH₃ is considerably more toxic than NH₄⁺ (U.S. EPA, 1998). This aqueous ammonia equilibrium is controlled primarily by pH and temperature; ionic strength is typically described as having a relatively minor influence. As pH and temperature increase and ionic strength decreases, the equilibrium shifts toward the NH₃ species. However, the toxicity of a certain concentration of NH₃ decreases as pH and temperature increase (U.S. EPA, 1985). These opposing effects have been accommodated in the development of water quality criteria for ammonia (U.S. EPA, 1985, 1998, and 1999).

Concentrations of T-NH₃ vary widely in time and space (vertically) in many lakes (Cole, 1994, and Wetzel, 1983) because of the reactive nature of this constituent. Biochemical processes that directly influence the T-NH₃ pool include sinks created by phytoplankton uptake (Harris, 1986) and nitrification (Cavari, 1977, and Hall, 1986) and ammonification (caused by decay of organic nitrogen, often localized within the sediments [DiToro et al., 1990]). Other loss pathways for T-NH₃ include export from a water body and volatilization of NH₃ (Effler et al., 1991b). Discharges from domestic wastewater treatment facilities can be particularly important sources of T-NH₃ for lakes that receive such effluent because of the relatively high (compared to fluvial inputs) concentrations that are typical of many of these effluents. Dynamics in NH₃ may be substantially different from those of the T-NH₃ pool because of uncoupled variations in pH (Brooks and Effler, 1990, and Effler et al., 1990). Furthermore, NH₃ (and NH₄⁺) is subject to substantial variations during a day in productive water because of diurnal variations in pH, driven by photosynthetic activity (Crumpton and Isenhardt, 1988).

The temporal distributions of T-NH₃ in the upper layer of a polluted hypereutrophic urban lake that receives discharge from a domestic wastewater treatment facility are documented and eval-

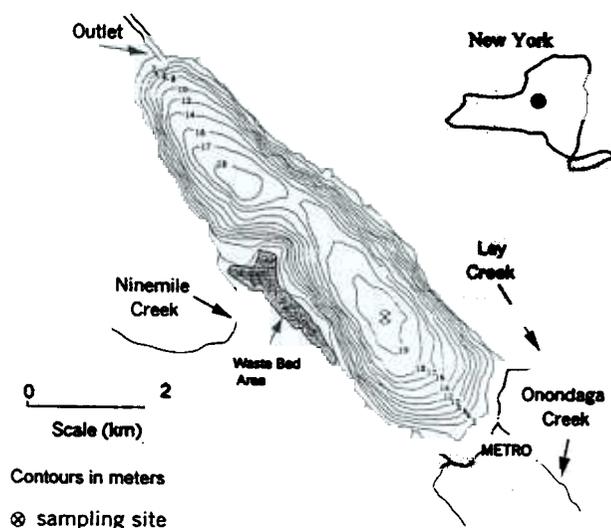


Figure 1—Onondaga Lake: bathymetry, lake sampling site, tributaries, and METRO.

uated here over a period of 10 years, 1989 through 1998. Changes in the ambient water quality criteria for ammonia (Heber and Ballentine, 1992, and U.S. EPA, 1985, 1996, 1998, and 1999) that have evolved during the 1984 to 1999 period are reviewed. The implications of the omission of the influence of ionic strength in the most recent criteria for application to this ionically enriched lake are demonstrated. The status of the lake with respect to national ammonia criteria for chronic toxicity is evaluated within the context of the changes in the criteria. Interannual and seasonal variations in conditions that influence the lake's status with respect to these criteria are described.

Finally, the implications of diurnal pH variations for the occurrence of exceedances of the acute criterion and selection of the appropriate time of day for monitoring status with respect to the chronic criterion are preliminarily investigated. This case study is valuable because it demonstrates the implications of changing ammonia criteria for a particularly polluted lake and it identifies salient issues to be considered in assessing status for other affected systems.

Onondaga Lake

Onondaga Lake is a hard-water, alkaline, dimictic lake, located in metropolitan Syracuse, New York (Figure 1). The lake has a surface area of 12.0 km², a volume of 131 × 10⁶ m³, and a maximum depth of 19.5 m (Figure 1). The lake's watershed (642 km²) currently includes a population of approximately 450 000. Three natural tributaries—Ninemile, Onondaga, and Ley Creeks (Figure 1)—contribute approximately 70% on average to the total flow to the lake (Effler, 1996). The lake discharges to the Seneca River, which, after combining with the Oneida River, flows into Lake Ontario. Onondaga Lake was oligo-mesotrophic before European settlement in the late 1700s (Rowell, 1996). The reception of increasing loads of domestic and industrial waste from the watershed that accompanied development and urbanization led to profound degradation of the lake (Effler, 1996). The lake's commercial cold-water fishery was eliminated by the late 1800s (Tango and Ringle, 1996), and the lake was closed to ice harvesting in 1901, swimming in 1940, and fishing in 1970 (Effler and Harnett,

1996). The lake is now hypereutrophic and severely polluted as a result of inputs of domestic and industrial waste (Effler and Harnett, 1996; Effler and Hennigan, 1996; and Hennigan, 1991).

Treated domestic waste from the Metropolitan Syracuse Treatment Plant (METRO) is discharged directly to the southern end of the lake (Figure 1). This discharge (average flow approximately 3.5 m³/s [80 mgd]) contributes approximately 20% of the annual inflow and is often the single greatest input in late summer (Effler et al., 1996a). The METRO is the dominant source of phosphorus (P) and N for the lake, currently contributing 60, 90, and 80% of the total annual external loads of total P (TP), T-NH₃, and total N (TN), respectively (Effler et al., 1996a). The prevailing areal annual loads of TP (approximately 8 g/m²·a) and TN (approximately 200 g/m²·a) (Effler et al., 1996a) are among the highest reported in the literature (Brezonik, 1972, and Stauffer, 1985).

The METRO, which uses contact stabilization modification of activated sludge, was not intended to attain significant nitrification. However, substantial nitrification is currently achieved within METRO during the warmer summer months (Effler et al., 1996a), which causes seasonal shifts in the contributions of T-NH₃ and oxidized forms of N (nitrate, NO₃⁻ and nitrite, NO₂⁻) to the discharged N load. Substantial interannual differences in the timing and extent of nitrification achieved at METRO have been observed (Effler et al., 1996a, and Gelda et al., 1999).

Manifestations of hypereutrophy in the lake include severe phytoplankton blooms (Effler et al., 1996a), poor clarity (Perkins and Effler, 1996), rapid loss of dissolved oxygen (DO) from the hypolimnion (Effler et al., 1996a), subsequent hypolimnetic accumulations of reduced byproducts of anaerobic metabolism (hydrogen sulfide, methane, and ammonia), and DO depletion in the upper layers during the fall mixing period associated with the oxidation of these byproducts (Adress and Effler, 1996, and Effler et al., 1988). A large fraction of the lake's fish population exits to the Seneca River during the period of depressed DO in fall (Tango and Ringle, 1996).

The primary source of industrial waste to the lake has been a soda ash (Solvay Process)—chlor-alkali facility located on the lake's western shore (Figure 1). Until its closure in 1986, this facility discharged large quantities of ionic (mostly chlorine, Cl⁻; sodium, Na⁺; and calcium, Ca²⁺) and T-NH₃ waste directly to the lake and, later, to the lake via Ninemile Creek (Effler, 1987 and 1996). These discharges had profound effects on the lake's chemistry, including the level and composition of salinity (Effler, 1996, and Effler et al., 1986), and related effects on precipitation of calcium carbonate (CaCO₃), alkalinity, and pH (Driscoll et al., 1994). Salinity and its primary component concentrations decreased (Effler, 1996), alkalinity increased, and pH increased (as a result of reduced CaCO₃ precipitation [Driscoll et al., 1994]) following closure of the facility in 1986. Substantial residuals of these inputs continue to enter the lake, particularly from areas where the most recent waste beds were formed along Ninemile Creek (Effler et al., 1991a and 1996b; Figure 1). These residuals increase the lake's salinity (Doerr et al., 1994) and promote deposition of CaCO₃ in the lake (Womble et al., 1996) and development of salinity-based stratification in the Seneca River (Effler et al., 1997).

The lake is severely polluted with T-NH₃ (Brooks and Effler, 1990) as a result of the load received from METRO (Canale et al., 1996). Ammonia concentrations increase progressively in the hypolimnion, particularly after the onset of anoxia (approximately late May), mostly as a result of releases from the underlying sediments (Wickman, 1996). Increases in T-NH₃ are observed

Table 1—Summary of revisions of the CCC for T-NH₃.

CCC	Dependencies	Averaging period	Comments
1984–1985	pH, <i>T</i> ^a	4 days	As NH ₃ ; more stringent criterion for salmonids
1992	pH, <i>T</i> ^a	4 days	As NH ₃ ; CCC increased by 18.5%
1996	pH, <i>T</i> ^a	4 days	As NH ₃ ; TCAP eliminated, increased CCC at <i>T</i> > 20 °C
1998	pH	30 days ^b	As T-NH ₃ ; eliminated <i>T</i> dependency
1999	pH, <i>T</i>	30 days ^c	As T-NH ₃ ; separate criterion for early life stages

^a The effect of *I* on ammonia speciation could be accommodated in conversion from NH₃ to T-NH₃.

^b The 4-day average cannot exceed 2 × CCC.

^c The 4-day average cannot exceed 2.5 × CCC.

with the approach to the sediment–water interface; seasonal maxima greater than 7 mg N/L have been observed (Brooks and Effler, 1990). Concentrations greater than the national ammonia chronic criterion (U.S. EPA, 1985) were documented for the entire water column for the spring to fall period of 1988 (Effler et al., 1990). The margins of exceedance remained greater within the epilimnion than in the hypolimnion (despite lower T-NH₃ concentrations in the upper layers) because pH was substantially greater in the upper layers (Effler et al., 1990). The analysis presented here focuses on the upper layers of the lake because the anoxic–anaerobic conditions of the hypolimnion are considered to be the primary limiting condition for aquatic life in the lower layers. Concentrations of T-NH₃ (and NO₃⁻) remain greater than levels considered limiting to phytoplankton growth (Bowie et al., 1985) in the lake's upper layers.

Methods

Field and Laboratory. The lake was monitored weekly at a buoyed deep water (approximately 19.5 m) location (Figure 1) in the lake's southern basin for the April to October period from 1989 to 1998. This site is representative of lake-wide conditions (Effler, 1996). Temperature (*T*) and pH were measured in the field (Hydrolab Surveyor 3 [Hydrolab Corporation, Austin, Texas]) at 1-m depth intervals. Samples for laboratory analyses of T-NH₃ (U.S. EPA, 1983) and Cl⁻ (APHA et al., 1985) were collected at depth intervals of 1 to 2 m. Chloride is a reliable measure of salinity (*s*) and ionic strength (*I*, mol) in this lake (Effler, 1996). Sampling and field measurements were conducted at mid-morning (approximately 10:00). Hourly measurements of *T* and pH were recorded with a Hydrolab Datasonde 3 at a fixed depth of 1 m for the May 1 to 15 period in 1996.

Calculations. The water quality status of Onondaga Lake with respect to ammonia is evaluated here by comparing measured distributions of T-NH₃ to the various recent U.S. Environmental Protection Agency (U.S. EPA) ammonia criteria (Heber and Ballentine, 1992, and U.S. EPA, 1985, 1996, 1998, and 1999). The criteria, as NH₃, were established as a function of pH and *T*, according to the first three versions of the criteria (Heber and Ballentine, 1992, and U.S. EPA, 1985 and 1996). Previous calculations of free ammonia concentrations for Onondaga Lake were based on measurements of T-NH₃, pH, *T*, and Cl⁻ (as a measure of ionic strength [Effler et al., 1990]). Onondaga Lake currently lacks a well-oxygenated, cold-water habitat sufficient to support salmonid fish species. Therefore, only the less stringent non-salmonid ammonia criteria are addressed here. Margins of exceedance were calculated as the ratio of the observed ammonia concentration (T-NH₃, for U.S. EPA 1998 and 1999 criteria, and NH₃, for earlier criteria) to the criteria concentrations.

Review of Ammonia Criteria. National toxicity criteria developed by U.S. EPA have three components (U.S. EPA, 1991): (1) magnitude, the allowable concentration, (2) duration, the period of time (averaging period) over which concentrations are averaged to compare to the allowable value, and (3) frequency, how often the criteria can be exceeded. The allowable (upper bound) concentrations—the criterion continuous concentration (CCC) and the criterion maximum concentration (CMC)—are intended to protect aquatic life against chronic and acute toxicity effects (respectively) of the toxic substance (U.S. EPA, 1991).

An exceedance occurs whenever the instantaneous concentration is above the CCC (or CMC) (U.S. EPA, 1991). An excursion occurs whenever the average concentration over the specified duration of the averaging period is above the CCC (U.S. EPA, 1991). The prevailing applicable state standards for ammonia in New York correspond to the magnitude component of the 1984–1985 criteria (U.S. EPA, 1985). Changes in the state standards in response to the most recent revisions are presently under consideration.

The national toxicity criteria for ammonia have been revised five times in the past 15 years (Heber and Ballentine, 1992, and U.S. EPA, 1985, 1996, 1998, and 1999; Table 1). The 1984–1985 criteria incorporated, for the first time, the effects of both pH and *T* as they influence ammonia toxicity and the equilibrium between NH₃ and NH₄⁺ (U.S. EPA, 1985). The CCC and CMC values were functions of pH and *T*. The 1984–1985 criteria incorporated a factor that capped the effect of temperature on toxicity (TCAP) for *T* greater than 20 °C (greater than 15 °C for salmonid systems). The TCAP was a conservative assumption “incorporated as a provision against uncertainties stemming from lack of toxicity data at higher temperatures” (U.S. EPA, 1996). These criteria required that 4-day average NH₃ concentrations not exceed the CCC on an average of once every 3 years and that 1-hour average NH₃ concentrations not exceed the CMC on an average of once every 3 years (U.S. EPA, 1985).

The criteria were updated in 1992 (Heber and Ballentine, 1992), 1996 (U.S. EPA, 1996), 1998 (U.S. EPA, 1998), and 1999 (U.S. EPA, 1999). The 1992 update eliminated controversial toxicity results reported for the white sucker (a fish) that had been incorporated to the development of the 1984–1985 criteria. This resulted in an 18.5% increase in the CCC (Heber and Ballentine, 1992) (i.e., less stringent criteria). The 1996 revision eliminated TCAP based on additional toxicity testing (U.S. EPA, 1996). As a result, the CCC was raised significantly for *T* greater than 20 °C. The 1984–1985 criteria and the 1992 and 1996 revisions were developed and expressed primarily in terms of NH₃. Corresponding limits were also presented in terms of T-NH₃ concentrations,

determined from equilibrium calculations with $s = 0$ (Heber and Ballentine, 1992, and U.S. EPA, 1985 and 1996).

The national ammonia criteria were revised again in 1998 to take into account newer data, better models, and improved statistical methods (U.S. EPA, 1998). Two significant changes were made to create the 1998 criteria. First, these criteria were developed in terms of T-NH₃. Second, the values were dependent only on pH (U.S. EPA, 1998). These simplifications have clear advantages in facilitating application of the criteria. Furthermore, the averaging period applicable for the CCC was increased to 30 days, as long as the 4-day average within the 30-day period did not exceed 2 times the CCC (U.S. EPA, 1998). The 1999 ammonia criteria incorporate comments received from the 1998 update and include revisions of the pH and temperature relationship of the CMC and CCC (U.S. EPA, 1999). Like the 1998 criteria, the 1999 criteria were developed in terms of T-NH₃.

As a result of these revisions, the CMC is now dependent on pH and fish species, and the CCC is dependent on pH and temperature (U.S. EPA, 1999). At lower temperatures, the CCC is also dependent on the presence or absence of early life stages of fish (U.S. EPA, 1999). In addition, the averaging period for the CCC is now 30 days, as long as the 4-day average within the 30-day period does not exceed 2.5 times the CCC (U.S. EPA, 1999). The 1999 revisions represent substantial changes in CCC. The dependencies of the various criteria on pH and T are presented here in terms of T-NH₃ for $T = 20^\circ\text{C}$ (Figure 2a) and pH = 8.0 (Figure 2b, typical values for Onondaga Lake) for $s = 0$. The CCC was more sensitive to changes in pH (Figure 2b) than those in T (Figure 2a). The 1998 CCC is independent of T (Figure 2a). The CCC has increased (i.e., become less stringent) during the past 15 years (Figures 2a and 2b).

Ionic Strength Adjustments. Salinity is relatively low in most freshwater bodies (e.g., global mean salinity is approximately 0.12‰ for rivers [Wetzel, 1983]); so the effect of ionic strength on f is minor for these dilute systems (Figure 3). In fact, published calculations of the percent NH₃ in freshwater have omitted adjustments for ionic strength in several cases (e.g., Emerson et al., 1975, and Thurston et al., 1979). However, in more saline (i.e., hard) water, ionic strength can cause a significant decrease in the percent NH₃ (Messer et al., 1984).

The effect of ionic strength on ammonia speciation is of particular interest in Onondaga Lake because of its elevated salinity. Before the soda ash-chlor-alkali facility closed, Onondaga Lake had a salinity of approximately 3.3‰, corresponding to an I of approximately 0.075 mol, primarily as a result of ionic waste received from the facility (Effler, 1996). The lake continues to have an unusually high salinity (approximately 1.2‰ [Effler, 1996]) because of residual inputs from the facility and natural inputs associated with its hydrogeologic setting (Perkins and Romanowicz, 1996); the ionic strength is currently approximately 0.028 mol. If the effects of ionic strength on f were ignored or assumed to be negligible (i.e., $I = 0$ mol and $f = 0.038$), f would be overestimated by 27% for preclosure conditions and 17% for postclosure (present) conditions (Figure 3). Neglecting the effect of I for Onondaga Lake introduces a systematic error in f equivalent to a falsely reported pH that is high by approximately 0.1 units (e.g., Figure 2b).

Calculation of Status. The 1998 and 1999 revisions to the national ammonia criteria have fundamentally changed the calculation of status in water bodies with high ionic strength. The 1984–1985, 1992, and 1996 criteria were developed in terms of

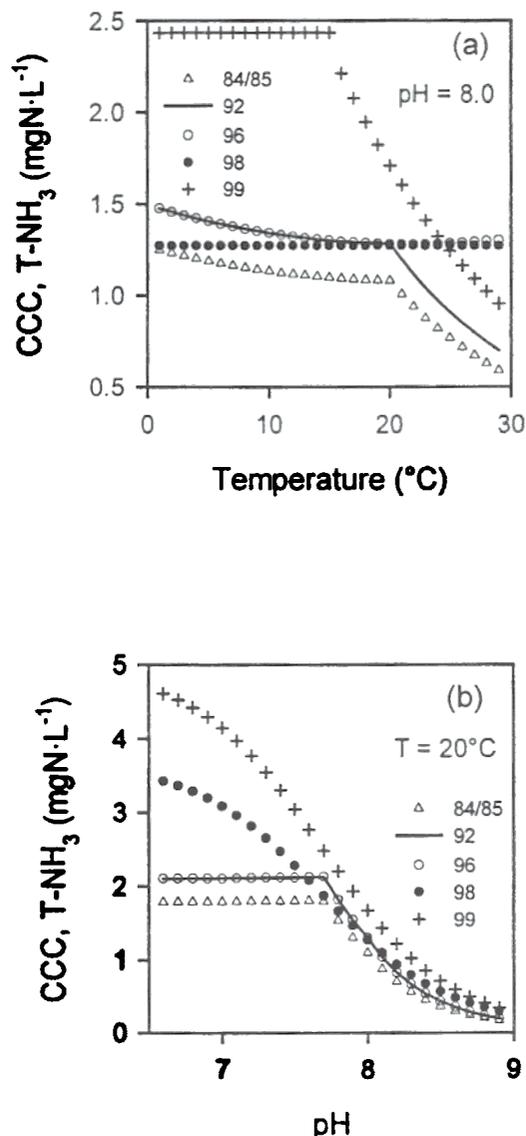


Figure 2—Dependencies of CCC for T-NH₃ on (a) temperature and (b) pH for five revisions of the criteria, identified by year ($I = 0.0$ mol).

NH₃. Thus, the effect of I on f could be accommodated (by specification of s , equation 2 [Effler et al., 1990, and Messer et al., 1984] in the calculation of NH₃ and back calculation to a T-NH₃ concentration that was thereby adjusted for ionic strength. Because the 1998 and 1999 criteria were developed in terms of T-NH₃, the influence of I on ammonia speciation and status with respect to criteria can no longer be explicitly accommodated.

Comparisons of the various CCC values are presented again in terms of T-NH₃ with fixed values of $T = 20^\circ\text{C}$, pH = 8.0, but with $I = 0.028$ mol (Figure 4, typical value for Onondaga Lake). The 1984–1985, 1992, and 1996 CCC values are 17% greater at this ionic strength (Figure 4), relative to the earlier representation ($I = 0.0$ mol, Figure 2). Ionic strength has no effect on the 1998 and 1999 CCC (Figures 2 and 4). Consequently, the 1998 and 1999 CCC can be more stringent than the earlier criteria (Figure 4) for saline systems (such as Onondaga Lake) because these revisions

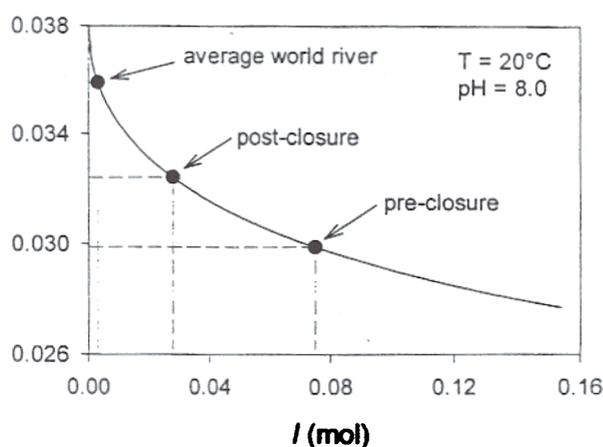


Figure 3—Dependence of the fraction of T-NH₃ as NH₃ (f) on I , for $T = 20\text{ }^{\circ}\text{C}$ and $\text{pH} = 8.0$. Three salinity conditions are identified for reference: average world river and Onondaga Lake before (pre-closure) and after closure (post-closure) of the soda ash–chlor-alkali facility.

do not allow explicit accommodation of I . This may be an unintended artifact of expressing the most recent criteria in terms of T-NH₃ that will be manifest in saline, ammonia-polluted systems such as Onondaga Lake.

To analyze the status of this system with respect to ammonia toxicity criteria, an additional hypothetical criterion that adjusts the most recent limits (U.S. EPA, 1998 and 1999) 17% higher is specified to accommodate the prevailing ionic strength conditions of the lake. This may be viewed as the minimum *matrix* effect of salinity, which recognizes the difference between the concentration and solution activity of ionic species (Messer et al., 1984).

Results and Discussion

Distributions of Total Ammonia. Substantial interannual differences in the temporal patterns of the T-NH₃ pool of the upper layers of the lake were observed for the April to October period during the 10 years of study, although certain recurring features have emerged (Figure 5). However, the overriding feature of these data is that T-NH₃ concentrations in this lake have been extremely high relative to other productive systems. For example, the average concentration over the April to June period for the 10 years was 2.3 mg N/L. Concentrations of T-NH₃ are reduced to below detection limits ($<10\text{ }\mu\text{g N/L}$) in the epilimnia of most eutrophic lakes during summer as a result of algal uptake (Wetzel, 1983). The high T-NH₃ concentrations of Onondaga Lake are primarily a result of T-NH₃ loads received by the lake from METRO (Canale et al., 1996, and Effler et al., 1996a).

Concentrations at spring turnover ranged from 1.5 to 3.5 mg N/L during the study period (Figure 5). These broad variations in concentration largely reflect changes in dilution of the METRO input associated with natural variations in antecedent tributary flow (Figure 6). A dilution model is supported for this relationship because the inverse of tributary flow during the December to March period explains 78% of the interannual variation observed in T-NH₃ at spring turnover during the 1989 to 1998 period (Figure 6). Dilution model relationships are characteristically manifest downstream of localized continuous inputs such as wastewater discharges (Johnson, 1979, and Manczak and Florczyk, 1971).

The interannual differences in the patterns reflect year-to-year differences in the relative magnitudes of the sources and sinks of T-NH₃. The sources of decay of organics and vertical mixing are relatively small during summer stratification and are approximately in balance with the loss of T-NH₃ by volatilization of NH₃ (Canale et al., 1996, and Gelda et al., 2000a). The decrease in the T-NH₃ pool from mid- to late summer observed in most years (Figure 5) is primarily a result of seasonal reductions in the effluent T-NH₃ concentration of METRO and the in-lake loss process of phytoplankton uptake (Canale et al., 1996). Interannual differences in the patterns for this interval are probably mostly associated with the wide year-to-year variations in the extent of nitrification achieved within METRO (Effler et al., 1996a, and Gelda et al., 1999).

Little nitrification occurs in the lake's upper layers during the spring to late summer period (Gelda et al., 1999). However, abrupt increases in nitrification (approximately 40%) occur in certain years during the fall mixing period (e.g., mid-September through October) that cause significant year-to-year differences in the in-lake T-NH₃ pattern during this portion of the study period

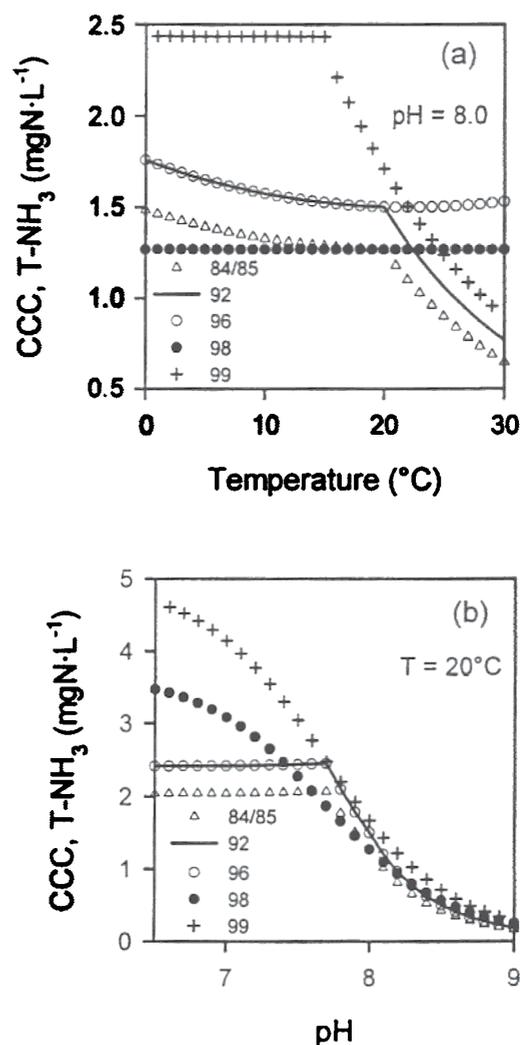


Figure 4—Dependencies for CCC of T-NH₃ on (a) temperature and (b) pH for five revisions of the criteria, identified by year ($I = 0.028\text{ mol}$).

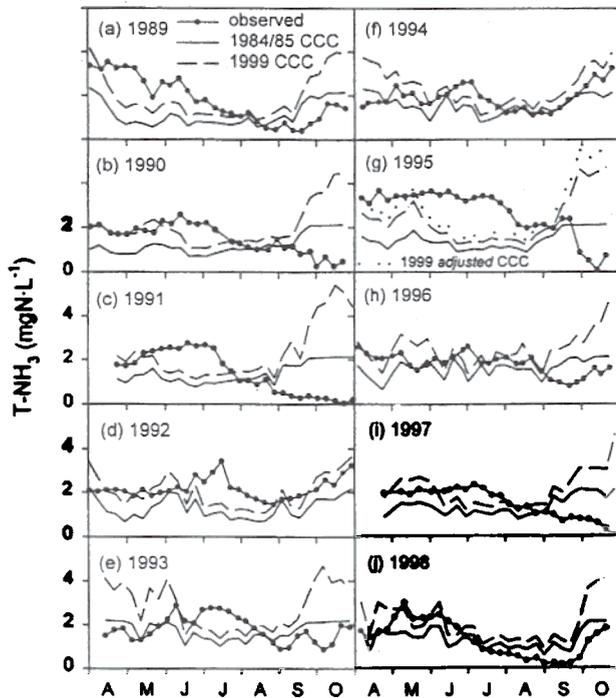


Figure 5—Time series of T-NH₃ and the 1984–1985 and 1999 CCC for T-NH₃ for the upper layers of Onondaga Lake: (a) 1989, (b) 1990, (c) 1991, (d) 1992, (e) 1993, (f) 1994, (g) 1995 with CCC for adjusted 1999 included for reference, (h) 1996, (i) 1997, and (j) 1998.

(Gelda et al., 2000a). For example, significant increases in the T-NH₃ pool occurred in September and October of 1992 (Figure 5d) and 1994 (Figure 5f) with the entrainment of the enriched hypolimnion, in the absence of nitrification events (Gelda et al., 2000a). In contrast, decreases in T-NH₃ were observed over the same interval of several years in response to nitrification events (Figure 5g [Gelda et al., 2000a]).

Lake Status with Respect to Chronic Criteria. The various chronic criteria for ammonia toxicity have been annually exceeded and by a wide margin during the study period (Figure 5 and Table 2). For example, T-NH₃ concentrations in the lake’s upper layers exceeded the 1984–1985 CCC, the 1999 CCC, and the adjusted 1999 CCC for intervals of at least 168, 147, and 133 days, respectively, in 1995 (Figure 5g). The average margin of exceedance of the 1984–1985 CCC during the 10-year study for the April to June period was 2.2 (Figure 5). Within the context of application of the toxicity criteria, the exceedances apparently have been continuous over extended intervals (Figure 5 and Table 2), thereby representing multiple excursions of the criteria and violations of prevailing state standards.

Undoubtedly, exceedances, excursions, and violations extended before monitoring began in each year during the 10-year study period (Figure 5). The CCC values for the 1999 criteria were greater (i.e., less stringent) than the 1984–1985 values throughout the 10-year study period; the differences were greatest for the colder months of April, May, September, and October (Figure 5). The less stringent adjusted 1999 criteria resulted in reduced margins and durations of exceedance (Figure 5g and Table 2). The differences between the 1984–85 and 1999 criteria were greater

by comparison (Figure 5g and Table 2). Two factors contributed to the CCC not being exceeded in the fall of 1995: (1) the abrupt reduction in the T-NH₃ pool in autumn associated with a nitrification event and (2) increased values of CCC. The first factor has previously been described as an irregular occurrence (nitrification event [Gelda et al., 2000a]); the second is typically recurring, attributable to a seasonal decrease in pH (Figure 7a; cf., Figure 2b).

The temporal pattern of pH in the upper layers of this lake during the spring to late summer period (Driscoll et al., 1994) and in other productive north temperate lakes (Wetzel, 1983) is primarily driven by the dynamics of primary production (consumption of CO₂). A peak in pH is often observed in spring, associated with the most significant phytoplankton bloom of the year (Figure 7a [Effler, 1996]). Substantial interannual differences in the detailed pattern of pH are observed as a result of differences in the timing of phytoplankton blooms. However, the decreases in pH during September and October (Figure 7a) are recurring, associated with the entrainment of layers enriched in CO₂ and reduced substances (Address and Effler, 1996, and Effler et al., 1988) that occurs during autumn mixing.

No long-term trends in pH were observed in the upper layers of the lake during the 1989 to 1998 period, as illustrated here for the months of April (Figure 7b) and June (Figure 7c). Interannual differences in the magnitude of the T-NH₃ pool, not variations in pH, have been primarily responsible for the year-to-year differences in the average margin of exceedance in Onondaga Lake for the April to August interval. Differences in the T-NH₃ pool explained 67% of the interannual variations in this average margin of exceedance.

Changes in the ammonia criteria during the past 15 years have not been great enough to substantially change the status of Onondaga Lake with regards to this water quality criterion (Figure 5g and Table 2). The effect of the decrease in the stringency of the criteria over time on the status of the lake is illustrated here within the context of maximum margins of exceedance of the CCC for each year, according to each of the criteria (Figure 8, adjusted CCC for 1998 and 1999 included). The reduced stringency effect has been progressive if the 1998 and 1999 revisions are adjusted

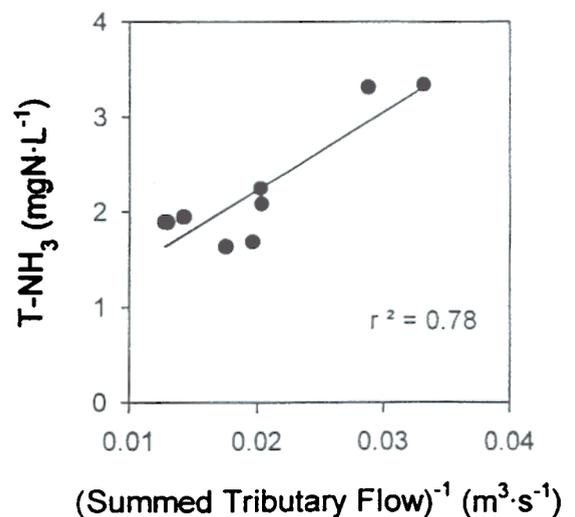


Figure 6—Evaluation of the relationship between T-NH₃ in Onondaga Lake in early April and antecedent summed tributary flow for the December to March period.

Table 2—Summary of features of exceedances of the CCC for T-NH₃ in the upper layers of Onondaga Lake for the 1989–1998 period.

Year	Maximum margin of exceedance			Duration of exceedance, d		
	84/85	99	99 adjusted	84/85	99	99 adjusted
1989	5.1	2.4	2.0	140	112	105
1990	3.2	2.1	1.8	140	77	35
1991	3.4	2.3	2.0	98	77	56
1992	3.1	2.3	2.0	196	119	98
1993	2.7	2.0	1.7	91	49	49
1994	2.6	1.8	1.5	154	49	35
1995	3.7	2.7	2.3	168	147	133
1996	3.1	1.9	1.6	147	63	35
1997	2.6	1.8	1.6	112	56	42
1998	2.3	1.4	1.2	77	35	28
10-year average	3.2	2.1	1.8	132	78	62

for the effect of ionic strength (Figure 8). If the influence of ionic strength is not accommodated, the 1998 revision is more (or at least as) stringent than the 1996 revision for the conditions of all 10 years. It would be more stringent than the 1992 revision for 4 years (Figure 8).

Maximum margins of exceedance were always greatest for the 1984–1985 CCC and least for the adjusted 1999 CCC. The 10-year average maximum margin of exceedance for the adjusted 1999 CCC was 15% less than the unadjusted (*I* = 0) 1999 CCC and 44% less than the 1984–1985 CCC (Table 2). In a few years (1990, 1994, and 1996), application of the adjusted 1999 CCC reduced the duration of exceedance by more than 100 days compared to application of the 1984–1985 CCC. Compared to the unadjusted 1999 CCC, application of the adjusted 1999 CCC resulted in substantial (>20 days) decreases in the duration of exceedance for 4 of the 10 years (1990, 1991, 1992, and 1996; Table 2). The implications of the changes in the criteria with respect to T-NH₃ loading reductions (i.e., treatment levels at METRO) required to avoid exceedances of the CCC are evaluated with a probabilistic mass balance modeling framework by Gelda and Effler (2000).

Diurnal Variations in pH. Variations in pH occur within a day in the productive depths of streams and lakes, associated mostly with changes in the concentration of CO₂. These dynamics are largely associated with plant metabolism and are driven by the diurnal cycle of incident light (Cole, 1994, and Wetzel, 1983). Diurnal patterns of pH have, in fact, been used as a basis to estimate primary production by calculating changes in the CO₂ pool. The classic diurnal pattern (Crumpton and Isenhardt, 1988, and Westlake, 1974) has the form of a sine wave, with a minimum pH value just before dawn, followed by progressive increases through late afternoon (daily maximum) and subsequent progressive decreases until the following dawn. The pH changes within a day are greatest when primary production is the highest, mixing-based exchanges of CO₂ with the atmosphere are minimal, and chemical buffering against pH changes is minimal, for example, when high concentrations of plant biomass and critical nutrients, clear skies, and calm conditions are present for a low-alkalinity system.

Diurnal changes in pH are problematic for the evaluation of status with respect to the ammonia criteria with regards to the appropriate timing of pH measurements. These problems are di-

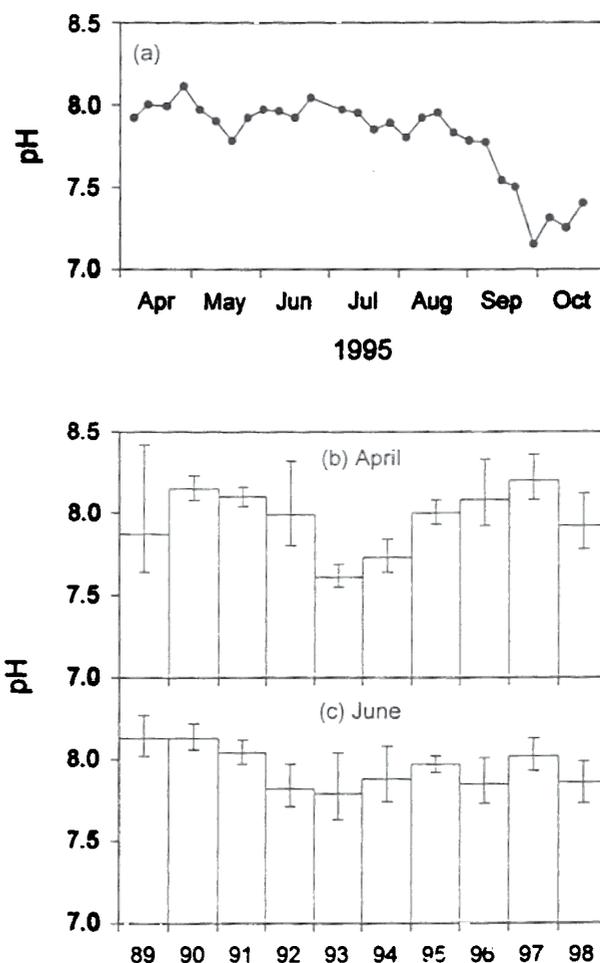


Figure 7—The pH conditions in the upper layers of Onondaga Lake: (a) time series for 1995, (b) pH corresponding to mean H⁺ concentration for April for the 1989 to 1998 period, and (c) pH corresponding to mean H⁺ concentration for June for the 1989 to 1998 period. Vertical bars correspond to ±1 standard deviation from mean H⁺ concentration.

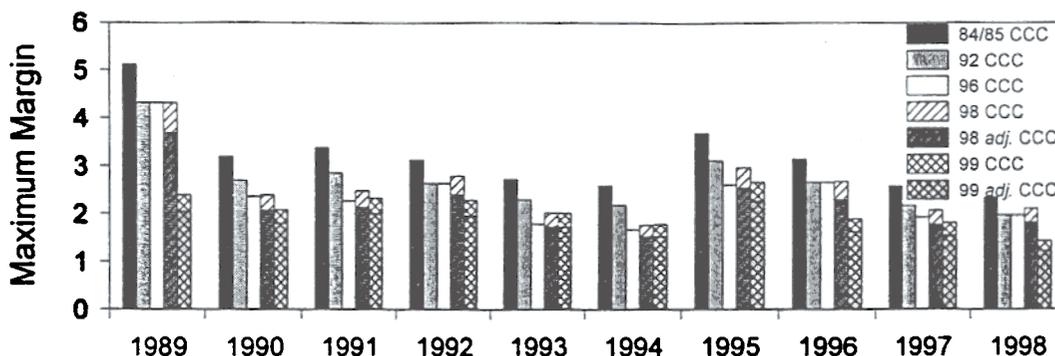


Figure 8—Comparison of annual maximum margins of exceedance of the CCCs for T-NH₃ in Onondaga Lake during the 1989 to 1998 period for revisions of the national criteria, identified by year.

rectly linked to the different time scales of the chronic and acute criteria (U.S. EPA, 1998). Appropriate application of the chronic criteria implicitly requires a pH value that corresponds to the daily average H⁺ concentration. Under ideal conditions (i.e., clear sky, uniform water surface turbulence, and uniform phytoplankton concentrations), this could be reasonably measured at mid-morning (Crumpton and Isenhardt, 1988, and Verduin, 1960). However, measured diurnal pH patterns have been observed to differ widely from the ideal (Verduin, 1960) because of natural variations in mediating conditions. Furthermore, daily maximum pH values are systematically greater than the value that corresponds to the daily mean H⁺ concentration. Thus, a measurement made at a time of day that is appropriate for representation of daily average conditions systematically understates the status with respect to the acute criterion and may result in a failure to identify exceedances of this criterion. These problems could be readily avoided with frequent measurements (e.g., hourly) within each day, but the necessary monitoring effort would be considered unrealistic in many cases.

Frequent and wide variations in pH and, therefore, status with respect to both the acute (CMC) and chronic (CCC) criteria occurred in the upper layers of Onondaga Lake during the 14-day period of hourly measurements in May 1996 (Figure 9). The range of pH values within a day was less than 0.2 units on nine days, greater than 0.3 units on four days, and approximately 0.9 units on May 8 (Figure 9a). Even larger variations in pH would be expected for a system of equal primary production and meteorological conditions but with less buffering capacity. The temporal patterns in the status with respect to the criteria were driven by the temporal structure in pH (Figures 9a through 9c) because T-NH₃ concentrations were relatively uniform by comparison during the period.

Little of this structure would have been resolved by the fixed frequency (weekly) long-term monitoring program (Figure 9). Hourly pH measurements resolved the occurrence of an exceedance of the acute criterion on May 8 (Figure 9b). It is likely that other exceedances of the acute criterion (U.S. EPA, 1998) occurred in 1996 and the other years of the monitoring program (Figure 5). First, T-NH₃ concentrations (Figure 5) and pH values (Figure 9a) in the lake during the early May period of 1996 were not unusual compared to other portions of the 1996 study period or other years (Figures 7b and 7c). Second, the 1996 hourly pH measurements were not made during a period of particularly high primary production. For example, the average chlorophyll concentration from the fixed frequency monitoring for that period (n = 3) was only 16.0 μg/L, compared to an average value for the April to

October period of 1996 of 49.6 μg/L (typical annual average for the overall study period [Effler et al., 1996a]).

Substantial deviations from the ideal daily sine wave temporal pattern were observed for pH during the period of hourly measurements (Figure 9a). Likely contributing factors are uncoupled dynamics in important mediating forcing conditions, including

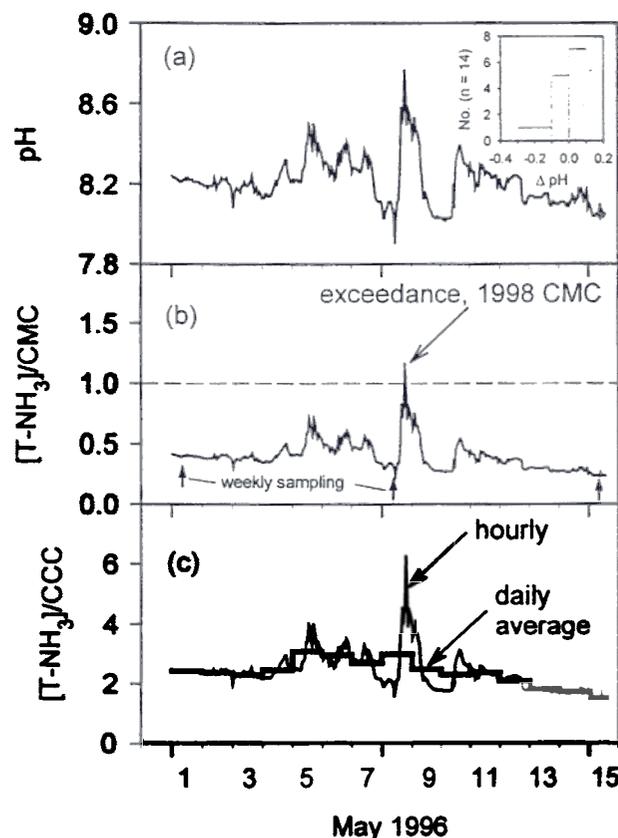


Figure 9—Time series for the upper layers (1 m) of Onondaga Lake, May 1 to 15, 1996: (a) pH with inset of the distribution of deviations between the pH determined from the mean H⁺ concentration and pH measured at 1000 hours, (b) the ratio of T-NH₃ to CMC (>1 is an exceedance), and (c) ratio of T-NH₃ to CCC, hourly and as a daily average.

incident light (e.g., cloud cover), turbulence at the air–water interface (e.g., wind speed and direction), and phytoplankton biomass. Increasing the number of days of hourly observations of pH will support mid-morning (or early afternoon, according to the sine wave characteristics) as the most representative time, on average, to measure the daily average H^+ concentration (Westlake, 1974). As evidenced here (see inset of Figure 9a), substantial and largely unavoidable uncertainty in the representation of daily average pH and, thereby, status with respect to the CCC accompanies a monitoring program design that adopts a fixed (even at the single most appropriate time) time of day for measurements. Measurements substantially shifted from this time of day (e.g., early morning to late afternoon) will result in systematic misrepresentation of daily average conditions and, thereby, the status with respect to the chronic ammonia criterion.

Some of the more subtle details of the application of criteria and standards, which are not particularly important in resolving the prevailing degraded conditions documented here (Figure 5g and Table 2), may become critical with respect to the level of treatment (cost) necessary to meet standards and water quality goals. For example, the significant diurnal changes in pH that can occur in this and other productive systems affect the duration component of the criteria and standards applied. The scientific literature supports the position that substantial fluctuations in the concentrations of toxic constituents result in increased adverse effects to aquatic organisms compared to temporally uniform conditions at the average concentration (U.S. EPA, 1991). This effect has been demonstrated specifically for ammonia (Thurston et al., 1981a). The diurnal changes in pH documented here (Figure 9a) translate to rather wide fluctuations in NH_3 concentrations (as equilibrium conditions between NH_4^+ and NH_3 [equation 1] are maintained [Thurston et al., 1981b]) and status with respect to the chronic criterion (Figure 9c). For example, on May 8, 1996, the margin of exceedance of the 1998 CCC increased by more than a factor of 3 as a result of the increase in pH (Figure 9c). This form and time scale of fluctuation should be considered for productive systems for protective application of criteria and standards.

The most recent revision of the criteria (U.S. EPA, 1999) may not be protective in this regard as a result of the increase to a 30-day averaging period, as long as the 4-day average T- NH_3 concentration does not exceed 2.5 times the CCC. Fluctuations of a magnitude of 2.5 times CCC could well occur within individual days in this lake and other productive systems, associated with diurnal variations in pH, and yet not be manifest on the time scale of 4 days. Until research is conducted to evaluate the relationships among frequency and period of fluctuations of NH_3 and its toxic effect, it may be prudent (and protective) to apply the 4-day (rather than the 30-day) averaging period to productive ammonia-polluted surface waters that experience substantial diurnal changes in pH. Adoption of this policy results in substantially more stringent requirements for treatment in the case of METRO and Onondaga Lake (Gelda and Effler, 2000). Further documentation of diurnal pH changes over longer periods will contribute to resolution of this issue for this system.

Management Perspectives. A mass-balance model for the primary forms of N was developed and successfully tested for Onondaga Lake by Canale et al. (1996) to support evaluation of various remediation strategies to eliminate violations of standards. The model accommodates the important transport features of the lake, quantifies the effects of the primary processes regulating the T- NH_3 pool in the lake, and provides the appropriate seasonal

resolution to address the T- NH_3 issue for the lake's upper layers (Canale et al., 1996). This model has been embedded in a larger probabilistic framework that accommodates important sources of variability, including interannual variations in tributary flow, in-lake nitrification, and pH (Gelda et al., 2000b).

Applications of these predictive frameworks establish that significant reductions in the external loading of T- NH_3 from METRO will be necessary to eliminate excursions of criteria and violations of standards (Effler and Doerr, 1996, and Gelda et al., 2000b). However, if the less stringent 1999 ammonia criteria were adopted as the standard in New York, these reductions would be significantly reduced, particularly during the colder months when nitrification is more difficult to achieve. Nonpoint sources are not a focus for these rehabilitative efforts because of their small contribution (<10% of external load presently) and lack of susceptibility to substantive reductions (Effler, 1996). Analyses conducted with the probabilistic framework (Gelda and Effler, 2000) indicate *regulatory discretion*, related to the interpretation and application of the standards, could play an important role in establishing the effluent concentrations necessary to meet ammonia goals for the lake.

A U.S.\$350 million cleanup plan for Onondaga Lake was recently approved. This plan represents the single greatest public works project ever undertaken in Onondaga County. The plan calls for reductions in METRO effluent concentrations in two stages during a 15-year period. The METRO effluent limits starting in 2004 will be 3.3 mg N/L during the November to May period and 1.65 mg N/L during the June to October period (as 30-day moving average values). In 2012, the limits will be reduced to 2 and 1 mg N/L for these intervals, corresponding to a reduction of approximately 85% from prevailing loading conditions. Extensive denitrification is not recommended to avoid significant reductions in the N:P ratio in the lake that could promote proliferation of nuisance filamentous N_2 -fixing cyanobacteria (Smith, 1985).

Conclusions

Concentrations of T- NH_3 in the upper waters of Onondaga Lake were extremely high during the study period of 1989 to 1998 because of discharges from METRO. The average T- NH_3 concentration during the April to June period for the 10 years was 2.3 mg N/L. Concentrations at spring turnover ranged from 1.5 to 3.5 mg N/L; interannual differences for this time of year were primarily regulated by the dilution of the METRO input provided by antecedent (i.e., December to March) tributary flow.

Review of the revisions ($n = 5$) of the national ammonia criteria for chronic toxicity made during the past 15 years established that the criteria have become progressively less stringent for low ionic strength conditions. The most recent (1998 and 1999) revisions can be more stringent for Onondaga Lake and other high ionic strength systems because they do not allow explicit accommodation of I. The various chronic criteria and the prevailing state standard were annually exceeded in the lake by a wide margin during the study period. For example, the 1984–1985 CCC (existing New York standard) was exceeded by an average margin of 2.2 for the April to June period and for durations longer than 75 days during the 10-year study. Significant reductions in external loading of T- NH_3 from METRO will be necessary to eliminate violations of the present, or future revisions of, state standards.

Substantial diurnal variations in pH occurred in the lake's upper layers during the 14-day period of hourly measurements, including a maximum that resulted in an exceedance of the 1998 acute

criterion. These diurnal changes in pH are important with respect to the appropriate timing of pH measurements and should be considered in the design of programs to assess status and in application of criteria for productive systems. The toxicity implications of fluctuations in free ammonia driven by diurnal variations in pH need to be further evaluated to guide effective application of related criteria and standards to productive systems. A more comprehensive study of diurnal pH underway for this system will resolve the appropriate timing for pH measurements and provide more complete documentation for exceedances of the acute criterion.

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