

Development and Testing of a Nitrogen Model for Onondaga Lake

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ABSTRACT

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A dynamic two-layer mass balance model for total nitrogen (N) and various species of N is developed and tested for Onondaga Lake, NY, a system in which high concentrations of total ammonia (T-NH₃) prevail. The model simulates concentrations of T-NH₃, nitrate plus nitrite, particulate organic N (PON), dissolved organic N, total Kjeldahl N, and total N. Processes of the N cycle accommodated include net phytoplankton growth, nitrification, denitrification, ammonification, decay of PON, volatilization of free ammonia, sediment release of T-NH₃, settling of PON, and vertical mixing-based exchange between the layers. Model testing is supported by a comprehensive monitoring database of lake concentrations of the N species, and tributary and waste discharge concentrations for calculation of loads. Model credibility is enhanced by the independent determination of several important model coefficients based on field and laboratory experiments, which greatly reduces the role of calibration. Model verification is established by the successful simulation of the distinctly different distributions of various N species documented for the lake in 1989 and 1990. The model is particularly successful in simulating T-NH₃ concentrations in the upper waters, and is thus appropriate to evaluate various related remediation strategies for the lake.

Key Words: nitrogen, mass balance model, nitrogen species, ammonia, model simulations, calibration, verification.

Nitrogen exists in a number of different forms in aqueous environments. Many of these forms have important water quality implications. For example, NH₄⁺ and NO₃⁻ ions are the principal forms of N used for plant nutrition (Harris 1986, Wetzel 1983), NH₄⁺ and its organic precursors can represent an important sink for O₂ (Bowie et al. 1985, Harris 1986), unionized ammonia (here designated NH₃; USEPA 1985) and NO₂⁻ are toxic to fish at rather low concentrations. Ammonia is a terminal product in the decomposition of organic material (Kelly et al. 1988). The distribution among the different forms of N in lakes is mediated largely by a number of biochemical processes such as plant assimilation, nitrification, denitrification, and ammonification, as well as the input of these forms of N from a watershed. The N cycle is complex because of

the large number of chemical species of N (Harris 1986) and biochemical processes (Sprent 1987) that are involved in the cycle, and the great sensitivity of these processes to ambient environmental conditions (Hutchinson 1957, Sprent 1987, Wetzel 1983).

Lake N models have usually been one of a number of nutrient submodels in lake phytoplankton models (Canale et al. 1976, DiToro and Connolly 1980, DiToro et al. 1987; also see reviews of Bowie et al. 1985 and Zison et al. 1978). These models have been developed to address cultural eutrophication issues. In sharp contrast, the primary water quality issue for N in Onondaga Lake is the violation of NH₃ standards that protect against toxic effects on fish. These conditions are a result of the very high concentrations of total ammonia (sum of NH₄⁺ and NH₃; here designated T-NH₃) that prevail in the lake (Effler et al. 1990, 1996).

Here we document the development and testing of

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a N model for Onondaga Lake, NY. The model is intended to support evaluation of various remediation strategies to eliminate violations of the NH_3 standard in the lake. The principal focus of this modeling effort is the prediction of the seasonal dynamics of T- NH_3 in the upper waters of the lake as a function of ambient forcing conditions and waste inputs. Ammonia concentrations in the lower waters are of less direct concern, because prevailing anoxic conditions are the primary resource limiting factor for this layer (Effler 1996). However, all the major transformation and transport processes and the other N species of the overall total N cycle are accommodated in both layers of the lake by the model in order to support credible simulations of T- NH_3 .

Onondaga Lake

Onondaga Lake is a high flushing rate, dimictic, eutrophic lake that adjoins Syracuse, NY (Effler and Hennigan 1996). Effler and Hennigan (1996) have reviewed the history of the development of the surrounding area, and the lake setting, morphometry, hydrology and water quality. The external load of total N to the lake is about $200 \text{ g m}^{-2} \text{ yr}^{-1}$ (Effler et al. 1996). Approximately 45% of the annual N load is in the form of T- NH_3 (Effler and Whitehead 1996). The Metropolitan Syracuse Wastewater Treatment Plant (METRO) discharges about 80 MGD directly to the lake (Effler et al. 1996), and is the dominant source of N. It contributes approximately 80% of the annual total N load, and 90% of the T- NH_3 load (Effler et al. 1996).

The T- NH_3 , NH_3 , NO_3^- and NO_2^- concentrations in the epilimnion of Onondaga Lake are high compared to concentrations reported for many other lakes (Brooks and Effler 1990, Effler et al. 1990, Effler et al. 1996). The concentrations of T- NH_3 and NO_3^- in the upper waters always exceed levels associated with N limitation of phytoplankton growth (Auer et al. 1996). The standard to protect against the toxic effects of NO_2^- is violated routinely in the lake's upper waters in summer and early fall (Effler et al. 1996). However, the toxic effects of NO_2^- are known to be mitigated by Cl^- (Lewis and Morris 1986), which is also present in the lake in unusually high concentrations (Doerr et al. 1994). The standard to protect against the toxic effects of NH_3 is also violated annually; the most severe violations are observed in late spring/early summer (Effler et al. 1996). The related T- NH_3 standards established by the State of New York for the upper waters of the lake are 0.77 mg N/L in the summer and 1.07 mg N/L in the winter (see Effler and Doerr 1996).

Conceptual Framework

Model credibility is a major concern in this effort because it is intended that the model support the evaluation of costly management alternatives to remediate the NH_3 problem of the lake (see Effler and Doerr 1996). There is an important interplay between the complexity of mechanistic models and their performance characteristics and reliability (Auer and Canale 1986). Models can be too simple and they can be overly complex. Overly simple models do not provide an adequate description of important mechanisms and processes of the system. Models that are too complex compromise the accuracy of their predictions by the introduction of uncertainties associated with the estimation or specification of a large number of coefficients. Calibration of highly complex models is characterized by the "adjustment" or "tuning" of a large number of coefficients. The process is often constrained only by literature compilations of coefficient values used for other systems (Bowie et al. 1985, Zison et al. 1978). The N model presented here is of intermediate complexity. It accommodates the key processes regulating the T- NH_3 concentration in Onondaga Lake.

The conceptual framework of the N cycle model for Onondaga Lake, developed herein, is presented in Fig. 1. The individual processes and components involved in the N cycle model are represented

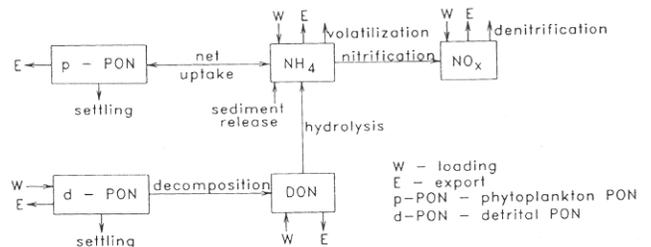


Figure 1.—Conceptual nitrogen model for Onondaga Lake.

schematically here by linkages and compartments. The components are particulate organic N (PON), dissolved organic N (DON), T- NH_3 , total Kjeldahl N (TKN = organic N + T- NH_3), NO_x , and total N (TN = TKN + NO_x). PON is partitioned into the phytoplankton fraction (p-PON) and the detrital fraction (d-PON), with total PON = p-PON + d-PON. It is assumed that the p-PON component is formed only from internal production, that is, there are no significant external sources. The other four N species have external sources (Fig. 1). Internal sources of d-PON are assumed to be insignificant. All components are subject to discharge from the lake through the outlet.

There are two pathways of loss to the atmosphere

(Fig. 1). Free ammonia is subject to loss through volatilization (see Effler et al. 1991). Also some of the N_2 gas formed through denitrification (loss from NO_x) in the anoxic hypolimnion is lost by gas ebullition (Address and Effler 1996). $T-NH_3$ is taken up by phytoplankton to support growth and converted to p-PON. DON is produced by decomposition of d-PON. $T-NH_3$ is produced from p-PON when phytoplankton net growth is negative (that is, when respiration and grazing losses exceed growth). Both forms of PON are subject to settling. $T-NH_3$ is produced from hydrolysis of DON and is released from the lake bottom sediments. $T-NH_3$ is converted to NO_x through the nitrification process. It is assumed that NO_x is not assimilated by phytoplankton in Onondaga Lake, because of the availability of $T-NH_3$, the form preferred for growth for energetic reasons (Wetzel 1983).

The transformations in the Onondaga Lake N model (Fig. 1) have been incorporated into other models (Baca and Arnett 1976 as cited by Bowie et al. 1985, Canale et al. 1976, Lean and Knowles 1987, Brezonik 1972 as cited by Chapra and Reckhow 1983, DiToro and Connolly 1980). However, there is no effort here to be mechanistically complete. Certainly other known, but poorly quantified, processes could be included in the model at the expense of overall model reliability. Rather, the emphasis here is to accurately quantify the important source and sink processes for $T-NH_3$.

The N model utilizes the same physical framework as employed for the total phosphorus (Doerr et al. 1996a) and dissolved oxygen (Gelda et al. 1996a) models developed for Onondaga Lake. The lake is modeled as two completely-mixed vertical layers, the

upper mixed layer (UML) and the lower mixed layer (LML). The dimensions of the layers are fixed. The demarcation depth separating the layers is 8.5 m, a depth that approximates the location of the thermocline for much of the summer stratification period (Effler 1996). The layers are connected by dispersive exchange flow. The seasonal variable exchange flow is calculated using measured surface and bottom layer temperatures. This two-layer representation of the lake water column has been widely adopted in modeling efforts for stratifying lakes (Chapra and Reckhow 1983, Thomann and Mueller 1987).

Monitoring Data/Process Studies

Extensive point source and tributary loading, and lake monitoring sampling programs were conducted in 1989 and 1990 to support model testing (Table 1). Average daily loads for METRO were determined from flow-weighted hourly samples. All tributary samples were grab type. Lake monitoring was conducted weekly from early spring to fall for both years at a single deep-water location representative of lake-wide conditions (Effler 1996).

Daily external loadings of $T-NH_3$, organic-N, and NO_x to Onondaga Lake were calculated using FLUX, a loading analysis software package developed by Walker (1987). In all cases interpolation was used to generate concentrations on days that were not sampled. Loading calculations used daily flows available for METRO and

Table 1—Monitoring data for Onondaga Lake N Model.

Component	Description
METRO*	$T-NH_3$, NO_x concentrations; 5d/wk TKN concentrations; 2d/wk Flow; continuously
Tributaries	Ninemile Cr.; 5d/wk March - Oct. 1989 other gauged tributaries and Ninemile Cr. outside this interval; 2/mo
Onondaga Lake monitoring	single deep-water station ** monitored April through October for 1989 and 1990 $T-NH_3$, NO_x , CHL - 2 m intervals; TKN, PON, DON - 1 and 16 m depths only; Temperature, pH, DO - 1 m interval

* reported by Onondaga County Department of Drainage and Sanitation as part of their operating permit requirements.

** found to be representative of lake-wide conditions (Effler 1996).

the gauged tributaries. Daily loading estimates for various N species for 1989 are presented here (Fig. 2a-c). METRO plays a dominant role in the magnitude and seasonality of the loads of these N species (particularly T-NH₃ and NO_x). The loading of T-NH₃ was relatively high, and NO_x relatively low, from January through mid-June. The loadings of T-NH₃ and T-NO_x were dramatically lower and higher, respectively, from July through September, because substantial nitrification is achieved within METRO only during these warmer months (Effler et al. 1996). The tributaries were the major source of NO_x to the lake during the spring. Short-term peaks in tributary loading generally corresponded to runoff events, while those for METRO were associated with abrupt changes in effluent concentrations.

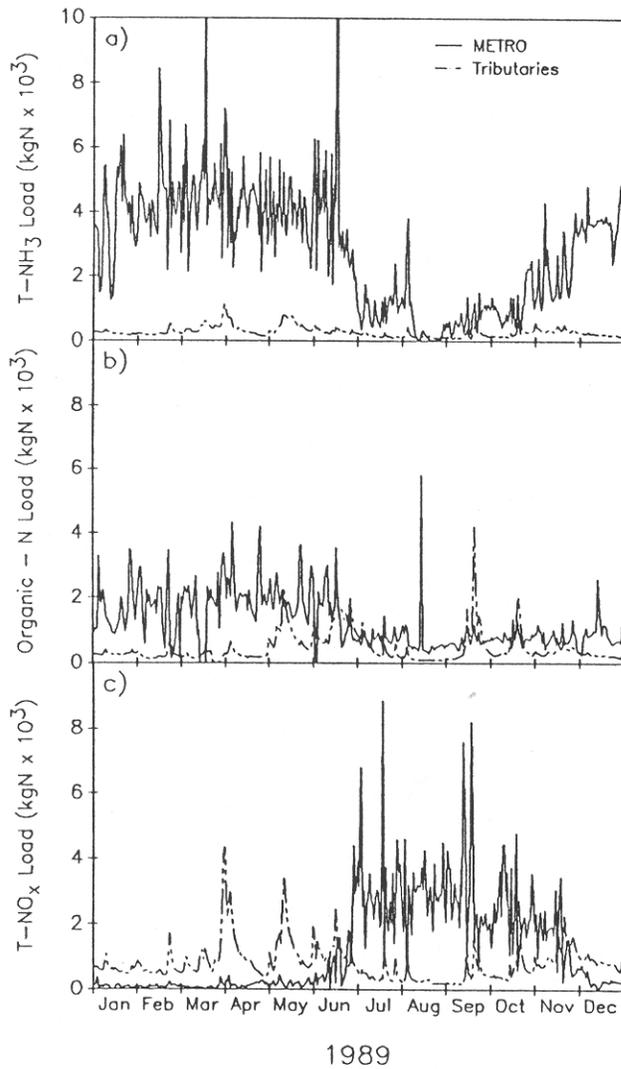


Figure 2.—Daily estimates of loading to Onondaga Lake from the Metropolitan Syracuse Wastewater Treatment Plant (METRO) and the sum of four tributaries for 1989: a) T-NH₃, b) organic N, and c) NO_x.

There were substantial differences in loads for 1989 compared to 1990 that were the result of differences in METRO effluent concentrations (Effler and Whitehead 1996). In particular, the T-NH₃ and organic-N loads were higher and the NO_x load lower in the summer and fall of 1990 compared to 1989 (see Fig. 3). As a result, the volume-weighted UML lake concentrations of T-NH₃ and NO_x are distinctly different for 1989 compared to 1990 (see Fig. 4). Concentrations of T-NH₃ were much higher in the spring, and again in October, in 1989 compared to 1990. The concentrations of NO_x were substantially higher in the late summer of 1989 compared to 1990. These differences present a good opportunity for testing the simulation capabilities of the model.

The model is also supported by a comprehensive program of field and laboratory studies (Table 2), to determine the various model inputs and coefficients. While this program has not entirely eliminated the

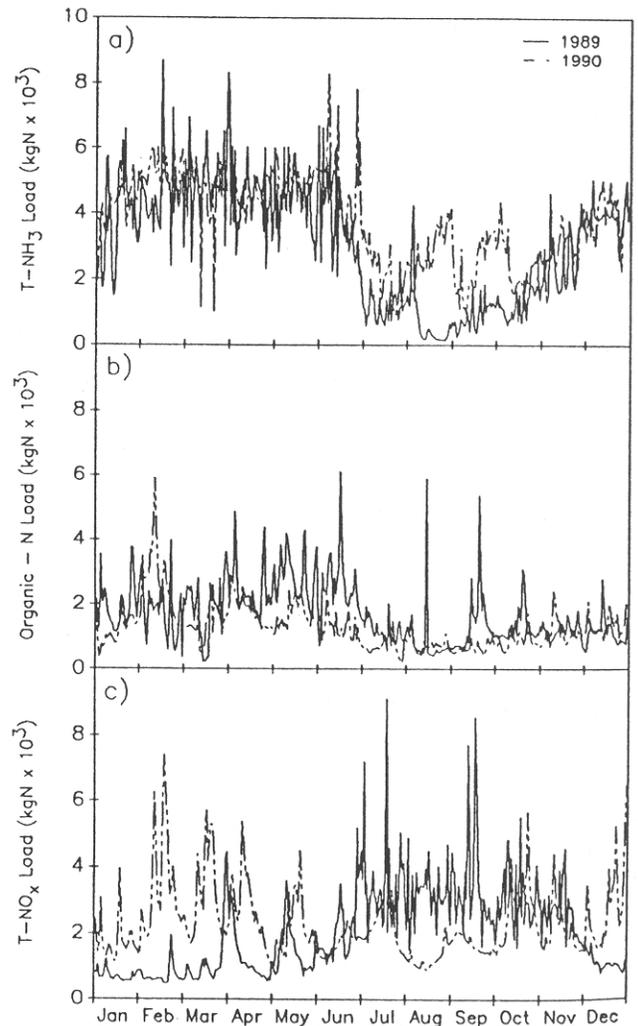


Figure 3.—Comparison of daily estimates of total loading to Onondaga Lake for 1989 and 1990: a) T-NH₃, b) organic N, and c) NO_x.

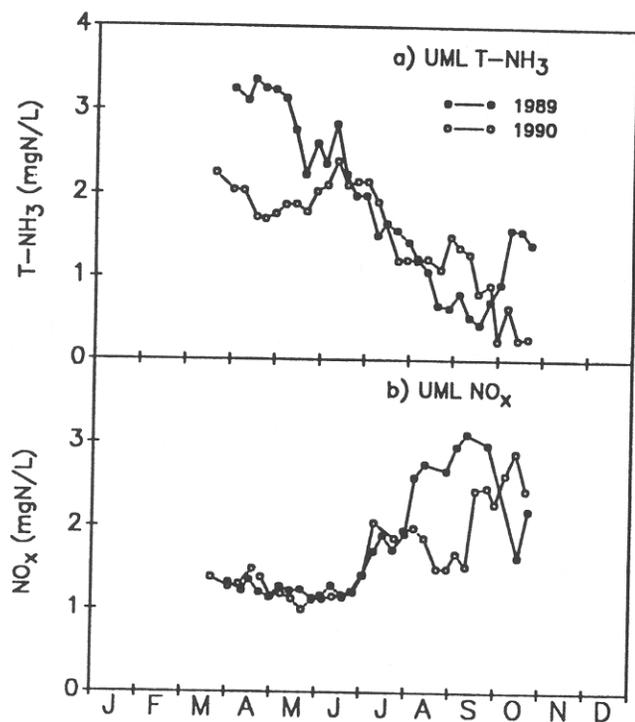


Figure 4.—Comparison of distributions of volume-weighted concentrations in the upper mixed layer (UML) of Onondaga Lake in 1989 and 1990: a) T-NH₃, and b) NO_x.

need for estimating some of the coefficients in the N model through calibration, it has substantially constrained this process, reduced the degrees of freedom of the model, and thereby enhanced model credibility. In particular, most of the primary processes regulating the cycling of T-NH₃ in the lake have been independently quantified. These processes and the supporting studies are further described as part of the development of the model.

N Model Components

p-PON and Phytoplankton Net Growth

The net effect of phytoplankton production and loss processes on T-NH₃ concentrations is accommodated in the N model (Fig. 1). Phytoplankton models consider growth and several sink terms including respiration, excretion, settling, grazing, and nonpredatory mortality (or decomposition) losses. A general equation which includes all of these processes and forms the basis for many phytoplankton models (Bowie et al. 1985) can be expressed as:

$$\frac{dP}{dt} = (G - D - e_x - s - m - z_g) \cdot P \quad (1)$$

Table 2.—Summary of procedures used to evaluate various model inputs.

Model Input	Procedure
geometry (V,A)	direct measurement
loads (W)	direct measurement (see Table 1)
flow (Q)	direct measurement (see Table 1)
settling velocity (vel_N)	deposition - cylindrical sediment traps, aspect ratio 6:1, deployed at 10 m depth, PON and CHL collected weekly, (Effler 1996)
vertical exchange (v_t)	calculated using temperature profiles (Doerr et al. 1996a)
sediment release (S_r)	sediment release of T-NH ₃ - intact sediment core experiments, accumulation of T-NH ₃ in overlying anoxic water (Penn et al. 1993)
net algal growth (G_{NET})	calculated using chlorophyll measurements
decomposition of PON (K_{decomp})	model calibration
hydrolysis of DON (K_{hyd})	model calibration
nitrification rate coef (k_{in})	nitrification - intact sediment core experiments, T-NH ₃ depletion in overlying oxic water (Penn et al. 1993)
volatilization rate coef (K_{L,NH_3})	calculated using oxygen transfer (Effler et al. 1991)
denitrification rate coef (K_{fd})	model calibration

in which P = phytoplankton biomass ($\text{mg chlorophyll}/\text{m}^3$), G = gross growth rate ($1/\text{d}$), D = respiration rate ($1/\text{d}$), e_x = excretion rate ($1/\text{d}$), s = settling rate ($1/\text{d}$), m = nonpredatory mortality rate ($1/\text{d}$), and z_g = loss rate due to grazing ($1/\text{d}$).

Several environmental factors, such as temperature, light, and nutrients affect the kinetics of the growth and loss processes. Many phytoplankton models combine several of the processes of Eq. (1) into a single term, thereby simplifying the expression (Bowie et al. 1985). The simplified version of Eq. (1) used here is:

$$\frac{dP}{dt} = (G_{\text{NET}} - s) \cdot P \quad (2)$$

in which G_{NET} = net growth = $G - D - e_x - m - z_g$ ($1/\text{d}$). The magnitude of G_{NET} varies seasonally in the lake because of temporal changes in mitigating environmental factors. The seasonality in G_{NET} and phytoplankton is not mechanistically modeled here, but instead is determined by calibration. Further research, particularly in quantifying zooplankton grazing and the dynamics of nutrient availability, is needed to develop a predictive phytoplankton model for Onondaga Lake.

The details of the calibrated time distributions of G_{NET} for the UML and LML for 1989 and 1990 were quite different (Fig. 5). However, spring and fall phytoplankton blooms (i.e., peaks in the concentration of total chlorophyll (CHL); e.g., see Fig. 5) are generally observed (Auer et al. 1996). There may be substantial

interannual variability in the magnitude of the fall bloom (Auer et al. 1996). This causes substantial interannual differences in the depletion of T-NH_3 in the upper waters during fall (Driscoll et al. 1996). Much of the temporal structure in CHL and therefore G_{NET} is regulated by zooplankton grazing (Siegfried et al. 1996), because only a modest degree of phosphorus limitation develops in the productive layers (Connors et al. 1996). The negative values of G_{NET} for the LML depict T-NH_3 recycle pathways.

The stoichiometry between p-PON and CHL was determined directly from paired measurements of PON and CHL made in the upper waters (1 m) of the lake between 1989 and 1991 (Fig. 6). The p-PON/CHL ratio is estimated as the slope ($= 5.2$) of the linear regression between PON and CHL. The intercept ($= 0.15 \text{ mgN} \cdot \text{L}$) is an estimate of the d-PON for the conditions of the measurements. The observations are nearly evenly distributed over the range of measurements. The regression explains 60% of the variations between CHL and PON. The relationship is used to calculate estimates of CHL from model predictions of p-PON. Some of the uncertainty in the regression is attributable to variations in the CHL content of the phytoplankton.

The mass balance expressions for p-PON in the UML and LML are:

$$V_1 \frac{d[\text{p-PON}]_1}{dt} = G_{\text{NET},1} \cdot [\text{p-PON}]_1 \cdot V_1 - Q \cdot [\text{p-PON}]_1 \quad (3a)$$

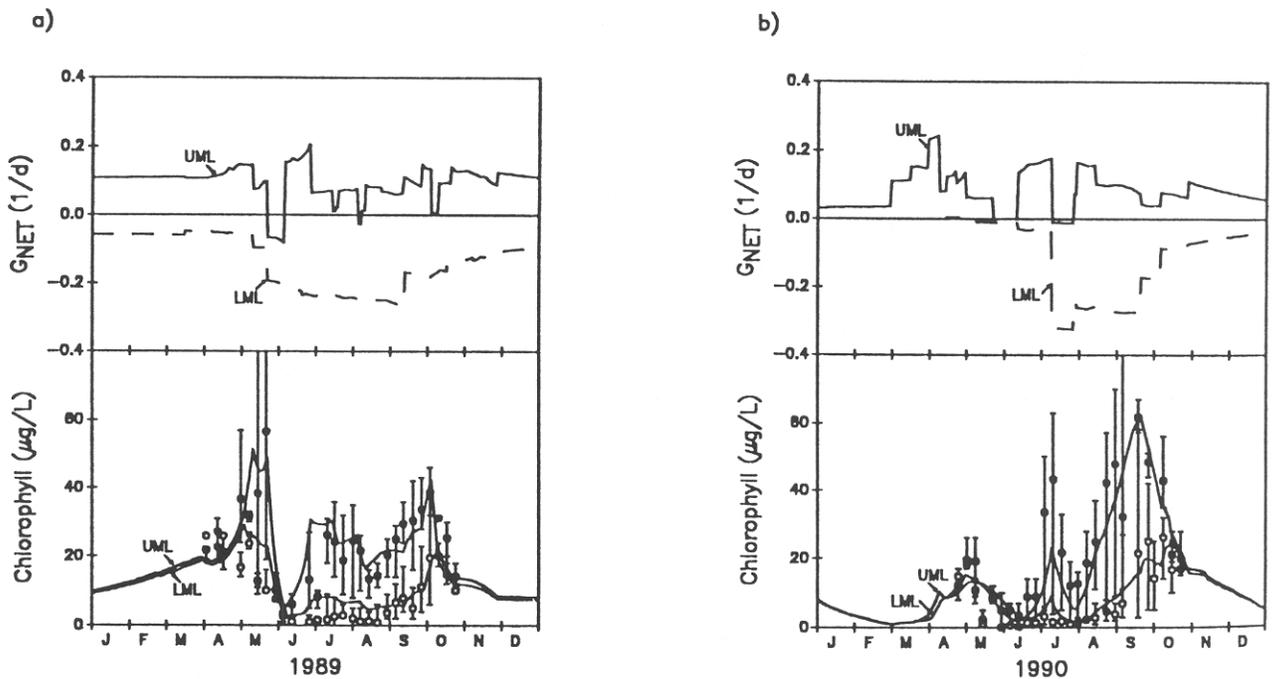


Figure 5.—Phytoplankton in Onondaga Lake: a) 1989, temporal distributions of net phytoplankton growth (G_{NET} ; see Eq. (2)) for the upper (UML) and lower mixed layers (LML) and performance in matching observed total chlorophyll (CHL) distributions, and b) 1990, temporal distributions of G_{NET} for the UML and LML and performance in matching observed CHL distributions. CHL points are volume weighted concentrations; dimensions of bars depict vertical range of observations within the layers.

$$\begin{aligned}
 & -vel_N \cdot A_i \cdot [p-PON]_1 \\
 & + v_t \cdot A_i \cdot ([p-PON]_2 - [p-PON]_1) \\
 V_2 \frac{d[p-PON]_2}{dt} = & G_{NET,2} \cdot [p-PON]_2 \cdot V_2 + vel_N \cdot A_i \cdot [p-PON]_1 \quad (3b) \\
 & - vel_N \cdot A_i \cdot [p-PON]_2 \\
 & + v_t \cdot A_i \cdot ([p-PON]_1 - [p-PON]_2)
 \end{aligned}$$

in which V_1, V_2 = volumes of UML and LML (m^3); Q = export flow from lake = sum of inflows to the lake (m^3/d); A_i = area of interface between the UML and LML (m^2); t = time (d); v_t = vertical mixing coefficient (m/d); $[p-PON]_1, [p-PON]_2$ = p-PON concentrations of the UML and LML (mg/L); $G_{NET,1}, G_{NET,2}$ = net growth of phytoplankton in UML and LML ($1/d$), and vel_N = average settling velocity of PON (m/d).

The time distributions of v_t for 1989 and 1990 were determined from temperature measurements by Doerr et al. (1996). The value of vel_N used for both p-PON and d-PON is 214 m/y . This corresponds to the settling velocity determined for particulate P in the total phosphorus (TP) model developed by (Doerr et al. 1996a). This is appropriate because particulate N and P are both largely associated with phytoplankton particles. This value of vel_N has additional independent support because it is quite close to an estimate based on paired measurements of PON and the downward flux of PON (Canale et al. 1993c).

d-PON

The model framework for d-PON includes terms for external loading, settling, and conversion to DON by decomposition processes. The major source of d-PON is loading from METRO. Total organic N (TON) in the METRO effluent was determined routinely during 1989 (calculated as the difference between unfiltered TKN and $T-NH_3$). Onondaga County (1990) reported an average TON loading rate of 1900 $kg\ N/d$ from

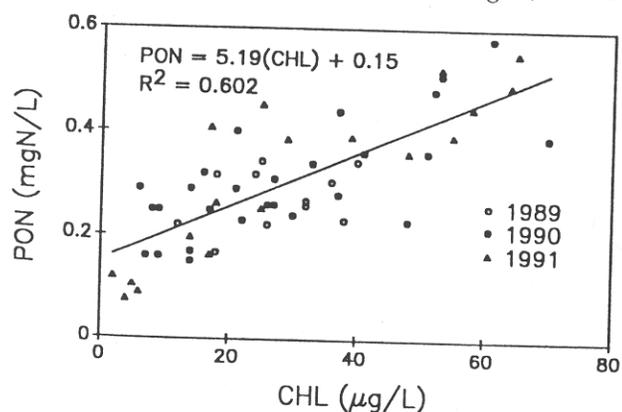


Figure 6.—Particulate organic nitrogen (PON) as a function of total chlorophyll (CHL) in Onondaga Lake.

METRO for 1989. Thirty-eight percent of the TON from all sources was reported to be PON and assumed to be d-PON in the model. This partitioning between d-PON and DON was adopted for all external loads in the model. The mass balance equations for d-PON in the two layers are:

$$\begin{aligned}
 V_1 \frac{d[d-PON]_1}{dt} = & W_{d-PON} - Q \cdot [d-PON]_1 \\
 & + v_t \cdot A_i \cdot ([d-PON]_2 - [d-PON]_1) \\
 & - vel_N \cdot A_i \cdot [d-PON]_1 - K_{decomp,T} \cdot V_1 \cdot [d-PON]_1 \quad (4a)
 \end{aligned}$$

$$\begin{aligned}
 V_2 \frac{d[d-PON]_2}{dt} = & vel_N \cdot A_i [d-PON]_1 \\
 & + v_t \cdot A_i \cdot ([d-PON]_1 - [d-PON]_2) \\
 & - vel_N \cdot A_i \cdot [d-PON]_2 - K_{decomp,T} \cdot V_2 \cdot [d-PON]_2 \quad (4b)
 \end{aligned}$$

in which $[d-PON]_1, [d-PON]_2$ = d-PON concentrations of the UML and LML (mg/L); W_{d-PON} = loading of d-PON (g/d), and $K_{decomp,T}$ = decomposition rate at temperature T ($1/d$).

The influence of temperature on $K_{decomp,T}$ is expressed in an Arrhenius format, according to:

$$K_{decomp,T} = K_{decomp,20} \cdot \Theta^{(T-20)} \quad (5)$$

Values of 0.1/d for $K_{decomp,20}$ and 1.08 for Θ were determined by model calibration.

DON

The sources of DON according to the model are external loading and decomposition of d-PON. The sinks of DON accommodated by the model framework include export and ammonification (hydrolysis). The mass balance equations for the two layers are:

$$\begin{aligned}
 V_1 \frac{d[DON]_1}{dt} = & W_{DON} - Q \cdot [DON]_1 + K_{decomp,T} \cdot V_1 \cdot [d-PON]_1 \\
 & - k_{hyd,T} \cdot [DON]_1 \cdot V_1 + v_t \cdot A_i \cdot ([DON]_2 - [DON]_1) \quad (6a)
 \end{aligned}$$

$$\begin{aligned}
 V_2 \frac{d[DON]_2}{dt} = & K_{decomp,T} \cdot V_2 \cdot [d-PON]_2 - k_{hyd,T} \cdot [DON]_2 \cdot V_2 \\
 & + v_t \cdot A_i \cdot ([DON]_1 - [DON]_2) \quad (6b)
 \end{aligned}$$

in which $[DON]_1, [DON]_2$ = DON concentration of the UML and LML (mg/L), W_{DON} = loading of DON (g/d), and $k_{hyd,T}$ = hydrolysis or ammonification rate constant at temperature T ($1/d$).

The influence of temperature on $k_{hyd,T}$ is expressed in an Arrhenius format, according to:

$$k_{hyd,T} = k_{hyd,20} \cdot \Theta^{(T-20)} \quad (7)$$

Values of 0.005 $1/d$ for $k_{hyd,20}$ and 1.08 for Θ were

determined by model calibration.

T-NH₃

The sources of ammonia include loadings from METRO and the four major tributaries, ammonification, zooplankton excretion (embedded in G_{NET}), and sediment release. The sinks of ammonia in the model are algal uptake, nitrification, export through the outlet and volatilization (Fig. 1).

The mass balance equations for T-NH₃ in the two layers are:

$$V_1 \frac{d[T-NH_3]_1}{dt} = W_{T-NH_3} - Q \cdot [T-NH_3]_1 + k_{hyd,T} \cdot [DON]_1 \cdot V_1 \quad (8a)$$

$$-G_{NET,1} \cdot [p-PON]_1 \cdot V_1 - k_{in,T} \cdot (A_s - A_1) \cdot [T-NH_3]_1 - K_{L,NH_3} \cdot A_s \cdot ff \cdot [T-NH_3]_1 + v_1 \cdot A_1 \cdot ([T-NH_3]_2 - [T-NH_3]_1)$$

$$V_2 \frac{d[T-NH_3]_2}{dt} = k_{hyd,T} \cdot [DON]_2 \cdot V_2 - G_{NET,2} \cdot [p-PON]_2 \cdot V_2 \quad (8b)$$

$$-k_{in,T} \cdot A_1 \cdot [T-NH_3]_2 + v_1 \cdot A_1 \cdot ([T-NH_3]_1 - [T-NH_3]_2) + S_{r,T} \cdot A_1$$

in which $[T-NH_3]_1$, $[T-NH_3]_2$ = T-NH₃ concentration of the UML and LML (mg/L), W_{T-NH_3} = external loading of T-NH₃ (g/d), $k_{in,T}$ = nitrification rate constant at T °C (m/d), A_s = surface area of the lake (m²), K_{L,NH_3} = surface transfer coefficient for NH₃ (m/d), ff = fraction of T-NH₃ as NH₃, and $S_{r,T}$ = sediment release rate of T-NH₃ (g/m²/d). The development of model inputs for nitrification, sediment release, and volatilization of T-NH₃, is treated below.

Nitrification

A number of researchers have reported that the nitrification process is localized at the sediment-water interface (Cavari 1977, Curtis et al. 1975, Hall 1986). Results of laboratory microcosm experiments indicate no significant nitrification occurs within the water column of Onondaga Lake (Auer and Brooks 1990). The kinetics of nitrification at the sediment-water interface were investigated in laboratory experiments with intact sediment cores, based on the depletion of T-NH₃ from overlying oxic lake water. A film transfer approach analogous to reaeration was used to describe the kinetics of the process (Bowie et al. 1985). Accordingly, the rate of nitrification is quantified by

$$\text{nitrification rate (g/d)} = k_{in} \cdot A \cdot [T-NH_3] \quad (9)$$

The film transfer nitrification coefficient (k_{in}) is determined by dividing the measured areal flux (g/m²/d) by the overlying bulk concentration (mg/L). This is an improvement over earlier models that have

treated the process as a first order water column phenomenon (Bowie et al. 1985, Zison et al. 1978).

The film transfer approach assumes that the rate limiting step for nitrification is diffusion-based transport of T-NH₃ from the overlying bulk liquid across a stagnant fluid layer (film) immediately overlying the sediments. Laboratory measurements of T-NH₃ flux suggest a range of k_{in} of 0.08 to 0.3 m/d. A value of k_{in} of 0.135 m/d was used in the model which is equal to that determined for the Seneca River (Canale et al. 1995). Temperature corrections were made according to the relationship

$$k_{in,T} = k_{in,20} \cdot \Theta^{(T-20)} \quad (10)$$

in which $\Theta = 1.06$. Zison et al. (1978) reported a range of Θ values for nitrification of 1.0548 to 1.0997.

The model assumes no nitrification for temperatures below 10°C because nitrifying bacteria do not multiply below this temperature (Thomann and Mueller 1987). Nitrification only occurs under oxic conditions. The area supporting nitrification in the UML (always oxic) is approximated by ($A_s - A_1$). The area of the lower layer during the oxygenated periods is A_1 . The area that supports nitrification in the LML during the summer stratification period decreases rapidly with the onset and vertical expansion of anoxia (Gelda et al. 1996a). Changes in the area of nitrification were determined from comprehensive oxygen measurements conducted since 1987 (Effler 1996).

Sediment Release

The sediment release rate of T-NH₃ ($S_{r,T}$) is applied across the entire LML sediment area. The flux has been measured directly in the laboratory at 8°C on cores (with intact sediment-water interfaces) collected from a single deep water location in the south basin of the lake. A value for $S_{r,T}$ of 92 mg N/m²/d has been determined by Penn et al. 1993. This value is close to a model calibration value of 70 mg N/m²/d. The modest difference between the laboratory and calibration values may reflect spatial differences in the release rate for the deep-water sediments of the lake. The influence of temperature is accommodated according to the Arrhenius relationship

$$S_{r,T} = S_{r,8} \cdot \Theta^{(T-8)} \quad (11)$$

with $\Theta = 1.085$.

NH₃ Volatilization

Free ammonia is lost to the atmosphere by volatilization (Effler et al. 1991, Thomann and Mueller

1987). The volatilization term in Eq. 8a is minor compared to the other sources and sinks, but it is included here for the sake of completeness. The fraction of T-NH₃ that exists as NH₃, (*ff*, dimensionless), is dependent primarily on pH and temperature (Effler et al. 1990). The temporal distribution of *ff* used in the model corresponds to the conditions documented for the upper waters of the lake in 1989 (Effler 1996). The surface air-water interface transfer coefficient for NH₃ was estimated from dissolved oxygen transfer coefficients determined independently for the lake (Gelda et al. 1996b). An average spring to fall value was used in the model as reported by Effler et al. (1991).

NO_x

The sources of NO_x are loadings from METRO and tributaries, and nitrification. The sinks of NO_x are denitrification and export through the outlet (Fig. 1). Algal uptake of NO_x is considered negligible because ammonia is favored by phytoplankton for energetic reasons (Wetzel 1983), and the T-NH₃ concentrations never fall to limiting levels. The management version of the N model accommodates a switch to utilization of NO_x for low T-NH₃ concentrations (Effler and Doerr 1996).

The mass balance equations for NO_x in the two layers are:

$$V_1 \frac{d[\text{NO}_x]_1}{dt} = W_{\text{NO}_x} - Q \cdot [\text{NO}_x]_1 + k_{\text{in},T} \cdot (A_3 - A_1) \cdot [\text{T-NH}_3]_1 + v_t \cdot A_1 \cdot ([\text{NO}_x]_2 - [\text{NO}_x]_1) \quad (12a)$$

$$V_2 \frac{d[\text{NO}_x]_2}{dt} = k_{\text{in},T} \cdot A_1 \cdot [\text{T-NH}_3]_2 - k_{\text{fd},T} \cdot A_1 \cdot [\text{NO}_x]_2 + v_t \cdot A_1 \cdot ([\text{NO}_x]_1 - [\text{NO}_x]_2) \quad (12b)$$

in which [NO_x]₁, [NO_x]₂ = NO_x concentrations of the UML and LML (mg/L), W_{NO_x} = loading of NO_x (g/d), and k_{fd,T} = denitrification rate constant at temperature T (m/d).

Denitrification, as with the nitrification process, is localized in the sediments (Seitzinger 1988). Therefore this process has also been modeled here according to film transfer theory, with the film transfer coefficient designated as k_{fd,T}. The denitrification process is the sole sink for NO_x in the hypolimnion. The value of k_{fd,T} determined by model calibration, is 0.4 m/d at T = 20°C. This corresponds to a first order water column process rate coefficient value of 0.06 1/d. This value is in the range reported by Bowie et al. (1985). The influence of temperature is quantified according to the Arrhenius expression

$$k_{\text{fd},T} = k_{\text{fd},20} \cdot \Theta^{(T-20)} \quad (13)$$

with $\Theta = 1.06$. This value falls in the range reported by

Bowie et al. (1985).

Total Kjeldahl and Total N

The concentration of TKN is the sum of predicted concentrations of PON, DON, and T-NH₃.

$$[\text{TKN}] = [\text{p-PON}] + [\text{d-DON}] + [\text{DON}] + [\text{T-NH}_3] \quad (14)$$

The concentration of TN in the system is the sum of the concentrations of organic and inorganic forms of N,

$$[\text{TN}] = [\text{PON}] + [\text{DON}] + [\text{T-NH}_3] + [\text{NO}_3^-] + [\text{NO}_2^-] \quad (15)$$

Inclusion of TKN and TN measurements in the supporting analytical program offers another level of testing of predictions of the model.

Model Performance

Model simulations were performed by solving Equations (3) to (15) using Euler's method with an integration step size of 1 day (Chapra and Canale 1990). Model performance was evaluated through calculation of the root mean square error (RMSE; Thomann 1982). RMSE is statistically well-behaved and is an indicator of average error between observations and predictions. RMSE is given by:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^N (X_{i,\text{obs}} - X_{i,\text{prd}})^2}{N}} \quad (16)$$

where, N = number of observations, X_{i,obs} = observed value of *i*th observation of parameter X, and X_{i,prd} = predicted value of *i*th observation of parameter X. Generally, a lower RMSE implies a better model fit to the observations.

Model simulations of the various N species and deposition in Onondaga Lake in 1989 are compared here to measurements (Fig. 7). Recall that the model calibration process was greatly constrained because of independent quantification of several important processes and detailed monitoring. The dynamics of PON largely reflect temporal patterns in phytoplankton biomass (in Fig. 7a) according to the p-PON/CHL stoichiometry (Fig. 6). Further, model-predicted patterns of PON and CHL deposition (Fig. 7b) approximately match observations. Model predictions of DON match observations for the UML, but overestimate LML measurements in late summer (Fig. 7c). Limited data are available to define vertically averaged concentrations of DON (Table 1) which may contribute to the apparent imprecision of the model.

The measured concentrations of T-NH₃ are

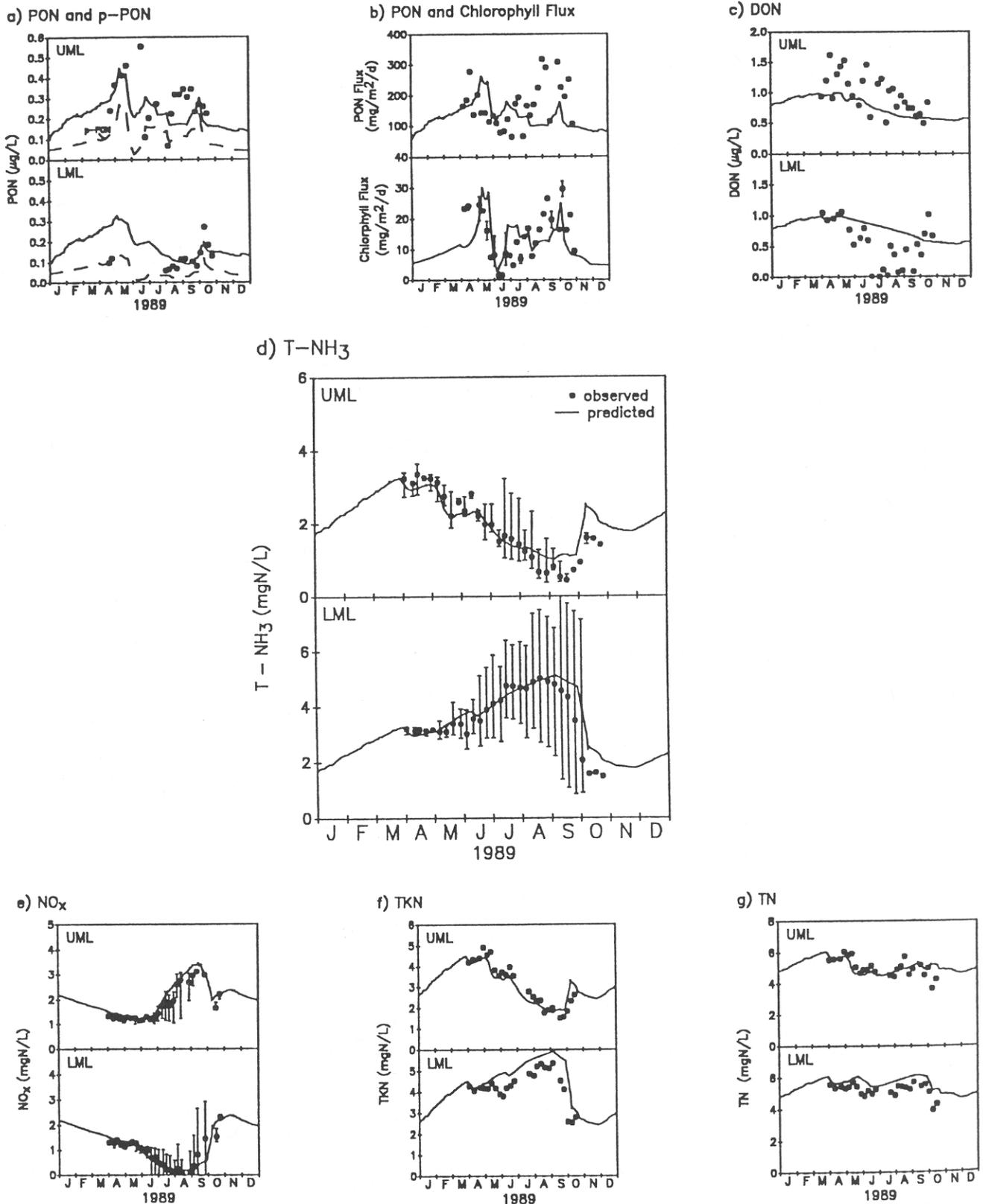


Figure 7.—Model performance (calibration) for 1989, comparison of simulations (lines) to measurements (points; dimensions of bars depict vertical range of observations within each layer): (a) concentrations of particulate organic nitrogen (PON), and the phytoplankton fraction of PON (p-PON; dashed line), (b) deposition of PON and total chlorophyll (CHL), as downward fluxes, (c) concentration of dissolved organic nitrogen (DON), (d) concentration of total ammonia (T-NH₃), (e) concentration of nitrate plus nitrite nitrogen (NO_x), (f) concentration of total Kjeldahl nitrogen (TKN), and (g) concentration of total nitrogen (TN).

particularly well matched by the model in both layers (Fig. 7d). The height of the vertical bars associated with the measurements of T-NH₃ (and NO_x) reflect the vertical range of concentrations observed in the two layers. The points are the volume-weighted concentrations. The fit of the data for the LML is in part a result of calibration. However, the simulation for the UML, the principal management focus of the N model, is much more independent of calibration procedures. The high spring concentration and the subsequent depletion of T-NH₃ in the UML until the fall mixing period is well simulated (Fig. 7d). The RMSE values of the model fit for the UML and LML for 1989 are 0.39 and 0.54 mgN/L, respectively. The seasonality of NO_x is also well tracked by the model simulations (Fig. 7c), especially the uniform concentrations in both layers through early summer, followed by increases in the UML and decreases in the LML. The model simulations also follow the dynamics of TKN and TN measurements in both layers (Fig. 7f, 7g).

Model verification results for 1990 (Fig. 8(a-g)) demonstrate the model captures the seasonality of the variations for most of the nitrogen species. The model calculations were performed using the same coefficient values used in 1989 and the G_{NET} distribution obtained from the measured CHL distribution in 1990 (Fig. 5). Again the model performs well for T-NH₃ in the UML in 1990, particularly for the critical spring/early summer (see Effler et al. 1996) period. The RMSE values of the model fit for the UML and LML for 1990 are 0.85 and 0.81 mgN/L, respectively. The deterioration in the model fit for the UML in 1990 compared to 1989 is associated mostly with the mid-summer to fall interval, i.e., after the critical spring to early summer period. The model performance for 1990 provides an additional test of the veracity of the linkages between phytoplankton activity and the various compartments of the N model.

Sensitivity Analyses

Sensitivity analyses have also been conducted to depict the importance of natural variations in environmental conditions and the uncertainty associated with the determination of model inputs and kinetic coefficients. The model exhibits substantial sensitivity in summer to interannual variations in the temporal distribution of phytoplankton activity (Fig. 9a), evaluated here by comparison of model predictions using the G_{NET} distributions for 1989 and 1990. Predictive capability for interannual differences in G_{NET} would entail development of a deterministic phytoplankton model (e.g., Bowie et al. 1985).

Subsequent sensitivity analyses (Fig. 9b-f) adopt the G_{NET} distribution for 1989 (Fig. 5a) and do not include the possible influence of changes in nutrient availability.

The sensitivity analysis for flows (Fig. 9b) uses the measured values for the tributaries for 1987 and 1976. These years correspond to the second lowest and highest annual runoff, respectively, over a 20-year period (Effler and Whitehead 1996). The sensitivity analysis for tributary flow (Fig. 9b) demonstrates substantial year-to-year differences in T-NH₃ concentrations are to be expected for the upper waters of the lake under prevailing METRO N loading conditions, as a result of natural variations in runoff (dilution; also see Effler et al. 1996).

Model simulations are moderately sensitive to \pm 10% variations in loading from METRO or errors in loading estimates from the facility of the same magnitude (Fig. 9c). The range of T-NH₃ in the UML is rather insensitive to reasonable levels of uncertainty in the sediment release rate (Fig. 9d). Uncertainty in ($k_{in,T}$), has a significant impact on the T-NH₃ concentration of the UML only during late summer (Fig. 9e), after the critical period of high T-NH₃ concentrations (Effler et al. 1990, 1996). Nitrogen model predictions of T-NH₃ in the UML were essentially insensitive to the uncertainties of the other model coefficients.

Management Summary

A dynamic two-layer mass balance model for N species in Onondaga Lake, that focuses primarily on T-NH₃, has been developed and tested. The model also simulates NO_x, PON, DON, TKN, and TN. The design of the model, including the processes accommodated, and its time and space scales, is consistent with the regulating phenomena, the character of the lake and its inputs, and the management needs and issues to be addressed (see Effler and Doerr 1996). Specifically, the model accommodates the important transport features of the lake, quantifies the primary processes regulating the T-NH₃ pool in the lake, and provides the appropriate seasonal resolution to address the T-NH₃ issue for the lake's upper waters.

The credibility of the model has been enhanced by the independent determination of several important model coefficients, thereby minimizing the introduction of uncertainties inherent in the calibration process. The successful verification of the N model for the lake, particularly for T-NH₃ for the upper waters during the critical late spring/early summer period, supports the model as a management tool to evaluate

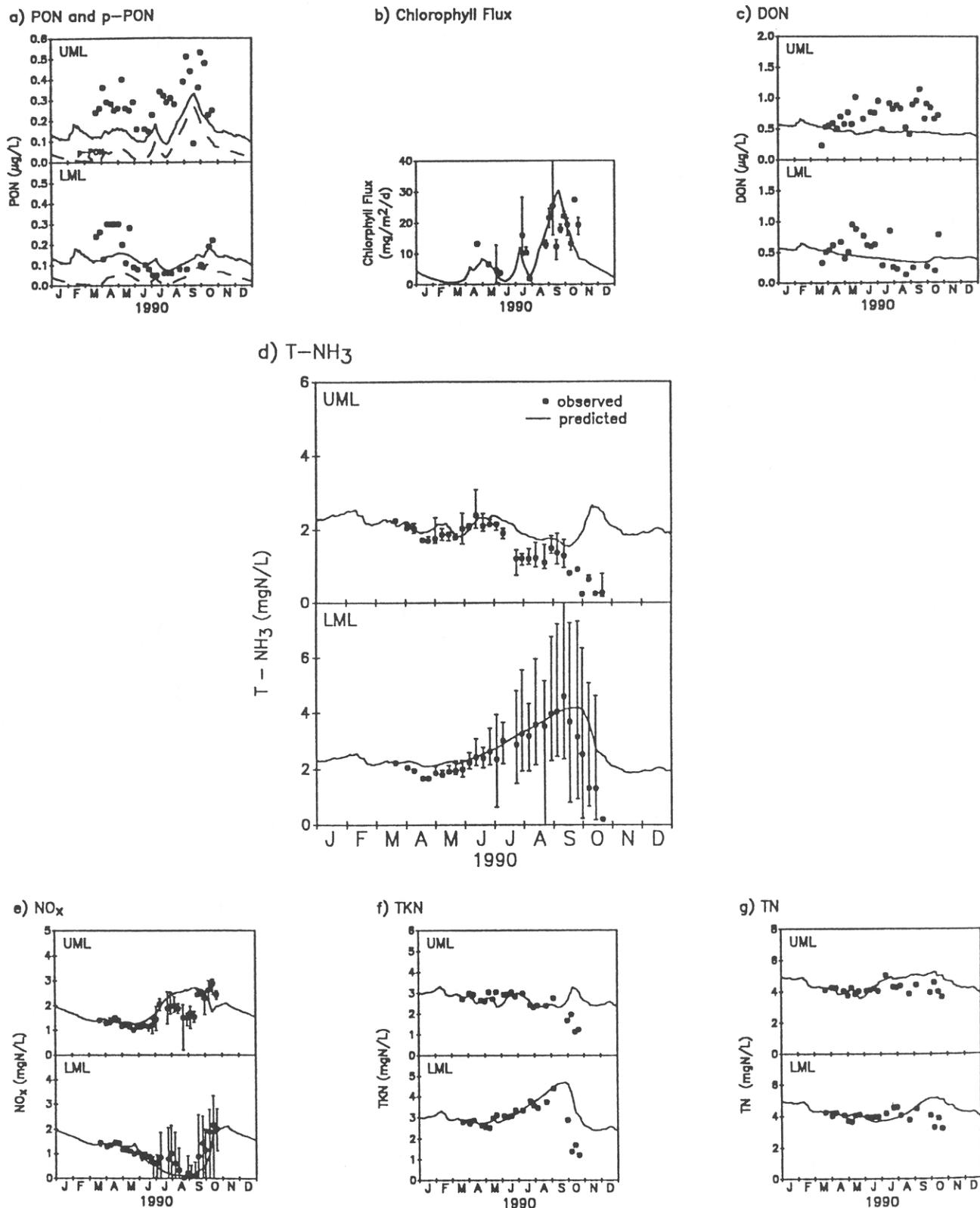


Figure 8.—Model performance (verification) for 1990, comparison of simulations (lines) to measurements (points; dimensions of bars depict vertical range of observations within each layer): (a) concentrations of particulate organic nitrogen (PON), and the phytoplankton fraction of PON (p-PON; dashed line), (b) deposition of total chlorophyll (CHL) as a downward flux, (c) concentration of dissolved organic nitrogen (DON), (d) concentration of total ammonia (T-NH₃), (e) concentration of nitrate plus nitrite nitrogen (NO_x), (f) concentration of total Kjeldahl nitrogen (TKN), and (g) concentration of total nitrogen (TN).

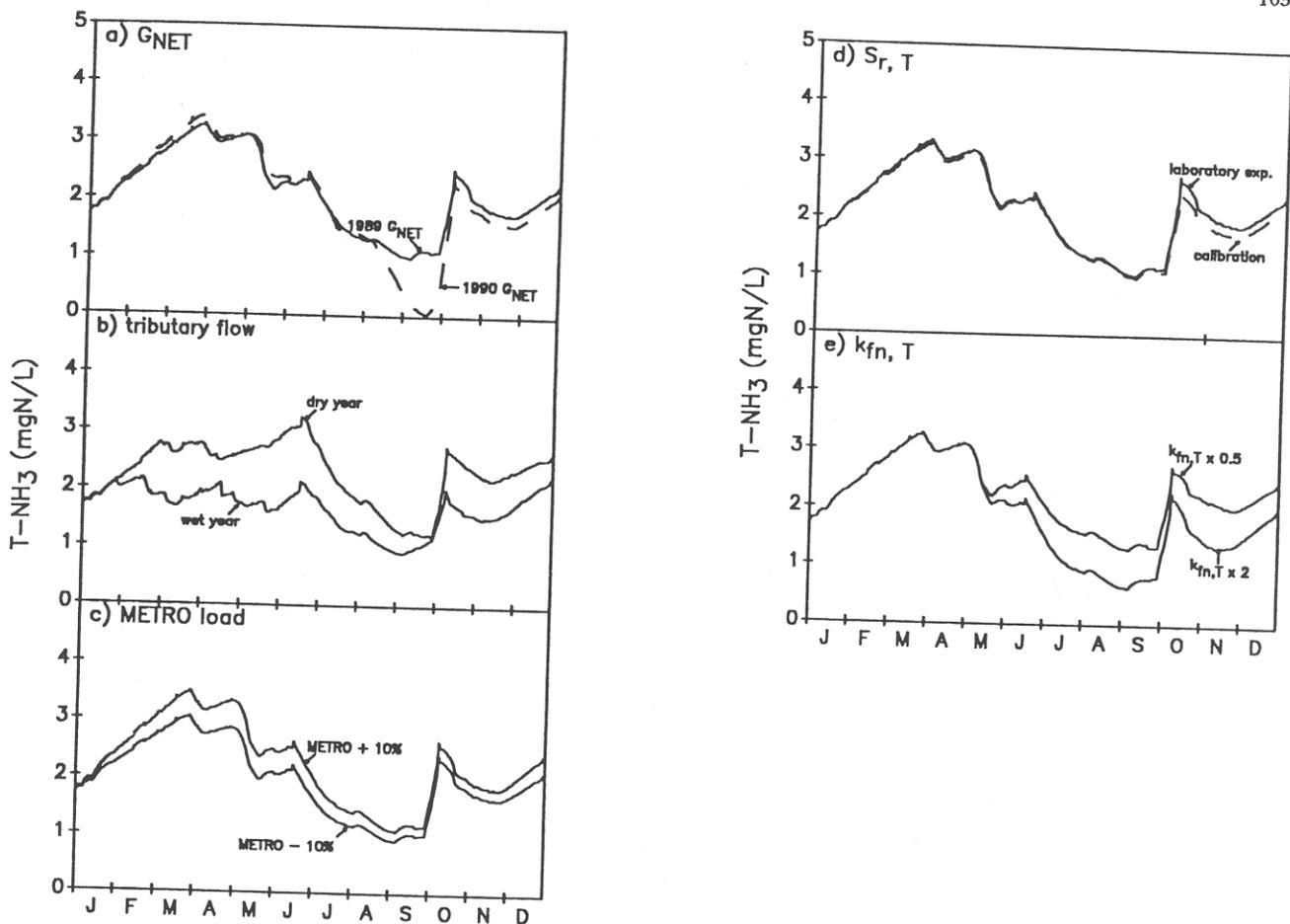


Figure 9.—Sensitivity analyses with nitrogen model for Onondaga Lake for total ammonia ($T-NH_3$) concentrations in the upper mixed layer (UML): (a) net phytoplankton growth (G_{NET} ; see Eq (2)), 1989 versus 1990 distributions, (b) tributary runoff, dry year (1987) and wet year (1976) flows, (c) $\pm 10\%$ $T-NH_3$ loading from the Metropolitan Syracuse Wastewater Treatment Plant (METRO), (d) sediment $T-NH_3$ release rate ($S_{r,T}$), laboratory rate versus calibration rate, and (e) film transfer nitrification coefficient ($k_{fn,T}$, $0.5 \times k_{fn,T}$ versus $2 \times k_{fn,T}$).

process. The successful verification of the N model for the lake, particularly for $T-NH_3$ for the upper waters during the critical late spring/early summer period, supports the model as a management tool to evaluate related remediation strategies. The sensitivity of model predictions of $T-NH_3$ for mid-summer to fall to interannual variation in net phytoplankton growth is not limiting for management applications because model performance is not influenced during the critical late spring/fall summer interval when the most severe violations are observed (Effler et al. 1996). Management actions that met the standard in the late spring/early summer interval would be protective for the entire interval.

The N model is applied in evaluating management alternatives in two contributions that appear subsequently in this issue. In the first instance the adequacy of selected reduced loading scenarios is evaluated (Effler and Doerr 1996). The other application, utilizing a modified transport framework

version of the model, forecasts the impact of an alternative to discharge the METRO effluent to the lake's hypolimnion (Doerr et al. 1996b).

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