



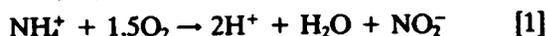
Nitrite and the Two Stages of Nitrification in Nitrogen Polluted Onondaga Lake, New York

Rakesh K. Gelda, Steven W. Effler,* and Carol M. Brooks

ABSTRACT

Nitrite (NO_2^-) concentrations in the upper waters of N polluted Onondaga Lake, New York, are documented for the April through October interval for a 10-yr (1989–1998) period. Inputs of NO_2^- from a domestic waste treatment facility (METRO) and tributaries (4) to the lake are quantified for four of the years (1991–1994). The NO_2^- concentrations measured in Onondaga Lake (e.g., annual maxima in the range 200–1000 mg N m^{-3}) are some of the highest reported for lakes and rivers in the literature. These levels represent severe violations of toxicity standards. Annual average concentrations in the METRO effluent ranged from 412 to 1097 mg N m^{-3} . The METRO load represented >90% of the total external NO_2^- load to the lake. A mechanistic mass balance model for NO_2^- and NO_3^- is developed and applied for the lake to identify occurrences, and quantify the rates, of the first and second stages of nitrification. Nitrite is found to behave in a nearly conservative manner in the upper waters of the lake over the April to July interval. The progressive increases in concentrations over this interval have been largely in response to inputs from METRO. Major deviations from conservative behavior occurred for NO_2^- in most years over the July to October interval as a result of the irregular operation of the two stages of the nitrification process. This has been manifested as large and abrupt changes in NO_2^- concentration in the July to October interval. Potential factors responsible for the observed dynamics in nitrification and the NO_2^- pool are considered.

NITRITE (NO_2^-) is an intermediate in the microbially mediated processes of nitrification—an aerobic process—and denitrification, which occurs mostly under anoxic/anaerobic conditions (Sprent, 1987; Wetzel, 1983). These are the two dominant processes regulating the formation and transformation of this form of N in soils and surface waters (Mackerness and Keevil, 1991; Wetzel, 1983). Though denitrification is not strictly limited to anoxic/anaerobic environments (Lloyd, 1993), nitrification is the primary pathway regulating the cycling of NO_2^- in oxic surface waters such as the epilimnia of lakes (Smith et al., 1995; Sprent, 1987; Wetzel, 1983). Nitrite is formed through oxidation of the ammonium ion, primarily by *Nitrosomonas* species.



Nitrite is oxidized to nitrate (NO_3^-), primarily by *Nitrobacter* species.



The first stage of nitrification (Eq. [1]) is usually the rate-limiting step of the overall process (Klapwijk and Snodgrass, 1982). Thus, NO_2^- is widely considered to be a labile material in surface waters, and is usually found in low concentrations (Meybeck, 1982; Wetzel, 1983).

Lake concentrations have been reported to usually fall in the range of 0 to 10 mg N m^{-3} (Wetzel, 1983). Meybeck (1982) reported a worldwide average concentration of 1 mg N m^{-3} for unpolluted rivers. Indeed, measurements of NO_2^- are often not included in water quality surveillance programs. Rather, this form is commonly lumped with NO_3^- in laboratory analysis and reported as the sum of $\text{NO}_3^- + \text{NO}_2^-$. The implicit assumption in such cases is that NO_2^- concentration is very low compared with NO_3^- concentration.

However, NO_2^- has been observed in relatively high concentrations in a limited number of surface water systems. These exceptions have reflected pollution inputs. Hutchinson (1957) indicated the occurrence of appreciable NO_2^- levels in surface waters was a manifestation of sewage contamination. Barica (1990) observed very high concentrations of NO_2^- (600–1200 mg N m^{-3}) near the outfall of the Hamilton sewage treatment plant in Hamilton Harbour, Lake Ontario; levels exceeded 50 mg N m^{-3} through most of the harbor for much of the 20-mo period of measurements. Meybeck (1982) reported concentrations of NO_2^- in major contaminated rivers of Switzerland in the range of 8 to 17 mg N m^{-3} . Smith et al. (1995) documented NO_2^- concentrations in the major rivers entering Lough Neagh (Northern Ireland) that were frequently in the range of 100 to 150 mg N m^{-3} . These levels were attributed largely to agricultural pollution, and were associated with direct inputs of NO_2^- (~40%) and internal production (~60%) from the first stage of nitrification (Smith et al., 1995, 1997a). In both cases the maintenance of high concentrations of NO_2^- were attributed to the inhibition of the second stage of nitrification (Eq. [2]) by high concentrations of free ammonia (NH_3 ; Barica, 1990; Smith et al., 1995, 1997a).

The occurrence of high concentrations of NO_2^- is an important water quality concern because this anion is highly toxic to fish, causing hypoxia by the oxidation of hemoglobin to methemoglobin (Rodríguez-Moreno and Tarazona, 1994; Russo, 1980; Russo et al., 1981). Related water quality standards in New York are 20 and 100 mg N m^{-3} for salmonid and nonsalmonid systems, respectively. Further, because NO_2^- is an intermediate in nitrification, occurrences of elevated levels offer an opportunity to evaluate various features of this important biochemical process of the N cycle. Here we document inputs of NO_2^- from a domestic waste treatment facility and tributaries to N polluted Onondaga Lake for the 1991 to 1994 period, and concentrations in the upper waters of the lake for the April to October inter-

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Abbreviations: CSO, combined sewer overflow; DO, dissolved oxygen; LML, lower mixed layer; METRO, Metropolitan Syracuse Wastewater Treatment Plant; UML, upper mixed layer; T, temperature; T-NH₃, total ammonia.

val over the period 1989 to 1998. The status of the lake with respect to a water quality standard for NO_2^- is evaluated. A mechanistic mass balance model is developed and applied to synthesize input and lake NO_2^- data, to delineate intervals over which source and sink processes for NO_2^- operate, and to estimate the dynamics of the rates of the first and second stages of nitrification. Potential forcing conditions responsible for the observed in-lake patterns of NO_2^- , and calculated variations in rates of nitrification, are evaluated.

ONONDAGA LAKE

Onondaga Lake is located in metropolitan Syracuse, NY. This hardwater, alkaline lake (Effler, 1996) has a surface area of 12 km², a volume of 131×10^6 m³, and a maximum depth of 19.5 m (Fig. 1). Onondaga Lake was oligo-mesotrophic before European settlement in the late 1700s (Rowell, 1996), and supported a cold-water fishery until the late 1800s (Tango and Ringler, 1996). Currently, the lake is hypereutrophic and severely polluted as a result of inputs of industrial and domestic waste from the watershed (642 km², ~450 000 people; Effler and Hennigan, 1996). It has been described as the most polluted lake in the USA (Onondaga Lake Restoration Act of 1989; Anon., 1989). The cold-water fishery has been lost, a number of numerical standards intended to protect fishing and contact recreation resources of surface waters are violated routinely, and other features of the ecosystem have been degraded that are not amenable to representation through numerical standards (Effler, 1996).

Three natural tributaries—Onondaga, Ninemile, and Ley Creeks (Fig. 1)—contribute ~70% of the flow into

the lake. Onondaga Creek (298 km² watershed) enters the southern end of the lake. The lower reaches of the creek drain a significant portion of the city of Syracuse, NY, and receive inputs of dilute untreated domestic waste during runoff events via approximately 40 combined sewer overflow (CSO) structures within the city (Canale et al., 1993). Ninemile Creek (298 km² watershed) empties into the lake on its western shore. Waste beds associated with soda ash production adjoin the lower 3 km of this stream. Various pollutants enter the stream from these industrial deposits, including ammonia (Effler et al., 1991). The headwaters of Ley Creek are located in wetlands. The watershed (77.4 km²) in the stream's lower reaches is residential and industrial. Two CSOs flow into the creek and an abandoned landfill adjoins the stream near its mouth. Harbor Brook (29.3 km² watershed) also enters the southern end of the lake (Fig. 1). This tributary is often included in water quality studies of the lake, despite its small flow (~2% of total inflow), because of elevated pollutant concentrations (Effler and Whitehead, 1996). Nineteen CSOs discharge to this stream during runoff events. None of these tributaries are considered trout fisheries in their lower reaches near the lake. Effluent discharged to the southern end of the lake from the Metropolitan Syracuse Wastewater Treatment Plant (METRO; Fig. 1; avg. flow $\sim 3.5 \text{ m}^3 \text{ s}^{-1}$) contributes almost 20% of the annual inflow, and often is the single largest input in late summer (Effler et al., 1996a). The hydrology of inputs to the lake is well quantified; about 90% of the inflow is continuously gauged (Effler and Whitehead, 1996). Wide seasonal and interannual variations in tributary flows occur, while the discharge from METRO is relatively uniform. Onondaga Lake flushes rapidly; e.g., the average for

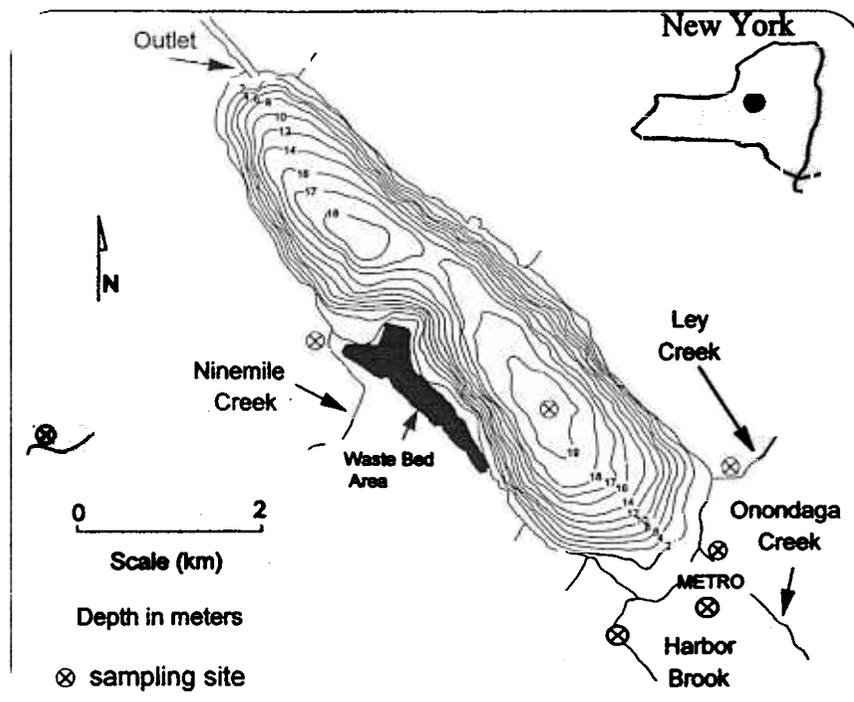


Fig. 1. Onondaga Lake and monitored inputs.

the 1971 to 1989 interval was 3.7 flushes yr^{-1} (Effler and Whitehead, 1996).

METRO is the dominant source of P and N to the lake (Effler et al., 1996a). The prevailing areal annual load of P from the facility ($\sim 5 \text{ g m}^{-2} \text{ yr}^{-1}$) represents about 60% of the total; this input is responsible for the lake's hypereutrophic condition (Effler et al., 1996a). Manifestations of hypereutrophy in the lake include severe phytoplankton blooms (Effler, 1996), poor clarity (Perkins and Effler, 1996), rapid loss of dissolved oxygen (DO) from the hypolimnion (Effler et al., 1996a), subsequent hypolimnetic accumulations of reduced by-products of anaerobic metabolism (hydrogen sulfide, methane, and ammonia), and oxygen depletion in the upper waters during the fall mixing period associated with the oxidation of these by-products (Address and Effler, 1996; Effler et al., 1988). A large fraction of the fish population of the lake exits to the river (Fig. 1) during the period of depressed DO in fall (Tango and Ringler, 1996). Oxygen concentrations in the upper waters (Effler, 1996) remain above levels considered limiting to the nitrification process (Bowie et al., 1985).

The METRO discharge represents 60, 90, and 80% of the total annual external loads of $\text{NO}_3^- + \text{NO}_2^-$, total ammonia (T-NH₃; defined as sum of NH_4^+ and NH_3), and total N, respectively (Effler et al., 1996a; Effler and Whitehead, 1996). Loads of NO_2^- from the facility and tributaries have not been comprehensively addressed previously. Substantial nitrification is achieved within METRO during the warmer months, which causes seasonal shifts in the contributions of T-NH₃ and $\text{NO}_3^- + \text{NO}_2^-$ to the facility's N load, though large interannual differences in the timing and extent of nitrification have been observed (Effler et al., 1996a). Denitrification is not achieved within METRO.

Temporal and spatial distributions of T-NH₃, NH₃, and $\text{NO}_3^- + \text{NO}_2^-$ for Onondaga Lake have been described for several years in the literature (Brooks and Effler, 1990; Canale et al., 1996; Effler et al., 1990, 1996a). However, descriptions of the patterns for NO_2^- for the lake have been more limited (Brooks and Effler, 1990; Effler et al., 1996a). Certain of the temporal features of the patterns of forms of N have strong interplay with the dynamics of the stratification regime. Concentrations of NO_3^- and NO_2^- have decreased progressively in the hypolimnion with the onset of anoxia, and are eliminated by midsummer, as a result of the operation of the denitrification process (Brooks and Effler, 1990; Effler, 1996). The progressive increases of ammonia concentrations in the hypolimnion (Brooks and Effler, 1990; Canale et al., 1996; Effler, 1996) are largely due to release from the underlying sediments (ammonification; Wickman, 1996). The maximum volume-weighted hypolimnetic T-NH₃ concentration observed annually, before the onset of fall mixing, approaches 5 g N m^{-3} (Effler, 1996). Vertical patterns for these constituents in the hypolimnion reflect localization of source/sink processes within the sediments (Gelda et al., 1995); i.e., $\text{NO}_3^- + \text{NO}_2^-$ has been depleted first, and maximum T-NH₃ concentrations (e.g., $>7 \text{ g N m}^{-3}$) have been measured, in the deepest layer(s).

Concentrations of T-NH₃ and NO_3^- in the upper productive layers (sum $>2 \text{ g N m}^{-3}$) remain well above levels considered limiting to phytoplankton growth (Canale et al., 1996; Effler, 1996). Year-to-year differences in T-NH₃ levels at spring turnover are largely driven by interannual differences in dilution provided by tributaries over the previous late fall to spring interval (Effler et al., 1996a). Subsequent seasonal epilimnetic patterns in T-NH₃ and $\text{NO}_3^- + \text{NO}_2^-$ through late summer can vary year-to-year in response to several factors, but primarily associated with differences in nitrification at METRO, phytoplankton growth, and lake flushing (Canale et al., 1996). Concentrations of ammonia in the lake's epilimnion have exceeded criteria (USEPA, 1985, 1998) to protect against related toxic effects by a wide margin for substantial portions of the spring to fall interval (Brooks and Effler, 1990; Effler et al., 1990, 1996a). Nitrification was found to be a minor source/sink process for the epilimnetic pools of T-NH₃ and $\text{NO}_3^- + \text{NO}_2^-$ over the spring to late summer interval (Canale et al., 1996). This is consistent with laboratory experiments that found nitrification to be localized at the (oxidized) sediment-water interface of the lake (Pauer, 1996). However, high rates of nitrification were demonstrated for the upper waters of the lake during the fall mixing period of certain years, that caused major interannual variations in the pools of T-NH₃ and $\text{NO}_3^- + \text{NO}_2^-$ (and oxygen) in these layers during this interval (Gelda et al., 1999). Brooks and Effler (1990) reported progressive increases in epilimnetic concentrations of NO_2^- through late summer in 1988 to more than 0.30 g N m^{-3} . Concentrations at a depth of 1 m demonstrated a similar trend in several other years (Effler et al., 1996a).

METHODS

Input Concentrations and Loads, and Lake Measurements

Estimates of mass loading rates of NO_2^- and NO_3^- to support mass balance model analyses for the 1991 to 1994 interval were based on flow and concentration data collected by three different monitoring programs (e.g., Effler and Whitehead, 1996): (i) tributary flow measurements made by the U.S. Geological Survey (USGS), (ii) effluent flow and NO_3^- concentrations measured at METRO as part of the facility's permit requirements, and (iii) measurements made by the authors of NO_2^- in the tributaries and METRO effluent, and of NO_3^- in the tributaries. Concentrations of NO_3^- in the METRO effluent were measured (APHA, 1992) once every 2 wk on daily flow-weighted composite effluent samples by the facility's personnel. Grab-type samples collected once every 2 wk from locations near the mouths of Onondaga Creek, Ninemile Creek, Ley Creek, and Harbor Brook (Fig. 1) were analyzed for $\text{NO}_3^- + \text{NO}_2^-$ and NO_2^- (USEPA, 1983); the concentration of NO_3^- was determined by difference. Aliquots of the daily flow-weighted composite samples collected at METRO were analyzed for NO_2^- at different frequencies over the interval; e.g., 2 d mo^{-1} in 1991 and 2 d wk^{-1} in 1994. The detection limit for all NO_2^- measurements in this investigation was 10 mg N m^{-3} . Tributary concentrations of NO_2^- for 1994 were represented here as the average of values measured in 1991, 1992, and 1993 to support loading calculations.

Loads of NO_2^- and NO_3^- were calculated at a daily time-

step for the 1991 to 1994 interval to support the mass balance model analyses (described subsequently). Daily estimates for METRO were the product of daily flows and daily concentrations. Effluent concentrations for days without measurements were estimated by time interpolation (e.g., Canale et al., 1996; Effler et al., 1996a; Effler and Whitehead, 1996). Tributary daily loading estimates were made using FLUX (version 4.4, 1990), loading analysis software developed by Walker (1987).

The lake was monitored weekly (at midmorning) over the April to October interval for the period 1989 to 1998, 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). Field measurements of temperature (T) and pH were made (Hydrolab Surveyor 3) at depth intervals of 1 m. Samples for laboratory analyses of T-NH₃, NO₃⁻ + NO₂⁻, and NO₂⁻ (USEPA, 1983) were collected at depth intervals of 1 to 2 m. Results of NO₂⁻ measurements are presented for the entire 10-yr monitoring period. Paired distributions of T-NH₃ and NO₃⁻ are presented here only for the 1991 to 1994 interval, to describe typical patterns for the lake, and support mass balance modeling analyses to estimate temporal distributions of the rates of the first and second stages of nitrification. Concentrations of NH₃ were calculated for the upper waters of the lake for the 1989 to 1998 period from the paired measurements of T-NH₃, pH, and T , according to protocols presented by Effler et al. (1990; also see Emerson et al., 1975; Messer et al., 1984).

Modeling

A mass balance model for NO₂⁻ and NO₃⁻ was developed to assess temporal patterns in the rates of the first and second stages of nitrification in the epilimnion of the lake. The mass transport framework of the model consists of two completely mixed vertical layers of fixed dimensions (demarcation depth of 8.5 m)—an upper mixed layer (UML) and a lower mixed layer (LML), corresponding approximately to the dimensions of the epilimnion and hypolimnion in summer (Effler and Owens, 1996). This type of representation has been widely used in mass balance simulation models for stratifying lakes (Chapra, 1997; Thomann and Mueller, 1987), and in other water quality models for Onondaga Lake (Canale et al., 1996; Doerr et al., 1996; Gelda and Auer, 1996). The velocity of mass transport between the two layers (v_i ; m d⁻¹) associated with vertical mixing processes was estimated by applying a heat (temperature) balance to the LML (Doerr et al., 1996). These calculations were performed iteratively until the time series of v_i resulted in a match between the observed and calculated values of T (Doerr et al., 1996).

The kinetic framework of the model includes NO₂⁻ and NO₃⁻ as state variables. Kinetic processes are limited to nitrification and denitrification. Nitrification requires aerobic conditions, thus limiting the process mostly to the epilimnion (UML) of Onondaga Lake (Canale et al., 1996), while denitrification operates under anoxia that prevails for most of the summer in the hypolimnion (LML; Effler, 1996). Denitrification is included to simulate the observed loss of NO₃⁻ + NO₂⁻ from the LML after the onset of anoxia, and thus concentration gradient-driven losses from the UML mediated by v_i (e.g., Jassby and Powell, 1975; Wodka et al., 1983). A sink process for these pools associated with phytoplankton uptake was not included. This simplification is supported by the high concentration of T-NH₃ maintained in the productive layers of the lake (Brooks and Effler, 1990; Canale et al., 1996), which is the form preferred for growth for energetic reasons (Wetzel, 1983). Rather than modeling T-NH₃, the temporal patterns of this form are specified according to the observa-

tions, since this pool is unaffected by concentrations of NO₂⁻ and NO₃⁻. The kinetics of both stages of the nitrification process are represented as first-order water column-based reactions. Other mechanistic water quality models have lumped the two stages together (i.e., one kinetic coefficient and NO₃⁻ + NO₂⁻), and most have represented the overall process by first order water column kinetics (e.g., Bowie et al., 1985; Brown and Barnwell, 1985; DiToro and Connolly, 1980; McCutcheon, 1987; Scott and Abumoghli, 1995; Thomann and Mueller, 1987). However, the results of a number of scientific investigations indicate nitrification is often localized at sediment surfaces (Cavari, 1977; Cirello et al., 1979; Cooper, 1984; Curtis et al., 1975; Hall, 1986). The water column representation (vs. sediment-based) for Onondaga Lake is supported by evidence recently presented by Gelda et al. (1999). Denitrification is localized at the sediment-water interface in the hypolimnion (Brooks and Effler, 1990; Effler, 1996; Seitzinger, 1988) and is represented as a sediment-based process in the model (e.g., Canale et al., 1996).

The mass balance equations of the model for the UML and LML are presented below.

$$V_1 \frac{d[\text{NO}_2^-]_1}{dt} = W_{\text{NO}_2} - Q[\text{NO}_2^-]_1 + v_i A_i ([\text{NO}_2^-]_2 - [\text{NO}_2^-]_1) + k_{n1} [\text{T-NH}_3]_1 V_1 - k_{d2} [\text{NO}_2^-]_1 V_1 \quad [3]$$

$$V_2 \frac{d[\text{NO}_2^-]_2}{dt} = v_i A_i ([\text{NO}_2^-]_1 - [\text{NO}_2^-]_2) + k_{n1} [\text{T-NH}_3]_2 V_2 - k_{d2} [\text{NO}_2^-]_2 V_2 \quad [4]$$

$$V_1 \frac{d[\text{NO}_3^-]_1}{dt} = W_{\text{NO}_3} - Q[\text{NO}_3^-]_1 + v_i A_i ([\text{NO}_3^-]_2 - [\text{NO}_3^-]_1) + k_{d2} [\text{NO}_2^-]_1 V_1 \quad [5]$$

$$V_2 \frac{d[\text{NO}_3^-]_2}{dt} = v_i A_i ([\text{NO}_3^-]_1 - [\text{NO}_3^-]_2) + k_{d2} [\text{NO}_2^-]_2 V_2 - k_{dn} [\text{NO}_3^-]_2 A_i \quad [6]$$

where subscripts 1 and 2 = UML and LML, respectively A_i = area of the interface between the UML and LML (m²) k_{n1} = first stage nitrification rate constant (d⁻¹) k_{d2} = second stage nitrification rate constant (d⁻¹) k_{dn} = denitrification rate constant (m d⁻¹) $[\text{T-NH}_3]$, $[\text{NO}_2^-]$, and $[\text{NO}_3^-]$ = layer volume-weighted average concentrations of T-NH₃, NO₂⁻, and NO₃⁻ (g N m⁻³) Q = total outflow (m³ d⁻¹) t = time (d) V = layer volume (m³) W_{NO_2} and W_{NO_3} = loading rates of NO₂⁻ and NO₃⁻ (g N d⁻¹).

Equations [3] to [6] were solved numerically using an Euler integrator (Chapra and Canale, 1988), with a time step of 1 d, to obtain time variable output of $[\text{NO}_2^-]$ and $[\text{NO}_3^-]$. Morphometric inputs (A_i , V_1 , and V_2) were obtained from available hypsographic data (Effler, 1996). External loading inputs are received by the UML and water is exported from the UML (Owens and Effler, 1996). The lake's outflow (Q) is assumed to equal the sum of the inflows (Canale et al., 1996). Temperature effects on rates were accommodated according to an Arrhenius relationship:

$$k_{x,T} = k_{x,20} \times \theta^{(T-20)} \quad [7]$$

where $k_{x,T}$ and $k_{x,20}$ are values of nitrification rate coefficients at temperatures T and 20°C, and θ is a dimensionless coefficient. A value of $\theta = 1.06$ was specified (Bowie et al., 1985; Canale et al., 1996).

Table 1. Statistics of NO_2^- concentrations (mg N m^{-3}) in METRO and tributaries to Onondaga Lake for 1991–1994.

| Year | Source | No. of samples | | Avg. conc. | | SD | | Max. conc. | | n < detection limit | |
|------|----------------|----------------|-----------|----------------------|-----------|-----------|-----------|------------|-----------|---------------------|-----------|
| | | Jan.–Dec. | June–Oct. | Jan.–Dec. | June–Oct. | Jan.–Dec. | June–Oct. | Jan.–Dec. | June–Oct. | Jan.–Dec. | June–Oct. |
| | | n | | mg N m ⁻³ | | | | | | | |
| 1991 | METRO | 18 | | 1097 | 1488 | 970 | 1120 | 3452 | 3452 | 0 | 0 |
| | Ninemile Creek | 18 | | 38 | 59 | 34 | 31 | 122 | 122 | 0 | 0 |
| | Onondaga Creek | 18 | | 6 | 7 | 2 | 3 | 12 | 12 | 13 | 6 |
| | Harbor Brook | 18 | | 20 | 19 | 19 | 14 | 69 | 48 | 0 | 0 |
| | Ley Creek | 18 | | 45 | 62 | 34 | 36 | 135 | 135 | 0 | 0 |
| 1992 | METRO | 25 | | 668 | 1315 | 1253 | 1713 | 5740 | 5740 | 0 | 0 |
| | Ninemile Creek | 25 | | 19 | 32 | 18 | 18 | 75 | 75 | 9 | 0 |
| | Onondaga Creek | 26 | | 6 | 6 | 4 | 3 | 22 | 12 | 23 | 9 |
| | Harbor Brook | 26 | | 11 | 16 | 6 | 5 | 28 | 28 | 11 | 0 |
| | Ley Creek | 25 | | 25 | 34 | 17 | 20 | 79 | 79 | 3 | 1 |
| 1993 | METRO | 49 | | 512 | 676 | 397 | 424 | 1853 | 1853 | 0 | 0 |
| | Ninemile Creek | 25 | | 34 | 46 | 44 | 49 | 149 | 149 | 8 | 3 |
| | Onondaga Creek | 25 | | 6 | 5 | 3 | 1 | 18 | 11 | 23 | 16 |
| | Harbor Brook | 24 | | 14 | 16 | 9 | 10 | 37 | 37 | 6 | 3 |
| | Ley Creek | 20 | | 22 | 21 | 12 | 11 | 48 | 44 | 3 | 2 |
| 1994 | METRO | 109 | | 412 | 779 | 430 | 437 | 2131 | 2131 | 0 | 0 |

A single value of k_{dn} was determined for the LML for each of the years of the 1991 to 1994 interval through calibration. This assumes that NO_2^- , an intermediary in the denitrification process (Wetzel, 1983), was lost at the same rate as NO_3^- , an appropriate assumption given the focus of this analysis on the pools of the UML. Temporal patterns in k_{n1} and k_{n2} were resolved for the UML by an iterative calibration procedure to match the observed temporal patterns of NO_2^- and NO_3^- . Simulations assuming conservative behavior for these constituents (i.e., $k_{n1} = k_{n2} = 0$) were conducted to depict the important role of external loading, and identify intervals of nitrification and imbalances in the rates of the two stages.

RESULTS AND DISCUSSION

Lake Inputs

Concentrations of NO_2^- in three of the four tributaries—Ninemile Creek, Ley Creek, and Harbor Brook—were often substantially above the detection limit (10 mg N m^{-3}) during the 3 yr of stream monitoring (Table 1). Prevailing concentrations in these streams are consistent with values considered indicative of contaminated systems elsewhere (Barica, 1990; Meybeck, 1982; Smith et al., 1995, 1997a). Levels in Onondaga Creek were substantially lower by comparison, often below the detection limit of measurement (Table 1). Concentrations were higher in the warmer months (June–October) in the contaminated tributaries (Table 1; e.g., Fig. 2). Average concentrations for the 3 yr of measurements (1991, 1992, and 1993) for the June to October interval were 17, 39, and 46 mg N m^{-3} , for Harbor Brook, Ley Creek, and Ninemile Creek, respectively. Violations of the non-salmonid standard for NO_2^- were documented on four occasions in Ninemile Creek during the 3 yr of measurements. The seasonality of NO_2^- concentrations observed in the contaminated tributaries suggest microbially mediated production of NO_2^- , as nitrification (and denitrification) operates more rapidly at higher temperatures (e.g., Bowie et al., 1985). The general seasonal pattern apparently was further modified by natural variations in stream flow; NO_2^- concentrations in the three contaminated tributaries tended to be higher at low flows (e.g.,

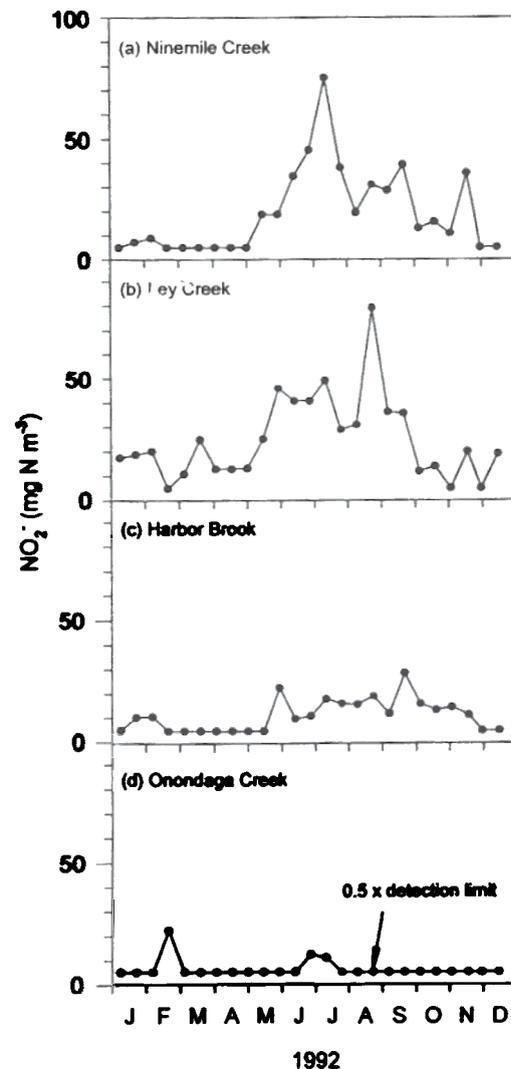


Fig. 2. Time-series of NO_2^- measurements for four tributaries to Onondaga Lake in 1992: (a) Ninemile Creek, (b) Ley Creek, (c) Harbor Brook, and (d) Onondaga Creek.

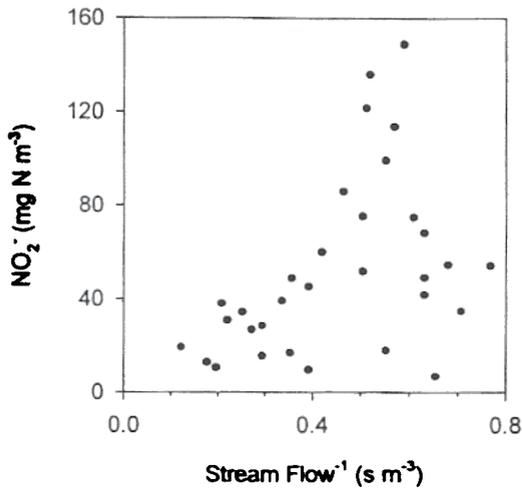


Fig. 3. Evaluation of the relationship between NO_2^- concentration and flow in Ninemile Creek for the June to October interval of 1991 to 1993, according to a dilution model (i.e., conc. vs. the inverse of stream flow).

Fig. 3). Relationships of this form (Fig. 3) suggest the dilution of sources (of T-NH₃, if nitrification is the primary source process) within these watersheds by runoff (e.g., Effler et al., 1996b; Manczak and Florczyk, 1971). The high concentrations of NO_2^- in Ninemile Creek may reflect the elevated T-NH₃ load received from the wastebeds (Fig. 1; Effler et al., 1991). Elevated NH₃ concentrations in this stream (Effler and Whitehead, 1996) may have inhibited the second stage of nitrification (e.g., Anthonisen et al., 1976). The high concentrations of NO_2^- measured in Harbor Brook are consistent with the elevated concentrations reported for this stream of other constituents common to domestic waste (Effler and Whitehead, 1996). The origins of NO_2^- in Ley Creek are more uncertain. Leachate from a landfill and partial nitrification of T-NH₃ released from earlier organic deposits (Effler and Whitehead, 1996) may be responsible.

Nitrite concentrations in the METRO effluent were also much greater in June to September (Table 1; e.g., Fig. 4a) associated with the seasonal operation of nitrification and no denitrification within the facility (Effler et al., 1996a). Nitrification during January to May and October to December is very low. The operation of this biochemical process has been clearly manifested as coincident and approximately stoichiometric increases in $\text{NO}_2^- + \text{NO}_3^-$ (Fig. 4b) and decreases in T-NH₃ (Fig. 4c) in the warmer months (decrease in T-NH₃ in March and April reflects dilution effect of high runoff inputs received by the facility; Fig. 4d). The extent and timing of nitrification in the facility has varied greatly year-to-year since the late 1980s. For example, nitrification was generally less complete and was achieved for a shorter duration in 1994 (Fig. 4) compared with 1988 and 1989 (Effler et al., 1996a). Nitrite has represented a substantial fraction of the effluent $\text{NO}_2^- + \text{NO}_3^-$ during the nitrification intervals (e.g., Fig. 4a and b). In 1994 NO_2^- was 23% of the $\text{NO}_2^- + \text{NO}_3^-$ load from the facility during the June to October interval. The average concentrations of NO_2^- in METRO's effluent during the

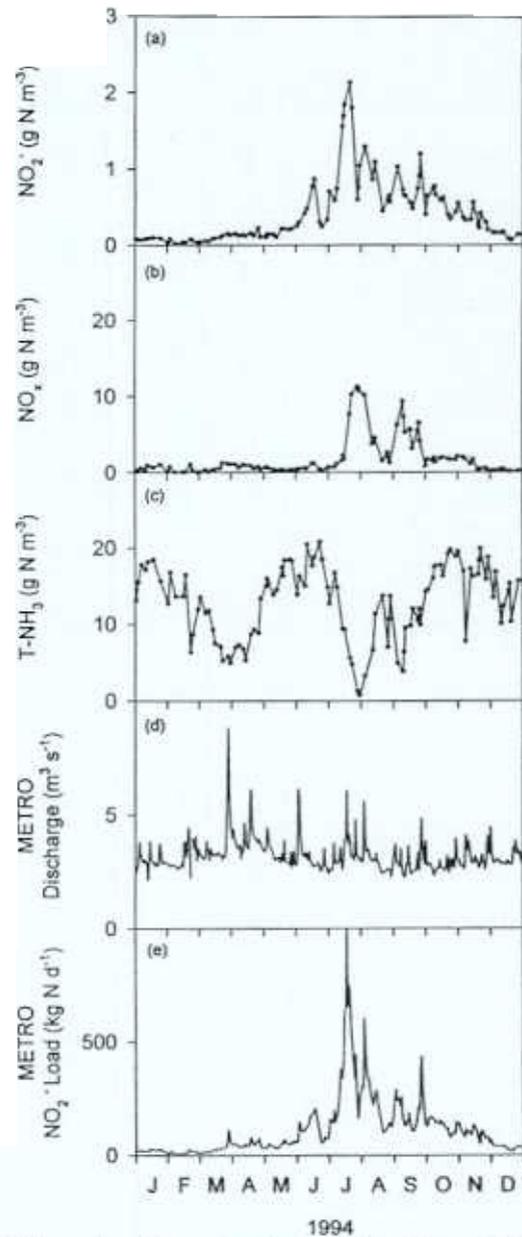


Fig. 4. Time-series of concentrations of three forms of N in the METRO effluent, METRO discharge, and NO_2^- loading in 1994: (a) NO_2^- , (b) $\text{NO}_2^- + \text{NO}_3^-$, (c) T-NH₃, (d) flow, and (e) NO_2^- loading. Note the different y axis scale for NO_2^- in (a).

June to October interval of 1991, 1992, and 1993 were more than an order of magnitude greater than in the contaminated tributaries (Table 1). High NO_2^- concentrations are widely encountered in biological treatment of domestic waste as a result of incomplete nitrification (Balmelle et al., 1992; Rols et al., 1994; Suthersan and Ganczarzyk, 1986). The high concentrations in the METRO effluent may reflect the transient effect of multiple initiations of nitrification and/or inhibition of the second stage (e.g., high NH₃ concentrations; Anthonisen et al., 1976; Balmelle et al., 1992; Rols et al., 1994; Suthersan and Ganczarzyk, 1986; Turk and Mavinic, 1989).

METRO has dominated the external loading of NO_2^- to Onondaga Lake (Table 2) because of the much

Table 2. The NO_2^- , NO_3^- , and $\text{NO}_2^- + \text{NO}_3^-$ loading from METRO and tributaries to Onondaga Lake for April–October period for 1991–1994.

| Year | Source | NO_2^- | | NO_3^- | | $\text{NO}_2^- + \text{NO}_3^-$ | |
|------|-------------|-----------------|------|-----------------|------|---------------------------------|------|
| | | tons N | % | tons N | % | tons N | % |
| 1991 | METRO | 52.9 | 95.0 | 165.7 | 62.0 | 218.6 | 67.7 |
| | Tributaries | 2.8 | 5.0 | 101.6 | 38.0 | 104.4 | 32.3 |
| | Total | 55.6 | 100 | 267.3 | 100 | 323.0 | 100 |
| 1992 | METRO | 52.9 | 94.0 | 71.7 | 31.4 | 124.6 | 43.8 |
| | Tributaries | 3.4 | 6.0 | 156.8 | 68.6 | 160.1 | 56.2 |
| | Total | 56.2 | 100 | 228.5 | 100 | 284.7 | 100 |
| 1993 | METRO | 21.9 | 90.4 | 51.8 | 47.1 | 73.7 | 54.9 |
| | Tributaries | 2.3 | 9.6 | 58.1 | 52.9 | 60.5 | 45.1 |
| | Total | 24.3 | 100 | 109.9 | 100 | 134.2 | 100 |
| 1994 | METRO | 28.8 | – | 94 | – | 122.8 | – |

higher concentrations found in the effluent compared with the tributaries (Table 1). This source represented more than 90% of the load in each of the 3 yr (1991, 1992, and 1993), during the April to October interval (Table 2), the period of primary concern for water quality in the lake (Effler, 1996). The time series of loads from METRO (Fig. 4e) tracked closely the distribution of concentrations (Fig. 4a) because of the relative uniformity of the effluent flow over the interval of high effluent concentrations (Fig. 4d). Interannual variations in nitrification at METRO are manifested as year-to-year differences in the $\text{NO}_2^- + \text{NO}_3^-$ load from the facility (Table 2). The METRO load of NO_2^- has not been tightly coupled to its $\text{NO}_2^- + \text{NO}_3^-$ load, indicating wide interannual differences in the completeness of nitrification. For example, NO_2^- was about 25% of the METRO $\text{NO}_2^- + \text{NO}_3^-$ load in 1991, but more than 40% in 1992 (Table 2). The NO_2^- loads from METRO were substantially greater in 1991 and 1992 than in 1993 and 1994 (Table 2). Under the input conditions documented for 1991 to 1993, the total external load of NO_2^- to the lake can be rather well specified by measurements of NO_2^- at METRO and adoption of average concentrations for the tributaries (e.g., 1991–1993; Table 1). The METRO 1994 NO_2^- data set (highest frequency monitoring) was manipulated to evaluate the influence of monitoring frequency on the representativeness of annual load estimates from this dominant source. Reductions in frequency from twice per week to weekly, biweekly, and monthly caused percent differences in this load of 0.6, 4.9, and 7.4%, respectively.

Lake Concentrations

Temporal patterns of NO_2^- and NH_3 concentrations in the upper waters (UML) of Onondaga Lake for the April to October interval are presented here for 10 consecutive yr as volume-weighted concentrations (Fig. 5a–j). Relatively minor vertical differences in NO_2^- were observed within these layers, as illustrated for 1991 (Fig. 5c). Certain features of the temporal pattern have been recurring, particularly over the first half of the April to October interval, while major interannual differences have occurred over the second half of the interval. Initial concentrations of NO_2^- in April have been in the range of 20 to 50 mg N m^{-3} ; a rather narrow range relative

to values observed later in the study interval (Fig. 5). These differences in part reflect interannual differences in dilution of the METRO input associated with natural variations in tributary flow over the preceding winter through March interval. Generally, progressive increases in NO_2^- have been observed annually through at least June, and usually July (Fig. 5). Two different types of patterns have occurred over the midsummer through October interval. Rather smooth and progressive patterns emerged in 3 yr [1992 (Fig. 5d), 1994 (Fig. 5f), and 1998 (Fig. 5j)]. In sharp contrast, abrupt changes in the NO_2^- pool of the upper waters (e.g., >100 mg N m^{-3} , over a 7-d period) were observed in this interval in the other 7 yr (Fig. 5a, b, c, e, g, h, and i). Multiple peaks occurred in 5 of these years. Peak concentrations exceeded 500 mg N m^{-3} in 6 yr. The highest maximum was ~1000 mg N m^{-3} in early October of 1993 (Fig. 5e). Concentrations remained <250 mg N m^{-3} in the 3 yr without abrupt changes (Fig. 5d, f, and j).

The concentrations of NO_2^- reported here for Onondaga Lake are the highest we encountered for lakes in review of the literature, except for values measured proximate to domestic waste discharges in Hamilton Harbour, Lake Ontario (Barica, 1990). These conditions represent severe violations of New York water quality standards (Table 3, Fig. 5). The maximum margin of violations (quotient of maximum observed and the standard) within the monitored interval of each year ranged from 1.9 (1992) to 10 (1993). The documented duration of violation exceeded 100 d in 8 of the 10 yr (Table 3). Violations undoubtedly extended beyond the monitoring interval in nearly all the years of the study (Fig. 5). The average margin of violation (average of quotients of observed and the standard) over the interval of violations ranged from 1.5 (1992 and 1998) to 3.2 (1993; Table 3).

A number of materials have been identified as mitigating against the toxic effects of NO_2^- (Lewis and Morris, 1986). The strongest documented interaction is for Cl^- (Lewis and Morris, 1986; Russo and Thurston, 1977). Onondaga Lake is unusually rich in Cl^- (~400 mg m^{-3}), as a result of industrial and natural inputs (Doerr et al., 1994; Effler et al., 1996b). Application of an empirical relationship developed to adjust NO_2^- toxicity results for the Cl^- mitigation effect (Lewis and Morris, 1986), for the Cl^- concentration of Onondaga Lake, indicates the documented NO_2^- levels (Fig. 5) would not be toxic. However, this interpretation should be considered highly uncertain because the relationship was extended in this case, beyond the upper bound of Cl^- incorporated in its development (Lewis and Morris, 1986). The New York state standard(s) for NO_2^- presently does not consider mitigating effects, including Cl^- .

Modeling

Model simulations of NO_2^- that treat this constituent as a conservative substance (i.e., no reactions) are compared here to the observed distributions for the UML for each of the 4 yr of the 1991 to 1994 period (Fig. 6a–d). The analysis is valuable in identifying intervals

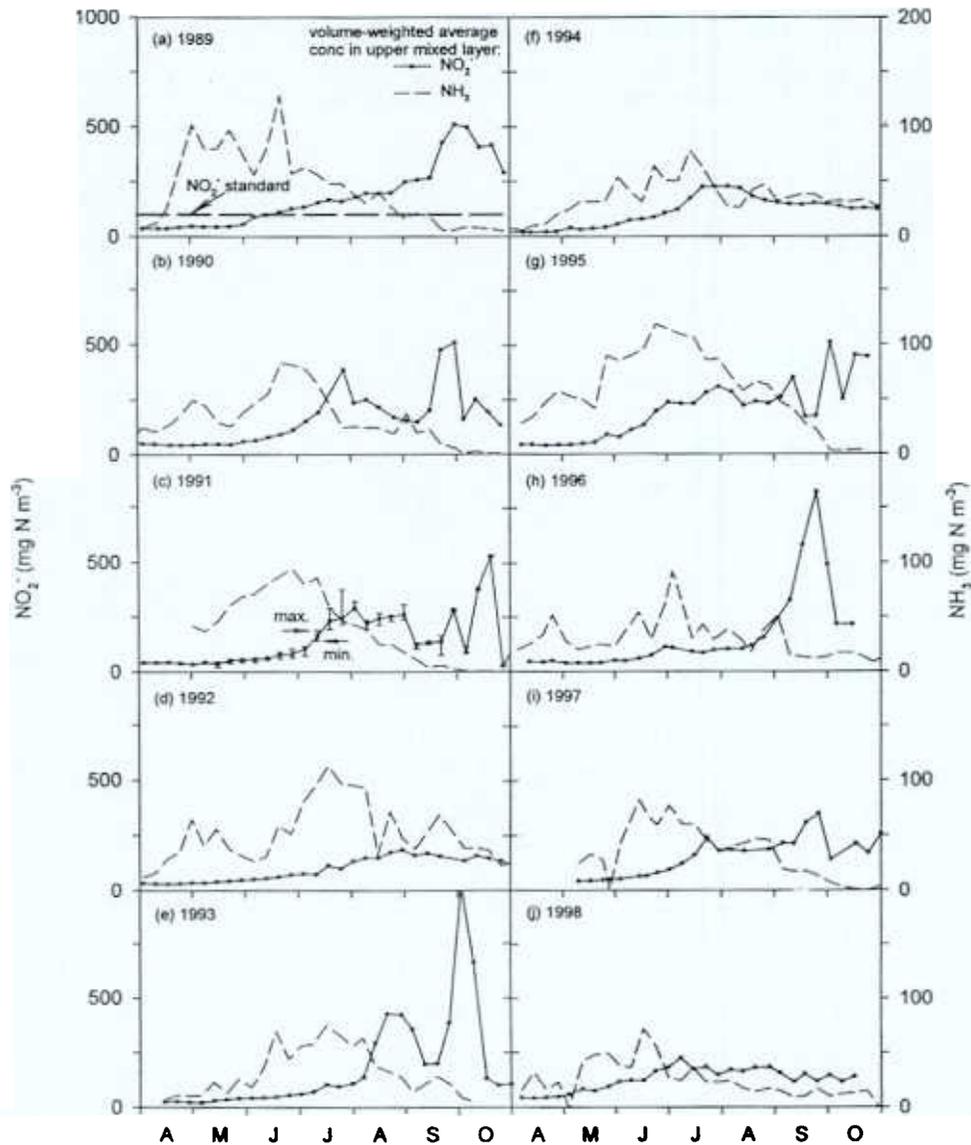


Fig. 5. Time-series of volume-weighted average NO_2^- and NH_3 concentrations in the UML of Onondaga Lake for the April to October interval of 10 yr: (a) 1989, (b) 1990, (c) 1991, (d) 1992, (e) 1993, (f) 1994, (g) 1995, (h) 1996, (i) 1997, and (j) 1998.

of the operation of source and sink processes and the relative effect of these reactions on the NO_2^- pool. The conservative simulations closely tracked the observations over the April to July interval of 1991, 1992, and 1993, but underpredicted concentrations over this interval in 1994 (Fig. 6a–d). Apparently NO_2^- behaved conservatively in the UML in most years over this interval. The alternate explanation, that sink/source processes are in balance throughout the interval, is unrealistic. Thus, the progressive build-up of NO_2^- in the upper waters of Onondaga Lake during this interval is driven by the METRO load, as modified by lake flushing/export and losses to the hypolimnion via vertical mixing. The deviations from conservative behavior over this interval in 1994 (Fig. 6d) indicate the source of NO_2^- (first stage of nitrification) exceeded the sink (second stage of nitrification) until late July, when the rate of the second stage apparently became greater. However,

these deviations from conservative behavior in 1994 were modest compared with those observed for the mid-summer through October interval of 1991 (Fig. 6a) and 1993 (Fig. 6c). The effects of in-lake reactions in these years were dominant. Increases/decreases in the lake's NO_2^- pool over brief intervals (1–2 wk) were greater in several instances in these 2 yr than the cumulative progressive increases observed from the METRO discharges during the April to July interval. These fluctuations in the NO_2^- pool reflect imbalances in the rates of the first (k_{n1}) and second (k_{n2}) stage of nitrification. The abrupt peaks in late September and early October in 1991, and in August through early October of 1993, reflect intervals of $k_{n1} > k_{n2}$, followed by $k_{n2} > k_{n1}$ (Fig. 6a).

Much lower concentrations of NO_2^- would have been observed in the lake, at least through midsummer, in the absence of the METRO load. A conservative simula-

Table 3. Violations of "New York water quality standards" for NO_2^- in Onondaga Lake during April–October for 1989–1998.

| Year | Max. margin† | Duration | Avg. margin‡ |
|------|--------------|----------|--------------|
| | | d | |
| 1989 | 5.1 | 127 | 2.6 |
| 1990 | 5.1 | 117 | 2.3 |
| 1991 | 5.3 | 98 | 2.3 |
| 1992 | 1.9 | 105 | 1.5 |
| 1993 | 10 | 105 | 3.2 |
| 1994 | 2.3 | 119 | 1.6 |
| 1995 | 5.1 | 133 | 2.7 |
| 1996 | 8.3 | 93 | 2.8 |
| 1997 | 3.5 | 112 | 2.1 |
| 1998 | 2.2 | 133 | 1.5 |

† Quotient of maximum observed NO_2^- and NO_2^- standard.

‡ Average of quotients of observed NO_2^- and NO_2^- standard.

tion of the model with the METRO input eliminated (e.g., diversion of the discharge) predicted a peak NO_2^- concentration of 21 mg N m^{-3} for the conditions of 1991 (Fig. 6a).

The unusually large pools of NO_2^- and NO_3^- —and the documented dynamics for these pools (Fig. 5 and 7)—that have prevailed in Onondaga Lake have offered a rare opportunity to resolve and quantify the operation of the two stages of the nitrification process through application of a mass balance model (Fig. 7a, e, i, and m). The two stages have not been comprehensively resolved previously for surface fresh waters. The findings for the selected 4 yr (1991–1994) are expected to be generally representative of the entire study period as conditions (e.g., pool sizes and dynamics) for this subset of years generally bracket those observed over the 10 yr of measurements (e.g., Fig. 5). Resolution of temporal patterns in nitrification rates (k_{n1} and k_{n2}) is limited by the frequency of lake measurements (weekly). The determined time-series of k_{n1} and k_{n2} resulted in a high degree of calibration for both NO_2^- and NO_3^- (Fig. 7). The slight overpredictions of NO_3^- in the fall of 1992 (Fig. 7h) and 1994 (Fig. 7p) may reflect utilization of this form of N by phytoplankton and/or overestimation of loads of this constituent during these intervals. These modest short-comings had very little effect on the determinations of k_{n1} and k_{n2} for these same intervals. This mass balance model analysis depicts widely different temporal patterns in k_{n1} and k_{n2} in the upper waters of the lake during the 1991 to 1994 interval (Fig. 7a, e, i, and m).

No nitrification occurred for the April to June interval of 1991 (Fig. 7a) and 1993 (Fig. 7i). Nitrification in this interval in 1992 (Fig. 7e) and 1994 (Fig. 7m) was limited to the first stage, and rates were very low (e.g., 0.0001 – 0.001 d^{-1}) relative to those determined for both stages for the July to October interval of 1991 (Fig. 7a; 0.01 – 0.7 d^{-1}) and 1993 (Fig. 7i; 0.01 – 0.8 d^{-1}). The very low magnitude of k_{n1} determined for the April to July interval of 1992 cannot be differentiated from a value of zero, as even the modest level of uncertainty in the METRO load associated with sampling frequency could explain this result. In contrast, the operation of the first stage of nitrification in June and July of 1994, in the absence of the second stage (Fig. 7m), is rather certain. This activity was responsible for the underprediction of

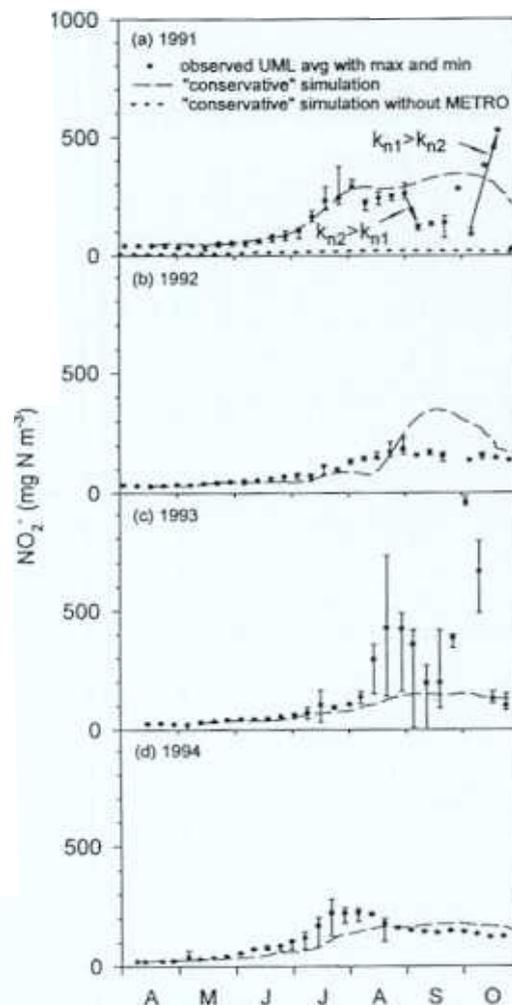


Fig. 6. Comparison of mass balance model simulations of NO_2^- concentrations to observations for the UML of Onondaga Lake for 4 yr, assuming conservative behavior of NO_2^- : (a) 1991, (b) 1992, (c) 1993, and (d) 1994.

NO_2^- concentrations by the conservative case over the same interval (Fig. 6d).

The modeling analysis demonstrates that the distinct seasonal and interannual differences observed in pools of NO_3^- and particularly NO_2^- in Onondaga Lake over the July to October interval (Fig. 5 and 7) have largely been the result of differences in the magnitudes and temporal patterns of the first and second stages of nitrification. The unusually large pool of T- NH_3 maintained in the lake by the METRO discharge (Table 2; Canale et al., 1996) has promoted the large fluctuations in NO_2^- levels. Under these conditions, k_{n1} must exceed k_{n2} for only a short interval and by only a small margin to cause these variations (Fig. 7). On an averaged basis, the paradigm that the first stage of nitrification is limiting (i.e., $k_{n2} > k_{n1}$; e.g., Klapwijk and Snodgrass, 1982) has been generally supported by this analysis. However, the very distinct peaks of NO_2^- concentration measured in September and October of 1991 (Fig. 7c) and in August and early October of 1993 (Fig. 7k) can only be explained, within the constraints of mass balance, by intervals in which k_{n1} approached or exceeded k_{n2} (Fig.

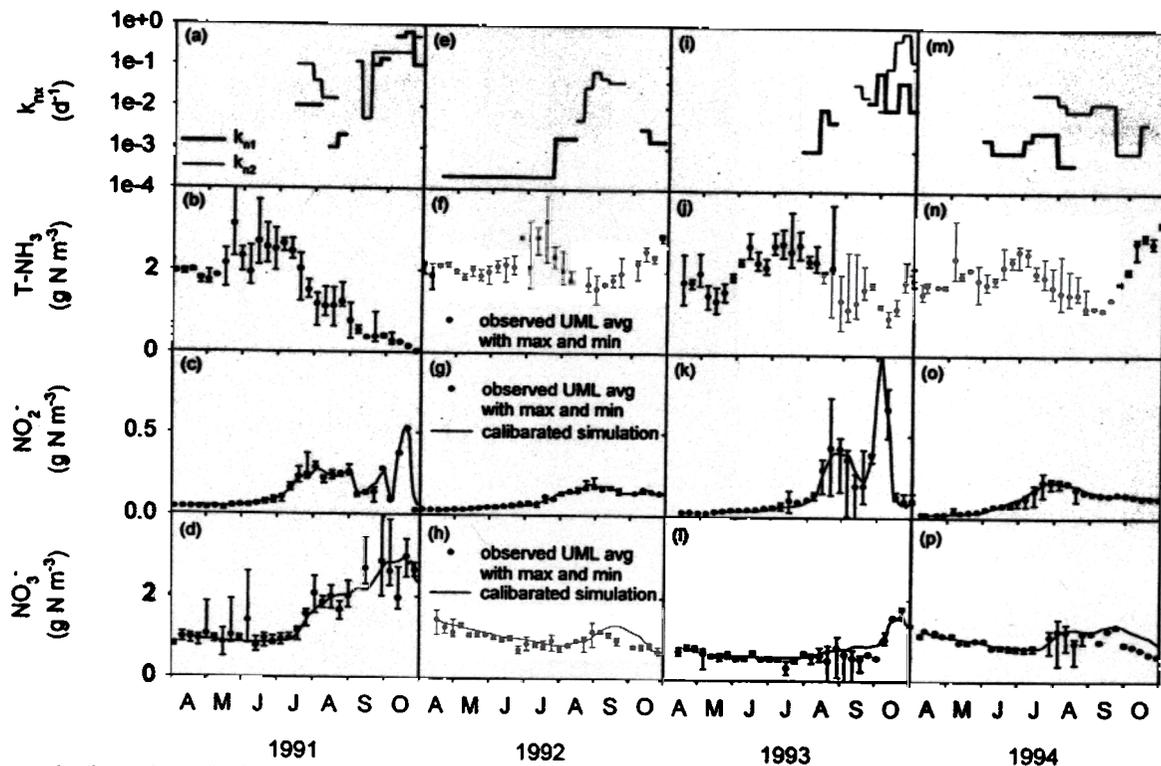


Fig. 7. Determinations of nitrification rate coefficients k_{n1} and k_{n2} for the UML of Onondaga Lake for the April to October interval of 4 yr from mass balance modeling, with measured T-NH₃ concentrations, and calibration performance for NO₂⁻ and NO₃⁻ concentrations: (a) determined time series for k_{n1} and k_{n2} for 1991, (b) measured T-NH₃ concentrations for 1991, (c) model calibration performance for NO₂⁻ for 1991, (d) model calibration performance for NO₃⁻ for 1991, (e) determined time series for k_{n1} and k_{n2} for 1992, (f) measured T-NH₃ concentrations for 1992, (g) model calibration performance for NO₂⁻ for 1992, (h) model calibration performance for NO₃⁻ for 1992, (i) determined time series for k_{n1} and k_{n2} for 1993, (j) measured T-NH₃ concentrations for 1993, (k) model calibration performance for NO₂⁻ for 1993, (l) model calibration performance for NO₃⁻ for 1993, (m) determined time series for k_{n1} and k_{n2} for 1994, (n) measured T-NH₃ concentrations for 1994, (o) model calibration performance for NO₂⁻ for 1994, and (p) model calibration performance for NO₃⁻ for 1994.

7a and i). These results (Fig. 7) support the findings of Smith et al. (1997b), based on mass balance modeling for a soil system, that the rate of the first stage has to exceed the second stage rate by only a small margin for NO₂⁻ to accumulate. Rates of nitrification were the highest in the September to October interval of 1991 and 1993, a period that included rapid deepening of the epilimnion and the onset of complete turnover (Effler and Owens, 1996). Coincident signatures from the operation of this (sink) process were imparted to the T-NH₃ pool in both years as conspicuous depletions (Fig. 7b and j). In contrast, major increases in T-NH₃ occurred in the UML over the same interval of 1992 and 1994 (Fig. 7f and n), when nitrification rates were much lower (Fig. 7e and m), largely in response to entrainment of the enriched hypolimnion (Brooks and Effler, 1990; Gelda et al., 1999).

Nitrification

The determinations of k_{n1} and k_{n2} presented here have provided a quantitative description of the operation of the two stages of nitrification in Onondaga Lake. Certain of the features manifested for this polluted system may be broadly representative for lakes. It is valuable to consider the results presented here of two general types, corresponding approximately to two time seg-

ments—the spring to midsummer (e.g., April–mid-July) and midsummer to fall turnover (e.g., mid-July to end of October) intervals. During the first interval NO₂⁻ behaves in a nearly conservative manner; i.e., there is essentially no, or very little, nitrification affected within the upper waters of the lake. There are two prominent potential explanations for this behavior, a lack of adequate nitrifier populations to affect these large pools of T-NH₃ and NO₃⁻ + NO₂⁻, and inhibition of the nitrification process.

System-specific measurements (Pauer, 1996) and results reported for other lakes and deep rivers support the position that nitrification rates for these systems are extremely low, because of relatively low concentrations of nitrifier biomass. Pauer (1996) observed essentially no nitrification in water column samples collected in summer from Onondaga Lake, but measured rather high rates for the sediment–water interface in deep stratified (hypolimnetic) portions of the lake (under oxic conditions). Pauer's (1996) position, that nitrification in the lake was localized at the sediments (in aerobic layers), was supported by enumeration of nitrifying bacteria; densities of $\sim 10^1$ and $\sim 10^5$ cells mL⁻¹ were reported for the water column and surface sediments, respectively. The results of a number of scientific investigations support the position that nitrification is usually localized at sediment surfaces (Cavari, 1977; Cooper,

1984; Cirello et al., 1979; Curtis et al., 1975; Hall, 1986). This localization is consistent with the observation that nitrification rates in lakes and deep rivers are low relative to rates in shallow turbulent streams (Bowie et al., 1985; Chapra, 1997; Cirello et al., 1979, Pauer, 1996).

Various constituents may inhibit the nitrification process (Anthonisen et al., 1976). Values of pH remained somewhat above neutral and outside of the range considered inhibiting to nitrification (Bowie et al., 1985). Free ammonia has received the most attention as an inhibiting substance contributing to the accumulation of NO_2^- in both waste treatment (e.g., Balmelle et al., 1992; Rols et al., 1994; Suthersan and Ganczarczyk, 1986; Turk and Mavinic, 1989) and surface water (e.g., Barica, 1990; Smith et al., 1995, 1997a) systems. The findings of Anthonisen et al. (1976), based on observations for waste waters, are most widely referenced as establishing NH_3 concentration ranges over which inhibition of nitrification is to be expected. The potential role of NH_3 in influencing the dynamics of NO_2^- concentrations and nitrification deserves attention for this system, because of the rather high concentrations of NH_3 that occur (Fig. 5; Brooks and Effler, 1990; Effler et al., 1990, 1996a) as a result of the METRO discharge (Canale et al., 1996).

Indeed, high concentrations of NH_3 occurred annually over the study period (particularly over the April to mid-July interval), and substantial nitrification (first and second stages) was not observed until NH_3 decreased (Fig. 5). Superficially, these conditions suggest the potential for an inhibiting effect of NH_3 in Onondaga Lake. However, additional considerations indicate this was probably not the primary factor responsible for the near absence of nitrification over the spring to midsummer interval. The second stage of nitrification is much more susceptible to inhibition than the first stage; *Nitrosomonas* does not become inhibited until concentrations of NH_3 reach 10 to 150 g N m^{-3} , while *Nitrobacter* becomes inhibited at concentrations in the range 0.1 to 10 g N m^{-3} (Anthonisen et al., 1976). Concentrations of NH_3 in the upper waters of the lake were well below the threshold of inhibition for the first stage of nitrification, and exceeded the threshold for the second stage on only several occasions (Fig. 5). Further, acclimation of NO_2^- oxidizers to NH_3 has been reported in waste water studies (e.g., Turk and Mavinic, 1989). If inhibition of the second stage prevailed, in the presence of adequate biomass of *Nitrosomonas*, greater accumulations of NO_2^- (beyond the observed nearly conservative behavior) would have occurred. It seems more likely that the near absence of the effects of nitrification in the upper waters of the lake over the spring to midsummer interval reflects a lack of nitrifier biomass.

The increased vertical mixing that attends the approach to fall turnover (Wetzel, 1983) may be critical in supporting the irregular occurrences of nitrification that have been reported here for the midsummer to fall interval (Fig. 5 and 7). This mixing is clearly manifested by the progressive deepening of the epilimnion observed during this interval (e.g., Effler and Owens, 1996). Increased nitrification has been reported for at least two

other lentic systems during turnover (Cavari, 1977; Roberts et al., 1982). These observations and the Onondaga Lake results may reflect the entrainment of resuspended bottom sediment enriched (e.g., Pauer, 1996) with nitrifying bacteria. Nitrifier biomass may also be contributed via the METRO discharge over this interval.

The driving forces for the irregularity of the occurrences of the nitrification events and their characteristics, including the erratic changes in the NO_2^- pool, remain uncertain. The potential influences of interannual differences in NH_3 concentrations during this interval (Fig. 5) cannot be discounted. However, these differences probably reflect the effects of irregular occurrences of nitrification rather than the cause. Interannual differences in the details of vertical mixing over this interval (Owens and Effler, 1996) may contribute to the observed variations, perhaps by supplying variable amounts of nitrifier biomass attached to resuspended sediment. The strong variations in the rates of the first and second stages of nitrification, and the resulting NO_2^- pool size (Fig. 7), can be described as transient behavior. The nitrification process apparently does not come into an equilibrium in the upper waters of Onondaga Lake (e.g., temporal uniformity in k_{s1} , k_{s2} , and NO_2^- concentrations). Such transient behavior (i.e., irregular occurrence of high concentrations of NO_2^-) is widely observed in nitrification treatment units during a *start-up* interval, before a balanced microbial population develops (Anthonisen et al., 1976; Neethling et al., 1997).

Nitrifying bacteria have an affinity for surfaces (Staley, 1989). Losses of nitrifier biomass that reaches the upper layers via deposition continues to work against the development of equilibrium conditions in a lake. Particle associations of these bacteria thus become critical to the development of high concentrations of biomass (e.g., attached to low density particles). Such characteristics may vary greatly and thereby contribute to the observed fluctuations in NO_2^- and rates of nitrification.

Summary/Management Considerations

Contamination of three tributaries of Onondaga Lake with high concentrations of NO_2^- has been documented. However, more than 90% of the NO_2^- load into the lake has been received from METRO, associated with the incomplete nitrification in the facility. Progressive increases in NO_2^- concentration, to levels exceeding the nonsalmonid standard for New York, occurred annually in the upper waters of the lake over the spring to midsummer interval for the period 1989 to 1998. These increases have reflected the near conservative (nonreactive) behavior of this constituent in the lake. In contrast, much more erratic patterns of NO_2^- concentrations (e.g., abrupt peaks) have been observed in the lake over the midsummer to early fall interval of most years in response to the irregular occurrence of nitrification events. Unusually high lake concentrations of T- NH_3 have promoted these events, but the identity and role of other driving conditions for these erratic patterns remain un-

certain. Temporal patterns of the rates of the first and second stages of nitrification responsible for the observed patterns of NO_2^- (and NO_3^-) have been resolved through the application of a mechanistic mass balance model.

METRO is responsible for the very high NO_2^- concentrations, and violations of the related water quality standard for nonsalmonid fisheries, documented here for Onondaga Lake. The progressive increases observed over the April to July interval annually, to levels exceeding the standard, have been almost entirely the result of loads of NO_2^- received from the facility. The extremely large pool of T- NH_3 maintained in the upper waters of the lake are a result of METRO discharges of T- NH_3 and P. The T- NH_3 load from the facility largely drives the lake's pool through late summer, while the P load promotes sediment release of T- NH_3 (a manifestation of cultural eutrophication) that augments (via vertical mixing) external inputs during the fall mixing period. Further, the possibility that this facility may promote the occurrence of nitrification events through the irregular discharge of nitrifier biomass cannot be discounted.

Managers plan to add increased nitrification treatment at METRO, with an interim effluent T- NH_3 goal of 3.3 g N m^{-3} in winter and 1.65 g N m^{-3} in summer, and a final goal of 2 g N m^{-3} in winter and 1 g N m^{-3} in summer. Major reductions in P loading from the facility are also planned. No effluent limits for NO_2^- have been set for the upgraded facility. Increased treatment at METRO can reasonably be expected to ameliorate the lake's NO_2^- problems. However, these expectations remain unquantified; e.g., whether the nonsalmonid standard will be met in the upper waters remains unknown. This uncertainty reflects uncertainty in the future NO_2^- concentrations of the effluent and in the forcing conditions for the late summer/early fall nitrification events. Decreases in the T- NH_3 pool should cause the NO_2^- peaks to diminish. The extent to which the fraction of the pool associated with sediment feedback will be reduced in response to the planned reduction in P loading remains uncertain. Inputs of NO_2^- from the facility over the spring to midsummer interval (and perhaps earlier) following increased nitrification treatment remain a concern because of the nearly conservative in-lake behavior documented here. Incomplete nitrification within the facility for extended periods, or transients in performance (e.g., *start-ups* after process *upsets*), could cause substantial inputs of NO_2^- and associated increases in lake concentrations.

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