PERGAMON
www.elsevier.com/locate/watres

PII: S0043-1354(99)00265-1

Wat. Res. Vol. 34, No. 4, pp. 1107–1118, 2000

Printed in Great Britain
0043-1354/00/$ - see front matter

INTERANNUAL VARIATIONS IN NITRIFICATION IN A HYPEREUTROPHIC URBAN LAKE: OCCURRENCES AND IMPLICATIONS

RAKESH K. GELDA[1]*, CAROL M. BROOKS[1], STEVEN W. EFFLER[1] and MARTIN T. AUER[2]

[1]Upstate Freshwater Institute, P.O. Box 506, Syracuse, NY 13214, USA and [2]Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI 49931, USA

(First received 1 November 1998; accepted in revised form 1 May 1999)

Abstract—The irregular occurrence of high rates of nitrification (nitrification events) in the upper waters of a nitrogen polluted urban lake, Onondaga Lake, NY, during the fall mixing period is documented. The analysis is supported by eight years (1988–1995) of measurements of total ammonia (T-NH_3) and oxidized forms of N (NO_x) in the lake and its inflows, and dissolved oxygen (DO) and temperature profiles. A tested system-specific mass balance model for N is used to estimate nitrification rates for these years, and a system-specific DO model is applied to demonstrate the impact of a nitrification event on the lake's oxygen resources for a single year. Rates of nitrification for different years ranged from near zero throughout the fall mixing interval (1994) to an average of about 0.18 d^{-1} for one month (1995). The nitrification events cause major interannual variations observed in the pools of T-NH_3 and NO_x in the lake's upper waters in fall, and are probably responsible for the particularly severe lake-wide depletion of DO observed in certain years during this interval. Nitrification was the dominant loss process for T-NH_3 and source for NO_x in years that the events occurred. The exacerbating effect of the events on the oxygen resources of the lake needs to be accommodated in related remediation efforts. © 2000 Elsevier Science Ltd. All rights reserved

Key words—ammonia, lake, modeling, nitrification, nitrate, nitrogen cycle, Onondaga Lake

INTRODUCTION

The oxidation of ammonia to nitrate (NO_3^-) by the microbially-mediated process of nitrification is a major pathway in the overall nitrogen cycle of freshwater systems (Curtis *et al.*, 1975; Harris, 1986; Sprent, 1987; Wetzel, 1983). The process has important water quality implications in systems enriched with ammonia, because: (1) this constituent is a key plant nutrient (Harris, 1986; Wetzel, 1983); (2) un-ionized ammonia (NH_3) is toxic to fish at rather low concentrations (USEPA, 1985, 1998); and (3) substantial oxygen demand can be exerted through nitrification (Bowie *et al.*, 1985; Chapra, 1997; Thomann and Mueller, 1987). Nitrification is a two step process carried out by aerobic autotrophic bacteria; almost entirely by species of *Nitrosomonas* (first stage) and *Nitrobacter* (second stage).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (1)$$

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^- \quad (2)$$

Nitrifying bacteria have relatively long generation times (Cooper, 1984). The first stage is usually the rate limiting step (Klapwijk and Snodgrass, 1982). Nitrite (NO_2^-) is considered to be labile and is present in low concentrations in most systems (Wetzel, 1983). Nitrification has been reported to be influenced by a number of ambient conditions including: temperature (T), pH, salinity, dissolved oxygen (DO), NH_4^+, NH_3, suspended solids, and light (Berounsky and Nixon, 1990; Sharma and Ahlert, 1977).

The findings of a number of diverse scientific investigations support the position that nitrification is usually localized at sediment surfaces (for example, Cavari, 1977; Cooper, 1984; Cirello *et al.*, 1979; Curtis *et al.*, 1975; Hall, 1986). Nitrifier densities have been shown to be several orders-of-magnitude greater in surface sediments than in overlying water columns (Curtis *et al.*, 1975; Hall, 1986; Pauer, 1996). Rates of nitrification in deep rivers and lakes, where the ratio of the sediment—water interface to the overlying volume is relatively low, have been observed to be small compared to rates in shallow turbulent streams (Bowie *et al.*, 1985; Chapra, 1997; Cirello *et al.*, 1979; Pauer, 1996). Despite these observations, nitrification has most

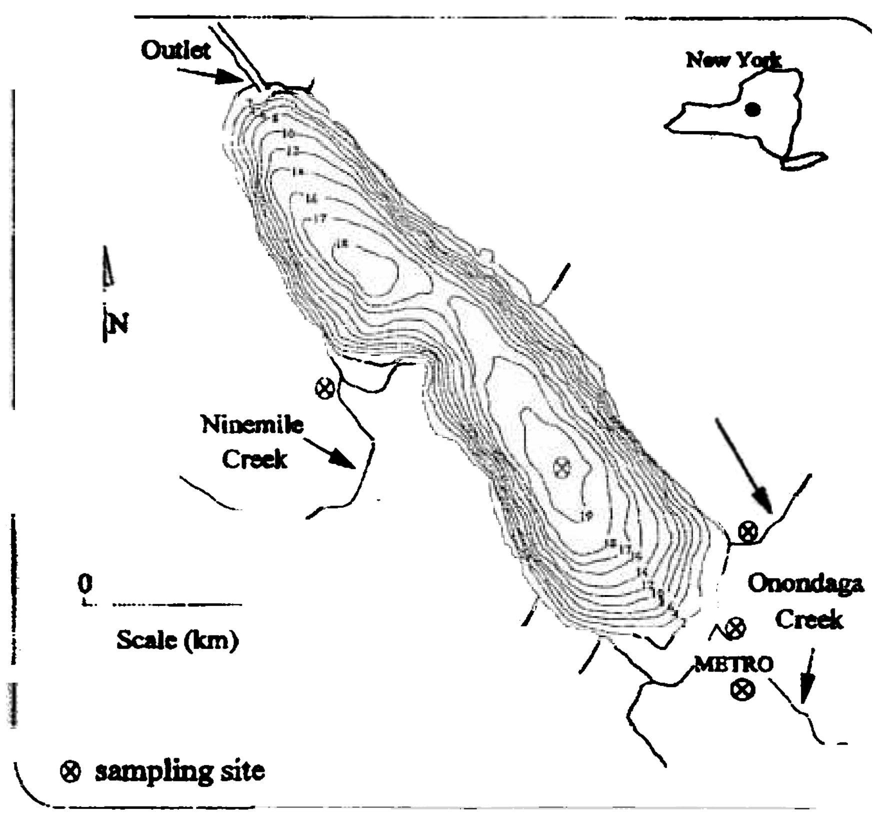
*Author to whom all correspondence should be addressed; e-mail: rkgelda@upstatefreshwater.org

often been represented in mechanistic models as a first-order water column process (for example, Bowie et al., 1985; Brown and Barnwell, 1985; DiToro and Connolly, 1980; McCutcheon, 1987; Scott and Abumoghli, 1995; Thomann and Mueller, 1987),

$$V\frac{d[NH_4^+]}{dt} = -k_N \times [NH_4^+] \times V \quad (3)$$

where V is the volume (m^3), $[NH_4^+]$ is the concentration of NH_4^+ (gm^{-3}), t is time (d), and k_N is a first-order decay coefficient (d^{-1}) for nitrification.

Nitrification rates have been reported for a limited number of freshwater systems; most have been for streams and rivers (Bowie et al., 1985). These rates have been estimated in a variety of ways, based on: (1) laboratory incubations of water and/or sediment samples; (2) in situ incubations; (3) analysis of paired distributions of measurements of ammonia [total (T-NH_3); sum of NH_4^+ plus NH_3] and NO_3^-; and (4) model calibration procedures. Incubations apparently often suffer from "container" effects that result in false high estimates (cf Pauer, 1996). The other non-manipulative techniques rely on the proper interpretation of conspic-



a volume of 131×10^6 m^3, and a maximum depth of 19.5 m (Fig. 1). Paleolimnological analyses (Rowell, 1996) established the lake was oligo-mesotrophic before European settlement in the late 1700s. Onondaga Lake supported a cold-water fishery until the late 1800s (Tango and Ringler, 1996). The lake watershed (642 km^2) presently includes a population of ~450,000. Treated domestic waste from the Metropolitan Syracuse Wastewater Treatment Plant (METRO; Fig. 1; average flow of 3.5 m^3 s^{-1}) presently contributes nearly 20% of the annual inflow; METRO often represents the single largest source of water during the low flow interval of late summer (Effler *et al.*, 1996). Onondaga Lake flushes rapidly; the average for the 1971–1989 interval was 3.7 flushes y^{-1} (Effler, 1996).

METRO is the dominant source of phosphorus (P) and N to the lake, presently representing 60, 90 and 80% of the total annual external loads of total P (*TP*), *T*-NH_3, and total N (*TN*), respectively (Effler *et al.*, 1996). The prevailing areal annual loads of *TP* (8 g m^{-2} y^{-1}) and *TN* (200 g m^{-2} y^{-1}) (Effler *et al.*, 1996) are among the highest reported in the literature (for example, Brezonik, 1972; Stauffer, 1985). Significant nitrification is achieved within METRO during the warmer summer months, that causes seasonal shifts in the contributions of *T*-NH_3 and NO_3^- to the facility's N load. Substantial interannual differences have been observed in the extent of nitrification achieved at METRO (Effler *et al.*, 1996).

Onondaga Lake has a dimictic stratification regime. Spring turnover extends from ice-out (for example, early March) usually through April. Peak density stratification is established by late July to early August. The summer thermocline depth average about 8.5 m (Effler, 1996). Deepening of the epilimnion usually commences in mid- to late August (that is, onset of fall mixing), and proceeds at an irregular rate, in response to the detailed time structure of meteorologically driven kinetic energy inputs (Owens and Effler, 1989, 1996), until the onset of complete (fall) turnover in mid- to late October (Effler and Owens, 1996).

Recurring manifestations of the present hypereutrophic state of Onondaga Lake include: high concentrations of forms of P (Connors *et al.*, 1996) and N (Brooks and Effler, 1990), high concentrations of phytoplankton (Effler *et al.*, 1996), limited light penetration (Perkins and Effler, 1996), rapid loss of DO from the hypolimnion (Effler *et al.*, 1996), subsequent hypolimnetic accumulation of reduced by-products of anaerobic metabolism (*T*-NH_3, H_2S, and CH_4), and lake-wide oxygen depletion during the fall mixing period associated with the oxidation of these by-products (Addess and Effler, 1996; Effler *et al.*, 1988). A large fraction of the fish population of the lake exits to the river during the period of depressed DO in fall (Tango and Ringler, 1996).

Concentrations of various forms of N are high in Onondaga Lake because of the inputs from METRO (Canale *et al.*, 1996). Further, conspicuous temporal and vertical patterns have been imparted to the N pools of the lake that offer a rare opportunity to identify, characterize and quantify mediating processes. Patterns reviewed in this section focus on the dynamics of the spring to late summer interval, that establish conditions at the onset of the fall mixing period. Certain of the temporal features of the patterns have strong interplay with the dynamics of the stratification regime and the timing of the onset of anoxia within the hypolimnion (Brooks and Effler, 1990). Concentrations of NO_3^- and NO_2^- (sum represented as NO_x) decrease progressively in the hypolimnion soon after the onset of anoxia (late May to early June; Effler, 1996), and are eliminated in less than a month, as a result of the operation of the denitrification process (Brezonik and Lee, 1968; Seitzinger, 1988). Ammonia concentrations increase progressively in the hypolimnion, particularly after the onset of anoxia, due to release from the underlying sediments (Wickman, 1996). The peak volume-weighted hypolimnetic *T*-NH_3 concentration observed annually, before the onset of fall mixing, has been between 4 and 5 mg N l^{-1} (Effler, 1996). The vertical patterns of these constituents in the hypolimnion (Brooks and Effler, 1990; Effler, 1996) reflect localization of source/sink processes within the sediments (Gelda *et al.*, 1995). The NO_x pool has been depleted first, and maximum *T*-NH_3 concentrations (for example, >7 mg N l^{-1}) have developed, in the deepest layer(s). Concentrations of *T*-NH_3 and NO_x in the productive layers of the epilimnion (sum >2 mg N l^{-1}) remain well above levels considered limiting to phytoplankton growth (Bowie *et al.*, 1985; that is, no N_2 fixation by cyanobacteria). The initial *T*-NH_3 concentration in spring varies greatly year-to-year (range of 1.5 to 4 mg N l^{-1}) in response to interannual differences in dilution of the METRO input provided by tributary flow over the preceding November to March interval (Effler *et al.*, 1996). Epilimnetic concentrations of *T*-NH_3 decrease during summer stratification to varying extents, and NO_3^- concentrations either increase progressively or remain nearly uniform (Effler, 1996). Concentrations of organic N have remained more uniform and generally lower than *T*-NH_3 and NO_3^- (Canale *et al.*, 1996). Concentrations of NO_2^- have usually increased progressively in the epilimnion through early August (Gelda *et al.*, 1999). Standards to protect aquatic life against the toxic effects of NH_3 (Effler *et al.*, 1990) and NO_2^- (Gelda *et al.*, 1999) have been violated by a wide margin routinely in the upper waters in summers.

Pauer (1996) measured a rather high nitrification rate for the sediment–water interface of Onondaga Lake (0.37 g N m^{-2} d^{-1}) in experiments with sediment cores (cf Auer *et al.*, 1993; Erickson and Auer, 1998), but observed no nitrification in water column samples collected in summer. His conclusion that nitrification in the lake was localized at the sediments (in aerobic layers) was supported by enumeration of nitrifying bacteria in experimental microcosms. Nitrifier densities of $\sim 10^3$ and $\sim 10^5$ cells ml^{-1} were reported for the water column and surface sediments, respectively (Pauer, 1996). The nearly conservative behavior of NO_2^- observed in the lake's epilimnion from April through mid-August in several years, an interval over which progressive increases in concentrations have been observed, indicated a lack of nitrification in the lake's water column for that interval (Gelda et al., 1999), consistent with Pauer's (1996) observations. However, abrupt changes (increases and decreases) in NO_2^- concentrations have been observed for the lake in a number of years over the mid-August through October interval, suggesting the irregular operation of the nitrification process (Gelda et al., 1999).

METHODS

Sampling, analyses, loads

Samples were collected weekly at 1 to 2 m depth intervals at a buoyed deep water (~19.5 m) location (Fig. 1) in the lake's southern basin, found to be representative of lake-wide conditions (Effler, 1996), for the April to October interval, over the period 1988–1995. This paper focuses on the fall mixing period; August to October. Laboratory analyses included $T\text{-}NH_3$ (USEPA, 1983), NO_x (USEPA, 1983), and total chlorophyll (Chl; Parsons et al., 1984). Temperature, pH, and DO were measured in the field, at 1 m depth intervals, with a Hydrolab Surveyor 3. Sampling and field measurements were conducted at mid-morning (for example, ~1000 h).

Loads of N forms from METRO were based on concentration data [total Kjeldahl N (TKN), $T\text{-}NH_3$, NO_x], collected by the facility on daily flow-weighted composite effluent samples, and daily average discharge flows of the facility. Concentration measurements for this effluent were made on samples collected from two (NO_x, TKN) to five ($T\text{-}NH_3$) times per week. Linear interpolation was used to estimate concentrations for days for which samples were not collected. Daily loads from the facility were calculated as the product of the daily concentrations and flows (Effler, 1996; Effler et al., 1996). Estimates of the smaller loading contributions from tributaries were based on a fixed-frequency (bi-weekly) sampling effort, using the same analytical protocols as specified for lake samples. Daily loads were estimated for these tributaries using the FLUX loading calculation software (version 4.4, 1990; Walker, 1987), as described by Effler (1996).

N and DO models

Mass balance models for forms of N (Canale et al.,

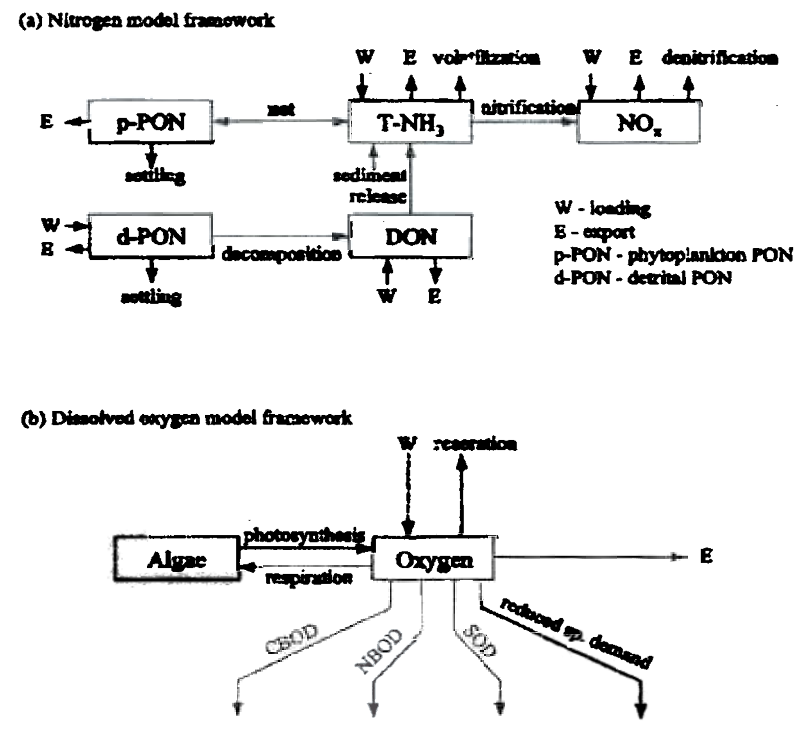


Fig. 2. Conceptual framework for the Onondaga Lake (a) nitrogen model, and (b) dissolved oxygen model.

1996) and DO (Gelda and Auer, 1996), developed and successfully tested for the lake, were utilized in this investigation (Fig. 2). These two models have the same physical framework. The water column is represented by two completely-mixed vertical layers of fixed dimensions (demarcation depth of 8.5 m), an upper mixed layer (UML) and lower mixed layer (LML), corresponding approximately to the dimensions of the epilimnion and hypolimnion in summer (Effler and Owens, 1996). This representation has been widely used in mass balance simulation models for stratifying lakes (Chapra, 1997; Thomann and Mueller, 1987). Vertical mixing-based exchange between the layers (includes diffusion and entrainment) was independently estimated by applying a heat balance to the lower layer (Doerr *et al.*, 1996).

The N model simulates in-lake concentrations of T-NH_3, NO_x, particulate (PON) and dissolved (DON) organic N. Components of the lake's N cycle accommodated in the model include: external loading, net phytoplankton growth (G_{NET}, d^{-1}), preferential loss (uptake) of T-NH_3 over NO_x to phytoplankton (for energetic reasons; for example, Wetzel, 1983), nitrification, denitrification, hydrolysis of DON, decomposition of PON, volatilization of NH_3, sediment release of T-NH_3, settling of PON, and vertical mixing-based exchange between the layers (Fig. 2(a)). The seasonality of the loss of T-NH_3 to phytoplankton growth was determined by Canale *et al.* (1996) by calibration to the observed distribution of Chl for 1989, a common temporal distribution for the lake (Effler, 1996). However, substantial interannual variations in temporal patterns of phytoplankton growth (for example, Chl concentrations) are known to occur in the lake over the late summer through early fall interval (Effler, 1996). This effect was not considered important in earlier applications of the model, that focused on the spring to mid-summer interval, the critical period for NH_3 toxicity concerns (Canale *et al.*, 1996; Effler and Doerr, 1996). The associated sink for T-NH_3 for the August to October interval is quantified here on a year-specific basis through the calibration procedures described by Canale *et al.* (1996). Originally, a film transfer approach, analogous to reaeration (Bowie *et al.*, 1985), was used to describe the kinetics of nitrification (Canale *et al.*, 1996)

$$V\frac{d[NH_4^+]}{dt} = -k_{fn} \times [NH_4^+] \times A \qquad (4)$$

where k_{fn} is the film transfer nitrification coefficient (m d^{-1}), and A is the area of the sediment–water interface across which nitrification-based exchange occurs. This representation is consistent with the observations of various investigators (Cavari, 1977; Cooper, 1984; Curtis *et al.*, 1979; Hall, 1986). The value of k_{fn} ($= 0.135$ m d^{-1}; model default value; Canale *et al.*, 1996) was established based on the system-specific experiments of Pauer (1996) with profundal sediments. Here we also evaluate alternate water column kinetics for nitrification of equation (3) for the fall mixing period. Several other kinetic coefficient values for the N model were determined through independent measurements, thereby enhancing the credibility of the model (Canale *et al.*, 1996).

The DO model accommodates the processes of reaeration (Gelda *et al.*, 1996), algal photosynthesis and respiration, carbonaceous biochemical oxygen demand, sediment oxygen demand (SOD; Gelda *et al.*, 1995), and water column oxidation of CH_4 and H_2S (Gelda and Auer, 1996). The effect of sediment-based nitrification was embedded within the independently measured value(s) of SOD (Gelda *et al.*, 1995). The model performed well in simulating the seasonal dynamics of DO observed in the lake in two years, including depletion of hypolimnetic DO in summer and epilimnetic depletion during the fall mixing period (Gelda and Auer, 1996).

Model application

Constituent concentrations were represented as volume-weighted values, determined from vertical profiles of measurements and hypsographic data (Doerr *et al.*, 1996), to evaluate model performance. The N model was applied for the August through October interval of seven consecutive years, 1989–1995 (1988 excluded because of incomplete loading data). Initial conditions were those measured on the first monitoring day of August in each year. Temporal distributions of vertical mixing were first determined from the T measurements, as described above (Doerr *et al.*, 1996). Next, temporal distributions of the G_{NET} sink for T-NH_3 were determined for each year for

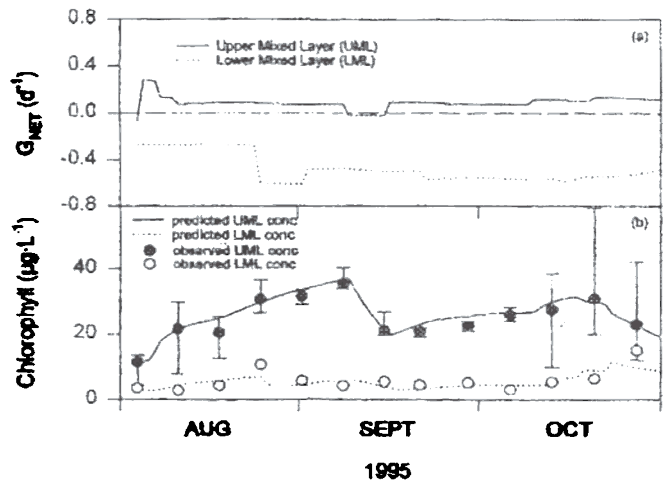


Fig. 3. Time series for phytoplankton for the August to October interval of 1995: (a) estimates of net phytoplankton growth in the UML and LML determined by model calibration procedures; and (b) model performance for Chl for the UML and LML from calibration procedures.

both lake layers (Fig. 3(a)) through model calibration (that is, by adjusting G_{NST} to match the observed Chl patterns; Fig. 3(b)). Temporal patterns of nitrification rates (k_N and k_{fn}) were resolved by an iterative calibration procedure (that is, by adjusting k_N and k_{fn} to match the observed T-NH_3 and NO_x patterns), in which all other rate processes in the model were specified according to coefficient values determined previously (Fig. 3(a); Canale et al., 1996). Temperature effects on nitrification rates were accommodated according to an Arrhenius relationship

$$k_{x,T} = k_{x,20} \times \theta^{(T-20)} \tag{5}$$

$k_{x,T}$ and $k_{x,20}$ are values of nitrification rate coefficients (k_N or k_{fn}) at temperatures T and 20°C, and θ is a dimensionless temperature coefficient. A value of $\theta = 1.06$ was specified (for example, Bowie et al., 1985; Canale et al., 1996). Nitrification rates determined seasonally and for different years are represented as $k_{x,20}$ values to facilitate comparisons.

The implications of high rates of nitrification on the oxygen resources of the upper waters of the lake during the fall mixing period were evaluated through application of the tested DO model for the conditions of 1995. An added oxygen sink of nitrification within the water column [equations (1)–(3)] was included with the time-series of k_N values determined for 1995 from application of the N model, as described above. The time series of vertical mixing was the same as determined for the N model application for the same year. All other inputs were as specified previously by Gelda and Auer (1996). Model performance was checked by comparing simulations with observations of DO. Comparisons of simulations for the UML with and without the added watercolumn nitrification sink formed the basis for delineating the effect of this process on the oxygen resources of the upper waters of the lake.

RESULTS AND DISCUSSION

Pools of T-NH_3 and NO_x

Patterns for the LML have had more recurring characteristics over the study period compared to those observed for the UML. Nitrogen oxides have essentially been absent from the LML and the annual maximum concentrations of T-NH_3 have been approached in this layer, by the beginning of August (Fig. 4). Concentrations of NO_x have increased progressively in the LML during the approach to fall turnover in each year (Fig. 4), reflecting the inclusion of oxygenated NO_x-enriched waters from the deepening epilimnion. The rates of increase in NO_x in the LML were relatively low in 1988 (Fig. 4(a)), 1992 (Fig. 4(e)), and 1998 (Fig. 4(g)), because concentrations remained low in the

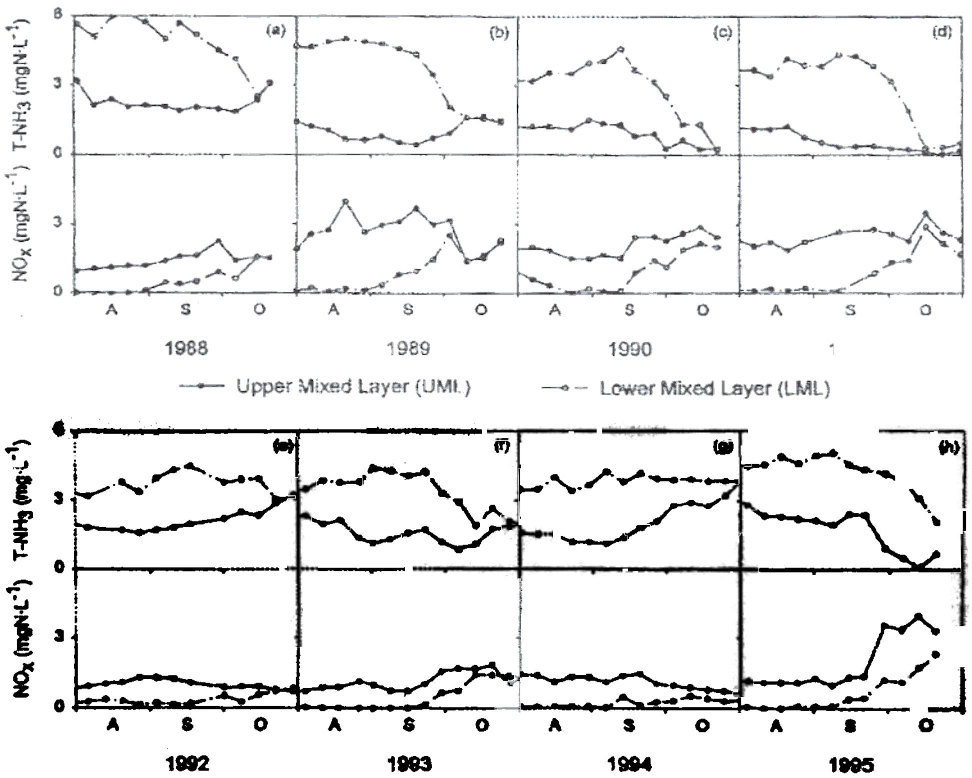


Fig. 4. Time-series of volume-weighted concentrations of T-NH_3 and NO_x for the upper (UML) and lower layers (LML; demarcated at a depth of 8.5 m) of Onondaga Lake for the August to October interval; (a) 1988; (b) 1989; (c) 1990; (d) 1991; (e) 1992; (f) 1993; (g) 1994; and (h) 1995.

UML in those years. Conspicuous decreases in the volume-weighted concentrations of T-NH_3, associated with the deepening of the epilimnion, were observed for the LML in six of the eight years (Fig. 4). The exceptions, 1992 (Fig. 4(e)) and 1994 (Fig. 4(g)), were a result of the very high concentrations maintained in the UML in those years.

Concentrations of T-NH_3 and NO_x remained vertically uniform within the epilimnion, and no localized process activity (for example, nitrification or denitrification) was manifested within the metalimnion over the study period. Concentrations of these constituents in the UML in early August varied greatly year-to-year (Fig. 4), reflecting interannual differences in the various sources and sinks over the preceding interval. Concentrations of T-NH_3 varied from ~1.5 mg N l^{-1} (Fig. 4(b)–(d)) to ~3.0 mg N l^{-1} (Fig. 4(h)) among the study years; concentrations of NO_x ranged from <1.0 mg N l^{-1} (Fig. 4(a), (e) and (f)) to nearly 2.5 mg N l^{-1} (Fig. 4(d)). The wide interannual differences in temporal patterns observed for these pools with the approach to fall turnover (that is, over the August to October interval) reflect year-to-year differences in the magnitudes of the source and sink processes. These disparate signatures offer an opportunity to resolve interannual variations in the mediating processes with the mass balance model. Concentrations of NO_x increased in most years to varying extents and with different temporal patterns (Fig. 4). In contrast, NO_x concentrations remained relatively uniform over the August to October interval of 1992 (Fig. 4(c)) and 1994 (Fig. 4(g)). Largely progressive decreases in T-NH_3 concentrations were observed in the UML in 1989 (Fig. 4(b)), 1990 (Fig. 4(c)), 1991 (Fig. 4(d)), and 1995 (Fig. 4(h)). Increases were observed in October in two of these years (Fig. 4(b) and (h)), at least in part associated with vertical mixing-based inputs from the shrinking hypolimnion. In sharp contrast, nearly progressive increases in T-NH_3 occurred in the UML in 1992 (Fig. 4(c)) and 1994 (Fig. 4(g)). Two minima in T-NH_3 concentrations were observed in 1993, one in late August, the other in early October (Fig. 4(f)).

The onset of complete fall turnover, manifested by essentially equivalent concentrations throughout the water column, was included within the monitored interval of seven of the eight years (Fig. 4). The exception was 1995 (Fig. 4(h)); the epilimnion had deepened to 15 m by the last sampling day in late October of that year. Interannual variations were clearly manifested in the pool sizes of T-NH_3 and NO_x at the onset of turnover (near turnover in the case of 1995). In three years, 1990, 1991, and 1995, the concentration of T-NH_3 was <1 mg N l^{-1}. The concentrations of NO_x were >2.5 mg N l^{-1} at turnover in those same years. In contrast, the concentrations of T-NH_3 and NO_x were >2.5 and <1.0, respectively, at turnover in 1988, 1992, and 1994.

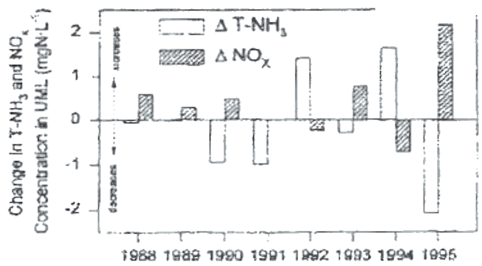


Fig. 5. Net changes in the concentrations of T-NH_3 and NO_x over the August to onset of complete fall turnover interval in Onondaga Lake for the period 1988–1995.

Comparison of net changes in T-NH_3 and NO_x concentrations in the UML for the early August to the onset of complete turnover (last observations for 1995) interval (Fig. 5), serve to further delineate salient aspects of the interannual differences in the dynamics of these pools. Major year-to-year variations emerge from this form of presentation (Fig. 5), that can only be the result of year-to-year differences in the magnitudes of the various sources and sinks of these constituents. There were almost no net changes in T-NH_3 for this interval in 1988 and 1989, and only modest increases in NO_x occurred in these years (Fig. 5). Net decreases in NO_x were observed in 1992 and 1994 (Fig. 5). Substantial increases (≥0.5 mg l^{-1}) in the concentration of NO_x were observed in the UML with the approach to fall turnover in three years (1990, 1993, and 1995; Fig. 5). Changes in T-NH_3 concentrations over this

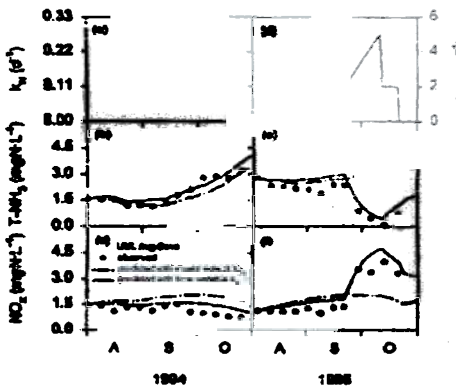


Fig. 6. Estimates of nitrification rate coefficient(s) (k_x; k_N or k_{fn}) values in the UML of Onondaga Lake for the August to October interval of two years, with calibration performance of the N model, and comparisons to predictions according to the original N model: (a) estimated time series of nitrification rate coefficient(s), 1994; (b) comparison of model simulations to observations of T-NH_3, 1994; (c) comparison of model simulations to observations of NO_x, 1994; (d) estimated time series of nitrification rate coefficient(s), 1995; (e) comparison of model simulations to observations of T-NH_3, 1995; and (f) comparison of model simulations to observations of NO_x, 1995.

interval were even more variable amongst the years; for example, major increases (for example, 1994) and decreases (for example, 1990, 1991 and 1995) were both observed over the eight-year period (Fig. 5). The greatest net differences for both constituents were observed in 1995. The substantial concurrent increase in NO_x and decrease in $T\text{-}NH_3$ in 1995 were approximately stoichiometric (within 5%), suggesting the operation of the nitrification process.

Variations in rate of nitrification

Widely different time-series of nitrification rates were determined for the fall mixing period of the study years through calibration with the N model, as illustrated for 1994 and 1995 (Fig. 6). The nitrification rate is represented in two alternate formats corresponding to a water column process (k_N) versus a sediment-based process (k_{fn}). The model analysis indicates essentially no nitrification occurred during the fall mixing period of 1994 (Fig. 6(a)). The time-series of $T\text{-}NH_3$ (Fig. 6(b)) and NO_x (Fig. 6(c)) concentrations were well simulated with the nitrification rate equal to zero. However, substantial increases in nitrification were determined for September and October in 1995 (Fig. 6(d)). These abrupt increases have an event-like character (for example, nitrification events). Rates during the events were 15 to 40 times greater than the sediment-based estimate (default value) originally incorporated in the N model, though the k_N values of 1995 (Fig. 6(d)) correspond approximately to the lower bound of the range (~0.3 d^{-1}) reported for suspended growth nitrification units in wastewater treatment facilities (Metcalf and Eddy, 1987). Simulations of the model with the default nitrification rate overpredict $T\text{-}NH_3$ (Fig. 6(e)) and underpredict NO_x (Fig. 6(f)) by a wide margin for the late September through October interval of 1995. The better fit of the zero nitrification rate compared to the default rate for NO_x in 1994 (Fig. 6(c)) suggests Pauer's (1996) experimental rates for profundal sediments may not be representative for sediments within the UML.

The irregular occurrence of nitrification events in the lake during fall mixing is further supported by the estimates of nitrification rates obtained for the other five years over the 1989–1995 period (Table 1). Nitrification events were manifested in two other years (1990 and 1991, Table 1); in each of these cases the nitrification rate increased abruptly over the late September to October interval (for example, Fig. 6(d)). This population (Table 1), though small ($n = 7$), reflects a bi-modal distribution, that is indicative of an event-like character. The authors are unaware of the previous resolution of interannual variations in nitrification rate in lakes, particularly over the duration of this study. Some uncertainty in these estimates (Table 1) is unavoidable associated with the limitations in model structure and sampling frequency. However, the conspicuous signatures imparted to the pools of $T\text{-}NH_3$ and NO_x in certain years (Fig. 4) provide compelling support for the event-like character manifested for the nitrification process in these results (Fig. 6(d), Table 1).

Table 1. Interannual differences in nitrification rate in Onondaga Lake during October

Year	Nitrification rate	
	k_{fn} (m d^{-1})	k_N (d^{-1})
1989	0.135[a]	0.0075
1990	2.0	0.11
1991	2.0	0.11
1992	0.0	0.0
1993	0.4	0.022
1994	0.0	0.0
1995	3.24	0.18

[a]Model default value (Canale *et al.*, 1996).

Resolution of the magnitudes of the individual source and sink processes for the UML pools of $T\text{-}NH_3$ and NO_x in 1994 and 1995 with the N model (Fig. 7) provides insight into the causes of the interannual differences and the role of nitrification events (for example, Fig. 6(d)). Sources of $T\text{-}NH_3$ include external loads (mostly METRO), hydrolysis of DON, and vertical mixing-based inputs from the enriched LML. Sinks include phytoplankton uptake, nitrification, export from the lake, and volatilization of NH_3 (Canale *et al.*, 1996). Sources of NO_x accommodated are external loads, and nitrification. Loss processes for NO_x include vertical mixing-based export to the depleted LML and hydrologic export (Canale *et al.*, 1996). Phytoplankton uptake of NO_x was assumed not to occur because concentrations of the energetically favored $T\text{-}NH_3$ (Wetzel, 1983) remained high relative to levels (~10 to 15 μg N l^{-1}) assumed to cause a switch to NO_3^- uptake (Canale *et al.*, 1996).

Hydrolysis and volatilization played minor, and nearly compensating, roles in mediating the $T\text{-}NH_3$ pool of the lake (Fig. 7(a) and (c)). External (METRO) loading was one of the two important sources of $T\text{-}NH_3$ in each of the years (Fig. 7(a) and (c)). The other major source was vertical mixing-based inputs from the LML (Fig. 7(c)), which largely reflects sediment feedback associated with the lake's hypereutrophic state (Wickman, 1996). The much larger magnitude of this source in 1995 compared to 1994 is not a result of interannual differences in the pool size of $T\text{-}NH_3$ in the lake's hypolimnion (Fig. 4(g) and (h)) or the magnitude of vertical mixing. Rather, the differences in this flux (and for NO_x; Fig. 7(b) and (d)) are attributable to the larger concentration gradients (cf Wodka *et al.*, 1983) between the LML and UML that prevailed in 1995 (Fig. 4(h)) compared to 1994 (Fig. 4(h)). Losses from phytoplankton uptake and export were of the same approximate magnitude, did not differ greatly for the two years, and were the dominant sinks in 1994 (Fig. 7(a)). The nitrification event was

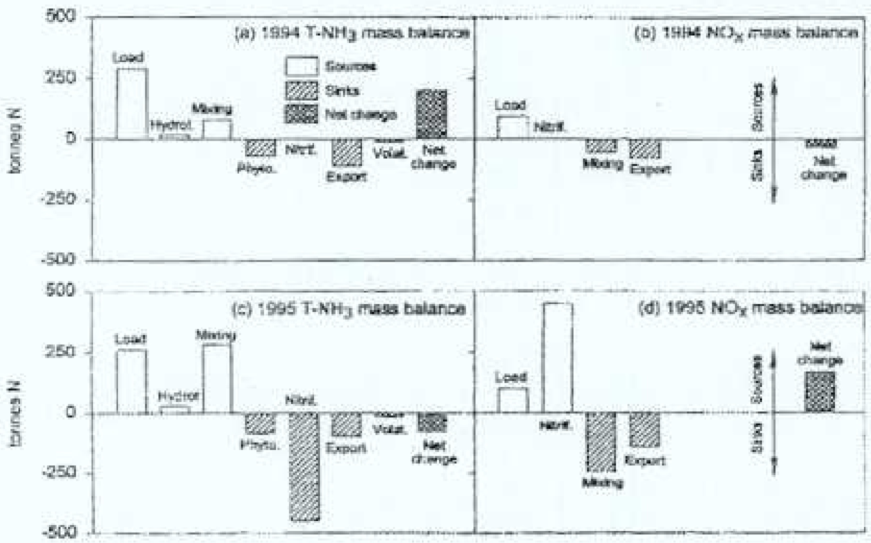


Fig. 7. Model simulated components (sources, sinks, and net change in lake storage) of the budgets for T-NH_3 and NO_x for the UML of Onondaga Lake for the August to October interval of three years: (a) T-NH_3, 1994; (b) NO_x, 1994; (c) T-NH_3, 1995; and (d) NO_x, 1995.

the dominant sink for T-NH_3 (Fig. 7(a)) and source of NO_x (Fig. 7(b)) in the UML in 1995, and in the other years in which the events occurred (Table 1). Nitrification events have been primarily responsible (for example, Fig. 7) for the major interannual variations observed for the pools T-NH_3 and NO_x within the upper waters of the lake during the fall mixing interval.

It is unlikely that the nitrification event phenomenon identified and quantified here is unique to Onondaga Lake. However, claims of potential broad occurrence need to be tempered by the unusually high concentrations of inorganic N forms that prevail in this lake as a result of pollution (Fig. 4). Perhaps the most conspicuous possibility for interference or feedback from the level of pollution that would limit the ubiquity of these findings is the known toxicity of NH_3 to the nitrification process (for example, Anthonisen *et al.*, 1976). A detailed analysis of this potential interplay for the UML of the lake concluded NH_3 concentrations, while unusually high and temporally variable in this polluted system, remain too low to inhibit the nitrification process (Gelda *et al.*, 1999). Qualitative evidence reported for other lakes supports the occurrence of nitrification events. Cavari (1977) observed increased nitrification in the water column of Lake Kinnert during turnover, and speculated this may have been in response to resuspension of bottom sediment enriched with nitrifying bacteria. Robarts *et al.* (1982) reported paired, nearly stoichiometric, decreases in T-NH_3 and increases in NO_x in a monomictic impoundment (Hartbeesport Dam, South Africa) following the onset of turnover, and concluded these patterns reflected extremely high rates of nitrification.

The cause(s), or trigger(s), for the observed nitrification events remains an open question that falls outside of the goals of this paper. A preliminary pursuit of the cause through analyses of a broad range of parallel measurement (cf. Bernunsky and Nixon 1990; Sharma and Ahlert, 1977) collected as part of the long-term monitoring programme for the lake (Effler, 1996) was inconclusive. The known affinity of nitrifying bacteria for surfaces (Staley, 1989) and the qualitative evidence for nitrification events in other lakes during turnover (Cavari, 1977; Robarts *et al.*, 1982), a period when sediment resuspension is known to increase (Bloesch, 1995), suggests that particle resuspension may be an important factor in the occurrence of these events. The fact that resuspension events are often coupled to random occurrences of particularly high winds (Bloesch, 1995) is consistent with the apparent event-like character of nitrification reported here. This issue deserves further research.

Water quality implications of nitrification events: DO

The DO model performed well in simulating the major depletion (for example "sag") in DO observed in the UML in late September and early October of 1995 (Fig. 8) by incorporating the oxygen demand associated with the time series of nitrification rates, as determined by application of the N model (Fig. 6(d)). This additional oxygen sink was represented as a water column process (k_N), as sediment-based nitrification is embedded in sediment oxygen demand (DiToro *et al.*, 1990), which

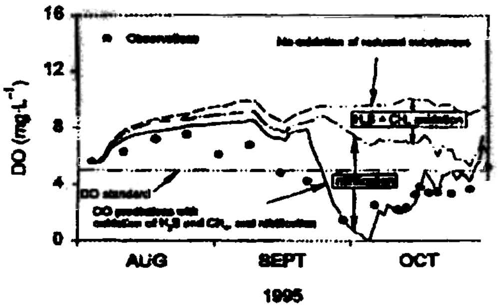


Fig. 8. Comparison of model simulations of DO concentrations for the UML of Onondaga Lake to observations for the August to October interval of 1995. Three simulation cases are presented to depict relative contributions of process to DO depletion: no oxidation of reduced substances, oxidation of H_2S and CH_4, and nitrification of T-NH_3 according to Fig. 5(d).

is already accommodated in the DO model (Gelda and Auer, 1996) and supported by independent measurements (Gelda *et al.*, 1995). The model overpredicted DO in September, but performed well in October. The simulation represented 82% of the observed temporal variations in DO in the UML over the August to October interval. The root mean squared error of the simulation was about 1.4 mg DO l^{-1}. This level of performance compares favorably with the initial testing of the model (Gelda and Auer, 1996). A simulation that did not accommodate the effects of the nitrification event on the oxygen budget of the UML grossly underpredicted the observed DO depletion (Fig. 8). The interconsistencies of the signals imparted to the pools of DO (Fig. 8) and forms of N (Fig. 6(e) and (f)) provide compelling evidence for the occurrence of nitrification events in the lake, as well as for the representativeness of the estimated time series of nitrification rates (Fig. 6(d)).

The model analysis (Fig. 8) demonstrates nitrification events have a highly negative impact on the lake's oxygen resources during the fall mixing period. Water quality standards for DO intended to protect fish (5 mg l^{-1} as a daily average, minimum of 4 mg l^{-1} within a day) were violated for more than a month as a result of the nitrification event in the fall of 1995. Undoubtedly, these conditions promote the reported exodus of fish from the lake (Tango and Ringler, 1996). The portion of the DO depletion attributed to oxidation of other reduced substances (H_2S and CH_4), received from the LML, was predicted to be less than associated with nitrification, and would not have caused violations in this year in the absence of nitrification (Fig. 8). Temporal features of the 1995 simulations (Fig. 8) indicate the oxygen demand of the nitrification event is shifted earlier than that associated with oxidation of H_2S and CH_4. This suggests that the nitrification event was initially supported in part by the T-NH_3 pool of the UML, as the kinetics of oxidation of H_2S and CH_4 are extremely rapid (Jannasch, 1975; Jorgensen *et al.*, 1979; Rudd *et al.*, 1976).

The observations that the DO depletion in the fall of 1990 was one of the more severe cases reported for the 1985–1993 interval (Effler *et al.*, 1996) and that the depletion in 1994 (unpublished data, Effler) was one of the least severe are qualitatively consistent with the presented estimates of nitrification (Table 1). We hypothesize that much of the substantial interannual variability observed for fall DO depletion in the UML of the lake (Effler *et al.*, 1996) has been caused by the irregular occurrence of nitrification events. If the existing population of nitrification rate determinations (Table 1) is representative, particularly severe DO depletions in the UML should be expected during fall mixing in about four of every ten years.

Model structure and management implications

Estimates of nitrification rates have been presented in two formats here, consistent with water column [equation (3)] and sediment-based [equation (4)] processes. While no strong position on these alternatives is taken here, circumstantial evidence indicates the reported nitrification events were water-column based. First, sediments within the UML (Auer *et al.*, 1996) could not support the SOD that would have been necessary to explain the DO depletion observed in 1995 (Fig. 8). Second, no significant seasonality emerged in SOD experimental results from profundal cores collected seasonally in the lake (Gelda *et al.*, 1995). Further, an unreasonably high transport rate across a boundary layer would be necessary (cf. Pauer, 1996) to accommodate the magnitude of these events within the constructs of a sediment–water interface process. These observations do not preclude a sediment-based representation of nitrification, which we believe operates in at least the profundal depths during oxic intervals. Rather, it appears the sediment-based process is augmented by its operation within the water column during the events (for example, consistent with a resuspension mechanism).

It is important for managers of this lake, and potentially other N polluted lentic systems, to be aware of the occurrence of nitrification events and the implications for DO resources and common measures of water quality. These apparently random events can interfere with trend/pattern analysis, and, if not recognized, could lead to incorrect interpretations of the conspicuous year-to-year differences in water quality signatures. Managers intend to use hypolimnetic oxygenation (for example, Prepas *et al.*, 1997) to remediate the particularly acute DO depletion of the fall mixing period (Fig. 8). It is recommended that related oxygenation capacity calculations adopt the nitrification event conditions of 1995 as a reasonable worst case for oxygen demand.

CONCLUSIONS

The irregular occurrence of intervals of high rates of nitrification, described as nitrification events, in the upper waters of polluted Onondaga Lake during the fall mixing period has been demonstrated, based on comprehensive measurements of forms of N in the lake and its inflows and application of a tested mass balance model for N. In some years essentially no nitrification has occurred in this interval, in others the rates have been high, approaching values reported for wastewater treatment facilities. Estimates of nitrification rates during an event have been independently supported by the closure this additional DO sink process brought to model simulations of the major DO depletion observed during the event. The irregular occurrence of the events is responsible for the major interannual variations observed for the pools of ammonia and oxidized forms of nitrogen in the upper waters of the lake during the fall mixing interval. Nitrification events exacerbate the lake's problem of low DO concentrations in the upper waters during the fall mixing period. Additional studies are recommended to identify causes of the events. The effect(s) of nitrification events should be included, as a representative worst case, for evaluating alternatives to remediate or reclaim the oxygen resources of the lake.

REFERENCES

Addess J. M. and Effler S. W. (1996) Summer methane fluxes and fall oxygen resources of Onondaga Lake, New York. *Lake and Reservoir Management* 12, 91–101.

Anthonisen A. C., Loehr R. C., Prakansam T. B. and Srinath E. G. (1976) Inhibitions of nitrification by ammonia and nitrous acid. *Journal of Water Pollution Control Federation* 48, 835–852.

Auer M. T., Johnson N. A., Penn M. R. and Effler S. W. (1993) Measurement and verification of rates of sediment phosphorus release for a hypereutrophic urban lake. *Hydrobiologia* 253, 301–309.

Auer M. T., Johnson N. A., Penn M. R. and Effler S. W. (1996) Pollutant sources, depositional environment, and the surficial sediment of Onondaga Lake, New York. *Journal of Environmental Quality* 25, 46–55.

Berounsky V. M. and Nixon S. W. (1990) Temperature and annual cycle of nitrification in waters of Narragansett Bay. *Limnology and Oceanography* 35, 1610–1617.

Bloesch J. (1995) Mechanisms, measurement and importance of sediment resuspension in lakes. *Marine and Freshwater Research* 46, 295–304.

Bowie G. L., Milles W. B., Porcella D. B., Campbell C. L., Pagenkopf J. R., Rupp G. L., Johnson K. M., Chan P. W., Gherini S. A. and Chamberlin C. B. (1985) *Rates, Constants, and Kinetic Formulations in Surface Water Quality Modeling*, 2nd ed. United States Environmental Protection Agency, Environmental Research Laboratory, Athens, GA, EPA/600/3-85/040.

Brezonik P. L. (1972) Nitrogen: sources and transformations in natural waters. In *Nutrients in Natural Waters*, eds H. E. Allen and T. R. Kramer, pp. 1–50. Wiley, New York.

Brezonik P. L. and Lee G. F. (1968) Denitrification as a nitrogen sink in Lake Mendota, Wis. *Environmental Science and Technology* 2, 120–125.

Brooks C. M. and Effler S. W. (1990) The distribution of nitrogen species in polluted Onondaga Lake, NY, USA. *Water, Air and Soil Pollution* 52, 247–262.

Brown L. C. and Barnwell T. O. (1985) *Computer Program Documentation for the Enhanced Stream Water Quality Model QUAL2E.* U.S. Environment Protection Agency, Athens, GA, EPA/600/3-85/065.

Canale R. P., Gelda R. K. and Effler S. W. (1996) Development and testing of a nitrogen model for Onondaga Lake, NY. *Lake and Reservoir Management* 12, 151–164.

Cavari B. Z. (1977) Nitrification potential and factors governing the rate of nitrification in Lake Kinnert. *Oikos* 28, 285–290.

Chapra S. C. (1997) *Surface Water-Quality Modeling*. McGraw-Hill, New York.

Cirello J., Rapaport R. A., Strom P. F., Matulewich V. A., Morris M. L., Goetz S. and Finstein M. A. (1979) The question of nitrification in the Passaic River, New Jersey: analysis of historical data and experimental investigation. *Water Research* 13, 525–537.

Connors S. D., Auer M. T. and Effler S. W. (1996) Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake, NY. *Lake and Reservoir Management* 12, 47–57.

Cooper A. B. (1984) Activities of benthic nitrification in streams and their role in oxygen consumption. *Microbial Ecology* 10, 317–334.

Curtis E. J., Durrant K. and Harman M. M. (1975) Nitrification in rivers in the Trent Basin. *Water Research* 9, 255–268.

DiToro D. M. and Connolly J. P. (1980) *Mathematical Models of Water Quality in Large Lakes. Part 2: Lake Erie.* U.S. Environmental Protection Agency, Duluth, EPA-600/3-8-065.

DiToro D. M., Paquin P. R., Subburamu K. and Gruber D. A. (1990) Sediment oxygen demand model: methane and ammonia oxidation. *Journal of Environmental Engineering Division ASCE* 116, 945–986.

Doerr S. M., Canale R. P. and Effler S. W. (1996) Development and testing of a total phosphorus model for Onondaga Lake, NY. *Lake and Reservoir Management* 12, 141–150.

Effler S. W. (1996) *Limnological and Engineering Analysis of a Polluted Urban Lake. Prelude to Environmental Management of Onondaga Lake, New York.* Springer-Verlag, New York.

Effler S. W., Brooks C. M., Auer M. T. and Doerr S. M. (1990) Free ammonia in a polluted hypereutrophic urban lake. *Journal of Water Pollution Control Federation* 62, 771–779.

Effler S. W., Brooks C. M. and Whitehead K. A. (1996) Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications. *Lake and Reservoir Management* 12, 127–140.

Effler S. W. and Doerr S. M. (1996) Water quality model evaluations for scenarios of loading reductions and diversion of domestic waste around Onondaga Lake. *Lake and Reservoir Management* 12, 181–193.

Effler S. W., Hassett J. P., Auer M. T. and Johnson N. A. (1988) Depletion of epilimnetic oxygen, and accumulation of hydrogen sulfide in the hypolimnion of Onondaga Lake, NY, USA. *Water, Air and Soil Pollution* 39, 59–74.

Effler S. W. and Owens E. M. (1996) Density stratification in Onondaga Lake: 1968–1994. *Lake and Reservoir Management* 12, 25–33.

Erickson M. J. and Auer M. T. (1998) Chemical exchange at the sediment water interface of Cannonsville Reservoir. *Lake and Reservoir Management* 12, 266–277.

Gelda R. K. and Auer M. T. (1996) Development and testing of a dissolved oxygen model for a hypereutrophic lake. *Lake and Reservoir Management* 12, 165–179.

Gelda R. K., Auer M. T. and Effler S. W. (1995) Determination of sediment oxygen demand by direct measurements and by inference from reduced species accumulation. *Marine and Freshwater Research* 46, 81–88.

Gelda R. K., Auer M. T., Effler S. W., Chapra S. C. and Storey M. L. (1996) Determination of reaeration coefficients: a whole lake approach. *Journal of Environmental Engineering Division ASCE* 122, 269–275.

Gelda R. K., Effler S. W. and Brooks C. M. (1999) Nitrite and the two stages of nitrification in nitrogen polluted Onondaga Lake, NY. *Journal of Environmental Quality* (in press).

Hall G. H. (1986) Nitrification in lakes. In *Nitrification*, ed. J. I. Prosser, pp. 127–156. IRL Press, Washington, DC.

Harris G. P. (1986) *Phytoplankton Ecology, Structure, Function and Fluctuation*. Chapman and Hall, New York.

Jannasch H. W. (1975) Methane oxidation in Lake Kivu (central Africa). *Limnology and Oceanography* 20, 860–864.

Jorgensen B. B., Kuenen J. G. and Cohen Y. (1979) Microbial transformations of sulfur compounds in a stratified lake (Solar Lake, Sinai). *Limnology and Oceanography* 24, 799–822.

Klapwijk A. and Snodgrass W. J. (1982) Experimental measurement of sediment nitrification and denitrification in Hamilton Harbor, Canada. *Hydrobiologia* 91, 207–216.

McCutcheon S. (1987) Laboratory and in-stream nitrification rates for selected streams. *Journal of Environmental Engineering Division ASCE* 113, 628–646.

Metcalf and Eddy Inc. (1987) *Wastewater Engineering: Treatment Disposal Reuse*. McGraw-Hill, New York. p. 920.

Owens E. M. and Effler S. W. (1989) Changes in stratification in Onondaga Lake, NY. *Water Resources Bulletin* 25, 587–597.

Owens E. M. and Effler S. W. (1996) Modeling the impacts of a proposed hypolimnetic wastewater discharge on stratification and mixing in Onondaga Lake. *Lake and Reservoir Management* 12, 195–206.

Parsons T. R., Maita Y. and Lalli C. M. (1984) *A Manual of Chemical and Biological Methods for Seawater Analysis*. Pergamon Press, New York.

Pauer J. J. (1996) Nitrification in lake and river systems. PhD-thesis, Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI. p. 105.

Perkins M. G. and Effler S. W. (1996) Optical characteristics of Onondaga Lake 1968–1990. *Lake and Reservoir Management* 12, 103–113.

Prepas E. E., Field K. M., Murphy T. P., Johnson W. L., Burke J. M. and Tonn W. M. (1997) Introduction to the Amisk Lake project: oxygenation of a deep, eutrophic lake. *Canadian Journal of Fisheries and Aquatic Sciences* 54, 2105–2110.

Roberts R. D., Ashton P. J., Thornton J. A., Taussig H. G. and Sephton L. M. (1982) Overturn in a hypereutrophic, warm, monomictic impoundment (Hartbeespoort Dam, South Africa). *Hydrobiologia* 97, 209–224.

Rowell C. (1996) Paleolimnology of Onondaga Lake: the history of anthropogenic impacts on lake water quality. *Lake and Reservoir Management* 12, 35–45.

Ruane R. J. and Krenkel P. A. (1978) Nitrification and other factors affecting nitrogen in the Holston River. *Journal of Water Pollution Control Federation* 50, 2016.

Rudd J. W., Furutani A., Flett R. J. and Hamilton R. D. (1976) Factors controlling methane oxidation in shield lakes: the role of nitrogen fixation and oxygen concentration. *Limnology and Oceanography* 21, 357–364.

Scott J. A. and Abumoghli I. (1995) Modelling nitrification in the River Zarka of Jordon. *Water Research* 29, 1121.

Seitzinger S. P. (1988) Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. *Limnology and Oceanography* 33, 702–724.

Sharma B. and Ahlert R. C. (1977) Nitrification and nitrogen removal. *Water Research* 1, 897.

Sprent J. I. (1987) *The Ecology of the Nitrogen Cycle*. Cambridge University Press, Cambridge, UK.

Staley J. T. (1989) *Bergey's Manual of Systematic Bacteriology*, 3. Williams and Wilkins, Baltimore, MA.

Stauffer R. E. (1985) Relationships between phosphorus loading and trophic state in calcareous lakes of southeast Wisconsin. *Limnology and Oceanography* 30, 123–145.

Tango P. J. and Ringler N. H. (1996) The role of pollution and external refugia in structuring the Onondaga Lake fish community. *Lake and Reservoir Management* 12, 81–90.

Thomann R. V. and Mueller J. A. (1987) *Principles of Surface Water Quality Modeling and Control*. Harper and Row, New York.

USEPA (United States Environmental Protection Agency) (1983) *Methods for Chemical Analysis of Water and Wastes*. EPA-600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

USEPA (United States Environmental Protection Agency) (1985) *Ambient Water Quality Criteria for Ammonia—1984*. Office of Water Regulations and Standards Criteria and Standards Division, Washington, DC.

USEPA (United States Environmental Protection Agency) (1998) *1998 Update of Ambient Water Quality Criteria for Ammonia*. EPA-822-R-98-008. Office of Water Regulations and Standards Criteria and Standards Division, Washington, DC.

Walker W. W. (1987) *Empirical methods for predicting eutrophication in impoundment; Report 4, Phase III: Applications Manual*. Technical Report E-81-9. Prepared for the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MI.

Wetzel R. G. (1983) *Limnology*, 2nd ed. Saunders College, New York, p. 767.

Wickman T. R. (1996) Modeling and measurement of nitrogen diagenesis and ammonia release from the sediments of a hypereutrophic lake. M.S. thesis, Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI. p. 105.

Williamson R. B. and Cooke J. G. (1985) The effects of storms on nitrification rates in a small stream. *Water Research* 19, 435–440.

Wodka M. C., Effler S. W., Driscoll C. T., Field S. D. and Devan S. D. (1983) Diffusivity-based flux on phosphorus in Onondaga Lake. *Journal of Environmental Engineering Division ASCE* 109, 1403–1415.