Development and Testing of a Dissolved Oxygen Model for a Hypereutrophic Lake[1]

Rakesh K. Gelda
Upstate Freshwater Institute
P.O. Box 506, Syracuse, NY 13214

Martin T. Auer
Department of Civil and Environmental Engineering
Michigan Technological University,
Houghton, MI 49931

ABSTRACT

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A mechanistic, two-layer mass balance model for dissolved oxygen (DO) in Onondaga Lake, a hypereutrophic, urban system, has been developed and tested. The model accommodates the processes of reaeration, algal photosynthesis and respiration, carbonaceous biochemical oxygen demand (CBOD), nitrogenous biochemical oxygen demand (NBOD), sediment oxygen demand (SOD) and water column oxidation of reduced species. Most model inputs, and many of the kinetic coefficients, were developed through a program of field monitoring and field and laboratory experimentation. The model was calibrated and verified using data collected in 1989 and 1990, respectively. Severe dissolved oxygen depletion is observed in the hypolimnion (lower mixed layer; LML) of Onondaga Lake during summer stratification. SOD and water column oxidation of reduced species diffusing from the sediment are together responsible for >70% of the summer depletion; CBOD, NBOD and algal respiration account for the balance. DO depletion occurs in the epilimnion (upper mixed layer; UML) in the fall. Oxidation of reduced species entrained from the LML is responsible for about 30% of the fall depletion, with algal respiration and mass transport to the LML accounting for about 25% each; CBOD and NBOD are minor sinks. Beyond those features of pollutant loading, fate, and transport, sensitivity analyses suggest that meteorological conditions importantly influence the character of the DO resources of the lake.

Key Words: dissolved oxygen, reduced chemical species, lake, modeling, eutrophication.

Maintenance of an adequate supply of dissolved oxygen (DO) is fundamental to the protection and propagation of aquatic life - a national goal specified by the Clean Water Act of 1972. Dissolved oxygen depletion and its impacts on ecosystem integrity such as extirpation of sensitive species and degradation of aesthetic conditions are no longer acceptable consequences of economic and cultural development. The establishment and enforcement of DO standards for rivers and streams have become common features of the regulatory process.

Mathematical models have long been recognized as valuable tools for the analysis of water quality (e.g., Streeter and Phelps 1925; Biswas 1981; Gromiec et al. 1983) and are routinely utilized in the permitting process for discharge of effluents to rivers (Krenkel and Novotny 1979). Various approaches and techniques for modeling oxygen in rivers have been outlined in water quality manuals (cf. Bowie et al. 1985) and texts (cf. Thomann and Mueller 1987). General purpose river modeling software is available for public use (e.g., QUAL2E; Brown and Barnwell 1985).

Dissolved oxygen conditions are also of importance in lakes, where hypolimnetic oxygen depletion in summer can lead to enhanced nutrient cycling, accumulation of obnoxious and toxic reduced chemical species, elimination of benthic macroinvertebrates, and extirpation of cold water fish. Despite the significance of oxygen resources to water quality, comparatively few attempts have been made to model DO in lakes (Symons et al. 1967; Bella 1970; DiToro and Connolly 1980; Snodgrass and Dalrymple 1985). In part, this may be due to the complicating interactions of the abiotic (reduced species accumulation), biotic (nutrient and trophic state dynamics), and meteorological (incident radiation and wind energy)

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phenomena mediating oxygen depletion and resupply in lakes. Many of these factors and their interrelationships are poorly understood. However, mathematical models for DO have been applied for management purposes; perhaps the most notable of these efforts being that for Lake Erie, where recovery from DO depletion was related to management of phosphorus loads (DiToro and Connolly 1980).

Lakes which exhibit accumulation of reduced chemical species (e.g., CH_4, HS^-, NH_4^+, Fe^{2+}) during seasonal anoxia have received little attention from those modeling oxygen dynamics (Effler et al. 1988). Hypolimnetic accumulation of oxygen-demanding reduced species is characteristic of the study system, Onondaga Lake (Effler et al. 1988; Gelda et al. 1995). At fall turnover, hypolimnetic waters, rich in reduced species, mix with the well-oxygenated waters of the epilimnion and exert an oxygen demand, resulting in epilimnetic oxygen depletion. Water column oxidation of reduced species, an important oxygen sink for Onondaga Lake (Gelda et al. 1995), is not traditionally accommodated in DO models.

Here we utilize measurements of the release and accumulation of reduced species as well as the rates, pathways and stoichiometry of their oxidation to support the development of a mathematical model which simulates seasonal DO dynamics in Onondaga Lake. The model is mechanistic in nature and is based on a mass balance approach. Model development was supported by an extensive program of field monitoring and process-level research to facilitate site-specific parameter determination and to minimize uncertainty in model predictions. The DO model works in concert with a nitrogen model for Onondaga Lake (Canale et al. 1996) which simulates phytoplankton production and biomass as well as concentrations of various nitrogen species. The DO model is capable of performing year-round simulations, thus, encompassing the critical periods of hypolimnetic oxygen depletion in summer and epilimnetic oxygen depletion in fall. The model is calibrated to a data set obtained in 1989 and verified using 1990 data.

Study System

Onondaga Lake is a dimictic, hypereutrophic (Auer et al. 1990) system located in metropolitan Syracuse, New York. The lake has an area of 11.7 km², a mean depth of 12 m and flushes 3-4 times per year. Effler and Hennigan (1996) describe the lake setting, its morphometry, hydrology, and water quality, and review the history of the development of the surrounding area.

Rates of hypolimnetic oxygen depletion are very high in Onondaga Lake (1.0 - 2.1 g/m²/d; Effler et al. 1986; 1988) and thus restoration of oxygen resources is a major management issue. Anoxic conditions are first encountered in the hypolimnion in mid-May and by late July the entire hypolimnion is devoid of oxygen. The State of New York does not have DO standards for the bottom waters of lakes, and thus hypolimnetic DO is not directly of regulatory interest. During the approach to turnover each fall, dissolved oxygen is depleted over the entire water column due to algal respiration and the entrainment and oxidation of reduced chemical species (cf. Effler et al. 1988). Minimum DO levels typically occur at turnover and are often in violation of New York State standards for surface waters (< 5 mg/L as a daily average; < 4 mg/L at any time within a day). Following turnover, oxygen levels gradually increase and approach saturation. Remediation alternatives seek to meet the surface water DO standard (Effler 1996) and to restore oxic conditions to the hypolimnion. Improvements in DO levels at turnover are expected as a first response to management efforts.

Model Framework

The Onondaga Lake DO model is developed from a conceptual framework based on the principles of mass balance (Fig. 1). Two oxygen sources are accommodated: photosynthesis and tributary loading. Oxygen sinks include export (hydraulic flushing), algal respiration, bacterial respiration (as manifested through carbonaceous, CBOD, and nitrogenous, NBOD, biochemical oxygen demand), sediment oxygen demand (SOD), and oxidation of reduced chemical species. Air - water exchange is quantified through a reaeration term. It is assumed that the lake volume is constant and that there is no significant horizontal variation in water quality constituents related to DO. These assumptions are supported by field observations (Effler 1996).

System Geometry

A fixed-volume, two-layer framework is applied, favored here over a variable-volume, multi-layer approach (cf. Snodgrass and Dalrymple 1985) for its simplicity and ease of application. The lake is segmented vertically, yielding two completely-mixed volumes, an upper mixed layer (UML) approximating the dimensions of the epilimnion, but including a portion of the metalimnion and a lower mixed layer (LML), comparable to the hypolimnion, but also containing

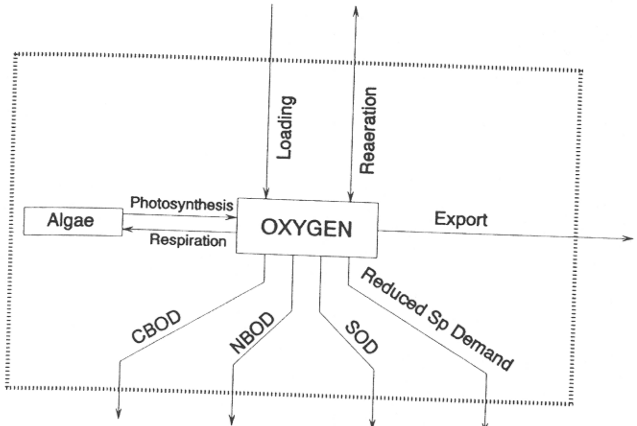

Figure 1.–Conceptual framework for the Onondaga Lake dissolved oxygen model.

part of the metalimnion. The size of the layers is kept constant, with the interfacial boundary set at 8.5 m, its position throughout most of the summer. This segmentation scheme treats the hypolimnion (i.e., LML) as a completely mixed volume and does not accommodate the significant vertical concentration gradients (e.g., for methane and sulfides) which develop there over the stratified period. Dissolved species are exchanged across the interfacial boundary, driven by the concentration gradient and mediated by the intensity of vertical mixing. The magnitude of vertical mixing is characterized by a seasonally-variable exchange coefficient. During the circulation period, a value for the vertical exchange coefficient sufficient to effect complete mixing and achieve equal concentrations in the two layers is adopted.

Boundaries for the UML and LML are defined to permit quantification of interfacial mass transport as well as those biochemical processes occurring at the sediment-water interface, e.g. SOD and the release of reduced chemical species. The lake surface area (A_o, m^2) is utilized in the reaeration calculation, the interfacial area (A_i, m^2) in estimating vertical mass transport and the area at the oxycline (oxic/anoxic boundary, A_x, m^2) in quantifying the corresponding areas for oxic ($A_e = A_i - A_x$; e.g. SOD) and anoxic (A_x; e.g. reduced species flux) sediment processes. Values for A_o and A_i are fixed and are determined by direct measurement (hypsographic data; Effler 1996). The position of the oxycline (and thus A_e and A_x) varies with the degree of anoxia in the LML and is determined by correlation with the LML volume-weighted average DO.

Loads and Export

Inputs to the lake are received exclusively by the UML; there are no loads to the LML. DO loads (W_{DO}; g/d) are quantified as the sum of the products of flow and DO concentration in each of the lake's major tributary (Onondaga Creek, Nine Mile Creek, Ley Creek and Harbor Brook) and point source (METRO: Syracuse Metropolitan Wastewater Treatment Plant) discharges:

$$\text{Load } (gO_2/d) = W_{DO} = \Sigma\, Q_{in}\, [DO]_{in} \tag{1}$$

where $[DO]_{in}$ is the tributary or point source input DO concentration (g/m^3) and Q_{in} is the tributary or point source inflow (m^3/d). Export (hydraulic flushing) is calculated as the product of outflow and the UML DO concentration:

$$\text{Export } (gO_2/d) = -\, Q_{out}\, [DO]_1 \tag{2}$$

where Q_{out} is the lake outflow (m^3/d) and $[DO]_1$ is the DO concentration in the UML (g/m^3). The LML is not connected to the lake outlet and thus has no export loss. Outflow cannot be measured directly in Onondaga Lake due to the complex hydrodynamic regime prevailing at the outlet (flow reversal; Effler and Driscoll 1986; Owens and Effler 1996), but may be estimated as the sum of the tributary and point source inflows. Net precipitation/evaporation has a negligible impact on the hydrologic budget of the lake (Effler 1996).

Vertical Mass Transport

Exchange of DO between the UML and LML is determined by the magnitude of the vertical exchange coefficient and by the DO concentration gradient at the interfacial boundary:

$$\text{Transport: UML}\rightarrow\text{LML } (gO_2/d) = v_t A_i\, ([DO]_2 - [DO]_1) \tag{3}$$

$$\text{Transport: LML}\rightarrow\text{UML } (gO_2/d) = v_t A_i\, ([DO]_1 - [DO]_2) \tag{4}$$

where $[DO]_2$ is the DO concentration in the LML (g/m^3) and v_t is the vertical exchange coefficient (m/d). The temporal distribution of v_t for the spring to fall intervals of 1989 and 1990 was determined using a heat balance model (Doerr et al. 1996a). In the fixed, two-layer framework utilized here, the vertical exchange coefficient collectively accommodates vertical exchange due to diffusion and due to entrainment (thermocline migration).

Reaeration

The rate of oxygen exchange at the air-water interface is quantified by:

$$\text{Reaeration } (gO_2/d) = k_L\, ([DO]_s - [DO]_1)\, A_o \tag{5}$$

where $[DO]_s$ is the saturation DO concentration in the

UML (g/m^3) and k_L is the liquid film transfer coefficient (m/d). $[DO]_s$ is calculated as a function of temperature (APHA, 1985). The coefficient k_L varies with temperature and with turbulence at the air-water interface. The temperature dependency of k_L is described by a logarithmic function:

$$k_{L,T} = k_{L,20}\ \theta^{(T-20)} \tag{6}$$

with θ = 1.024 (Bowie et al. 1985; Thomann and Mueller 1987). The influence of turbulence is a manifestation of wind-driven energy inputs to the lake (O'Connor 1983) and can be accommodated through empirical relationships (see Bowie et al. 1985 for a review) of the form:

$$k_L = \alpha\ U^{\beta} \tag{7}$$

where α and β are empirical coefficients and U is the wind speed (m/s) at a height of 10 m above the water. Gelda et al. (1996) have estimated and field-verified values for α and β for Onondaga Lake: α = 0.20 and β = 1 for U < 3.5 m/s, and α = 0.057 and β = 2 for U > 3.5 m/s. Wind speed data required for estimation of k_L were obtained from the NOAA Weather Station at Hancock Airport, located approximately 8 km from the lake.

Algal Photosynthesis and Respiration

The algal contribution to the oxygen budget is quantified through the rate of net photosynthesis. Net phytoplankton production ($gChl/m^3/d$), as calculated by the Onondaga Lake nitrogen model (Canale et al. 1996), is converted to a rate of net photosynthesis through application of stoichiometric coefficients describing the ratio of chlorophyll to carbon in the phytoplankton (a_{cp} = 43 gC/gChl; sediment trap data, Effler 1996) and the amount of oxygen produced per unit phytoplankton carbon fixed (a_{oc} = 2.67 gO_2/gC; Stumm and Morgan 1981). The resulting rate of net photosynthesis (Figure 2) is then input to the DO model:

$$\text{Net photosynthesis (UML; } gO_2/d) = P_{n1}\ V_1 \tag{8}$$

$$\text{Net photosynthesis (LML; } gO_2/d) = P_{n2}\ V_2 \tag{9}$$

where P_{n1} and P_{n2} are rates of net photosynthesis ($gO_2/m^3/d$) in the UML and LML and V_1 and V_2 are the UML and LML volumes (m^3).

Carbonaceous Biochemical Oxygen Demand

The kinetic framework employed here considers autochthonous (internally-produced) and allochthonous (externally-loaded) organic matter separately. The rate of net photosynthesis, determined by calibration using the Onondaga Lake nitrogen model (Canale et al. 1996), is equivalent to the amount of oxygen produced through gross photosynthesis less that consumed through algal and bacterial respiration of *autochthonous* organic matter. The microbial degradation of *allochthonous* organic matter is characterized through CBOD and quantified through a separate mass balance which accommodates loads, losses to outflow and oxidation, and exchange between the upper and lower mixed layers:

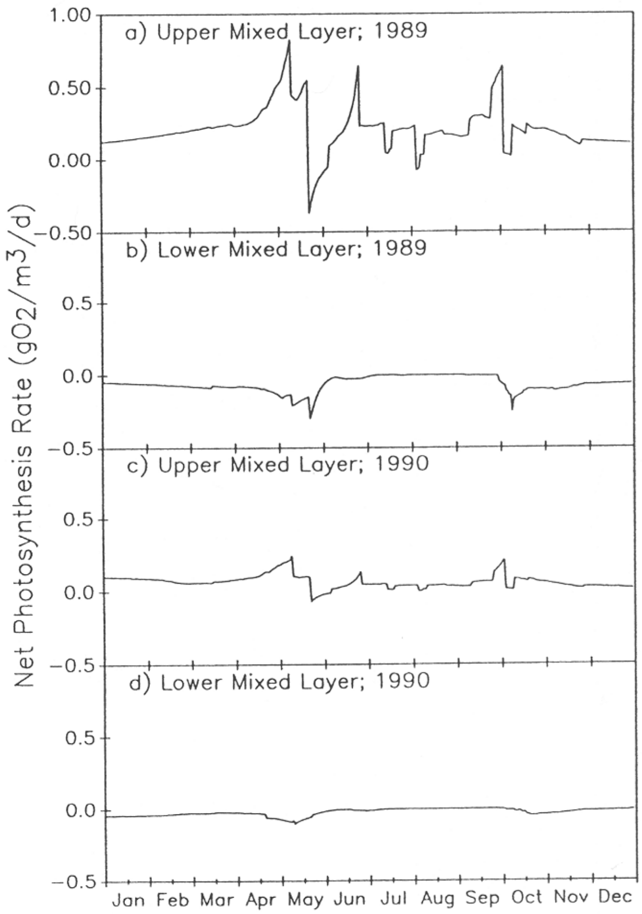

Figure 2.–Calculated rates of net photosynthesis for the UML and LML of Onondaga Lake in 1989 and 1990.

$$V_1 \frac{d[CBOD]_1}{dt} = W_{CBOD} - Q_{out}\ [CBOD]_1 - k_d\ [CBOD]_1\ V_1 + v_t\ A_i\ ([CBOD]_2 - [CBOD]_1) \tag{10}$$

$$V_2 \frac{d[CBOD]_2}{dt} = - k_d\ [CBOD]_2\ V_2 + v_t\ A_i\ ([CBOD]_1 - [CBOD]_2) \tag{11}$$

where CBOD is the carbonaceous biochemical oxygen demand (g/m^3) and W_{CBOD} is the CBOD loading (g/d).

The value for the CBOD oxidation coefficient (k_d = 0.28/d) was determined directly for mixtures of Onondaga Lake water and METRO effluent (Upstate Freshwater Institute, unpublished data); a temperature correction is applied (θ = 1.047; Bowie et al. 1985; Thomann and Mueller 1987). W_{CBOD} was estimated as the product of reported flow (Onondaga County 1990) and concentration data for METRO (CBOD = 16.0 g/m^3) and the major tributaries (CBOD = 2.5 g/m^3). Model-predicted, time-variable values for CBOD are used as input to the DO mass balance:

$$\text{CBOD oxidation rate (UML; gO}_2\text{/d)} = -k_d\,[\text{CBOD}]_1\,V_1 \qquad (12)$$

$$\text{CBOD oxidation rate (LML; gO}_2\text{/d)} = -k_d\,[\text{CBOD}]_2\,V_2 \qquad (13)$$

Measured and predicted levels of CBOD are generally low, approaching the limit of detection (APHA 1985) in both the UML and LML. Little seasonality was noted in measured or predicted values in either layer. The annual average simulated CBOD (0.35 ± 0.12 g/m^3) is of a magnitude comparable to, though statistically different from, that measured in the field (0.84 ± 0.32 g/m^3; N = 6). The difference between the simulated and measured CBOD may be attributed to uncertainty in the estimates of CBOD loading from METRO and the major tributaries.

Nitrogenous Biochemical Oxygen Demand

The microbial oxidation of ammonia (bacterial nitrification) results in the exertion of a nitrogenous biochemical oxygen demand (NBOD, g/m^3). Laboratory microcosm experiments conducted on water and sediment samples from Onondaga Lake (Penn et al. 1993) suggest that negligible nitrification occurs in the water column and that the process is largely confined to the oxic portion of the sediment-water interface. This is consistent with the conclusion of Hall (1986) that nitrification occurs primarily at the sediment surface and that water column nitrification contributes little to the nitrogen budget of lakes. The rate of NBOD exertion at the sediment-water interface may be calculated as the product of the film transfer coefficient for nitrification, the oxic sediment area, and the ammonia concentration, corrected for the oxygen stoichiometry of the process:

$$\text{NBOD oxidation rate (UML; gO}_2\text{/d)} = -a_{ON}\,k_n\,(A_o - A_i)\,[\text{NH}_3\text{-N}]_1 \qquad (14)$$

$$\text{NBOD oxidation rate (LML; gO}_2\text{/d)} = -a_{ON}\,k_n\,A_e\,[\text{NH}_3\text{-N}]_2 \qquad (15)$$

where a_{ON} is the stoichiometric oxygen equivalent for ammonia oxidation (4.57 gO_2/gNH_3-N), k_n is the film transfer coefficient for nitrification (m/d), (A_o - A_i) is the UML sediment area (m^2), A_e is the LML sediment area (m^2) in contact with oxic waters, and $[NH_3\text{-}N]_1$ and $[NH_3\text{-}N]_2$ are the ammonia-nitrogen concentrations (gNH_3-N/m^3) in the UML and LML, respectively. The value for the film transfer coefficient (0.135 m/d) was determined by calibration using the Onondaga Lake nitrogen model (Canale et al. 1996). This value is somewhat larger than those measured for Onondaga Lake in microcosm experiments (0.04 and 0.10 m/d), but within the range determined for the adjoining Seneca River (0.11 - 0.51 m/d; Penn et al. 1993). The film transfer coefficient is temperature corrected (θ = 1.085; Bowie et al. 1985) and set to zero for temperatures below 10°C (Thomann and Mueller 1987). Concentrations of NH_3-N used as model input are calculated by the Onondaga Lake nitrogen model (Canale et al. 1996).

Sediment Oxygen Demand

Organic matter delivered to the lake bottom by sedimentation is stabilized through biochemically-mediated aerobic and anaerobic processes which directly or indirectly exert a sediment oxygen demand (SOD, $gO_2/m^2/d$; see Hatcher 1986, for a review). A variety of complex kinetic formulations for simulating SOD have been proposed (Bouldin 1968; Bowie et al. 1985; Walker and Snodgrass 1986; DiToro et al. 1990). Here, a zero-order expression is adopted (Bowie et al. 1985):

$$\text{Sediment oxygen demand (gO}_2\text{/d)} = -\text{SOD}\,A_e \qquad (16)$$

SOD is included as a sink term only in the LML. Sediments in shallow locations are expected to exert a negligible demand on the well-oxygenated waters of the UML as they have substantially less organic matter than deep-water sediments (Auer et al. 1996). Exertion of SOD in the LML is limited to that fraction of the sediment surface in contact with oxic waters (A_e). Where LML sediments contact anoxic waters (A_x), SOD is manifested in the accumulation of reduced chemical species (unexerted oxygen demand), an oxygen sink treated separately as described below.

Techniques are available for the direct field and/or laboratory measurement of SOD (Bowman and Delfino 1980; Chiaro and Burke 1980; Gardiner et al. 1984; Hatcher 1986). Rates of sediment oxygen demand were measured in the laboratory on intact sediment cores collected from Onondaga Lake (Gelda et al. 1995). Measurements were made at 8°C, a representative mean annual hypolimnetic temperature, and converted to 20°C using θ = 1.065 (Bowie et al. 1985; Thomann and Mueller 1987). A seasonal temperature correction is applied in the model. Rates measured in Onondaga Lake (SOD; mean ± s.d. = 1.68 ± 0.56 $gO_2/m^2/d$ at 8°C; n = 15) are comparable to values observed in other systems of similar trophic state (Gardiner et al. 1984; Bowie et al. 1985; DiToro et al. 1990). Model simulations of reduced species and dissolved oxygen are performed using the mean measured SOD ± one standard deviation.

Reduced Chemical Species Oxygen Demand

Sediment oxygen demand is a manifestation of the aerobic decomposition of organic matter and the oxidation of reduced chemical species (e.g. CH_4, H_2S, NH_4^+, and Fe^{2+}). When the water overlying the sediment is depleted of oxygen, SOD cannot be exerted. However, anaerobic decomposition continues within the sediment, releasing reduced chemical species to the water column. These materials progressively accumulate in the LML in a nearly linear fashion over the stratified period (Addess and Effler 1996; Effler et al. 1988; Gelda et al. 1995). With the approach to fall turnover, LML waters, rich in reduced species, are entrained by the UML. Oxidation of these reduced species in the UML contributes to the lakewide oxygen depletion observed each fall. Simulation of the fall depletion event requires that the accumulation of reduced species in the LML and their transport to the UML be quantified. To this end, a submodel was developed, linking SOD and the phenomenon of reduced species accumulation. The simulation is based on an estimate of the rate of sediment production of reduced species:

$$W_{RS} = f_{RS}\, SOD\, A_x \tag{17}$$

where W_{RS} is the estimated reduced species internal loading expressed as oxygen equivalents (gO_2^*/d), f_{RS} is the fraction of the measured SOD accounted for by the flux of CH_4, H_2S, and Fe^{2+} and A_x is the anoxic sediment area. Ammonia flux is not included in the reduced species submodel as it is treated separately by the Onondaga Lake nitrogen model (Canale et al. 1996) and accommodated here through NBOD exertion. Values for f_{RS} (0.78 in 1989 and 0.94 in 1990) were estimated by quantifying the component contributions to SOD from reduced species (CH_4, H_2S, and Fe^{2+}), ammonia, and aerobic decomposition (Gelda et al. 1995). The value of f_{RS} is higher for 1990 than for 1989 due to an elevated sulfide flux (0.941 gO_2^*/d in 1990 versus 0.634 gO_2^*/d in 1989; Gelda et al. 1995). Reduced species data used for comparison to submodel output were derived from direct observations of the concentration of the individual chemicals in the LML, expressed as oxygen equivalents:

$$[RS]_{obs} = a_1\,[CH_4] + a_2\,[H_2S] + a_3\,[Fe^{2+}] \tag{18}$$

where $[RS]_{obs}$ is the observed reduced species concentration, expressed in oxygen equivalents (gO_2^*/m^3), $[CH_4]$ is the methane concentration (gCH_4/m^3), $[H_2S]$ is the sulfide concentration (gS/m^3), $[Fe^{2+}]$ is the ferrous iron concentration (gFe/m^3), and a_1, a_2, and a_3 are stoichiometric coefficients appropriate for the oxidation pathways of the individual reduced species (Gelda et al. 1995). The input of methane to the UML and LML associated with the dissolution of rising methane-enriched gas bubbles (ebullition; cf. Addess and Effler 1996) has been included for completeness.

The overall mass balance for reduced species can be written as:

$$V_1 \frac{d[RS]_1}{dt} = W_{1,eb} - Q_{out}\,[RS]_1 - k_{RS}\,[RS]_1\,V_1 + v_t\,A_i\,([RS]_2 - [RS]_1) \tag{19}$$

$$V_2 \frac{d[RS]_2}{dt} = W_{2,eb} + f_{RS}\,SOD\,A_x - k_{RS}\,[RS]_2\,V_2 + v_t\,A_i\,([RS]_1 - [RS]_2) \tag{20}$$

where $[RS]_1$ and $[RS]_2$ are the reduced species concentrations in the UML and LML, $W_{1,eb}$ and $W_{2,eb}$ are the redissolution rates for methane gas in the UML and LML, and k_{RS} is a first order rate coefficient for reduced species oxidation. The value for k_{RS} was set at 0.25/d through model calibration. Application of a single first order rate coefficient representing oxidation of methane, hydrogen sulfide, and iron is deemed appropriate here, because all three species are very rapidly oxidized (Jannasch 1975; Jorgensen et al. 1979). Further, sensitivity analyses (see below) indicate that the model is not particularly sensitive to k_{RS}. Values for $W_{1,eb}$ (3.77×10^5 gO_2^*/d) and $W_{2,eb}$ (2.38×10^5 gO_2^*/d) were estimated for 1989 (Addess and Effler 1996) and applied to both years. Output from the RS submodel is utilized as input to the DO model and the contribution to the oxygen budget of the UML and LML is given by:

$$\text{Reduced species oxidation rate (UML; } gO_2/d) = -k_{RS}\,[RS]_1\,V_1 \tag{21}$$

$$\text{Reduced species oxidation rate (LML; } gO_2/d) = -k_{RS}\,[RS]_2\,V_2 \tag{22}$$

Oxygen Limitation of Microbial Processes

Oxygen limitation of microbially-mediated processes is typically simulated through a Monod-type formulation (NBOD: Charley et al. 1980, Hall and Murphy 1980; CBOD: DiToro and Connolly 1980; SOD: Lam et al. 1984, Snodgrass and Ng 1985; CH_4 oxidation: Lidstrom and Somers 1984; H_2S oxidation: Wilmot et al. 1988), i.e.

$$f_{OL} = \frac{[DO]_2}{[DO]_2 + K_{s,DO}} \tag{23}$$

where f_{OL} is an oxygen limitation function (dimensionless) and $K_{s,DO}$ is the half-saturation constant for oxygen limitation (g/m³). The function is applied only to the LML, as oxygen limitation of microbial processes seldom occurs in the UML. A value for $K_{s,DO}$ = 3.5 g/m³ was determined by model calibration. This volume-weighted average value corresponds to an oxygen concentration at the sediment-water interface of < 1 g/m³. Snodgrass and Ng (1985) applied a value of $K_{s,DO}$ = 1.4 g/m³ at the sediment-water interface in studies of Hamilton Harbor.

Overall Model Framework

The complete mass balance equations for DO in the UML and LML can be written as:

$$V_1 \frac{d[DO]_1}{dt} = W_{DO} - Q_{out}[DO]_1 + k_L A_o ([DO]_s - [DO]_1) + P_{nl} V_1 - k_d [DBOD]_1 V_1 - a_{ON} k_n (A_o - A_i) [NH_3\text{-}N]_1 - k_{RS} [RS]_1 V_1 + v_t A_i ([DO]_2 - [DO]_1) \tag{24}$$

$$V_2 \frac{d[DO]_2}{dt} = f_{OL} P_{n2} V_2 - f_{OL} k_d [CBOD]_2 V_2 - f_{OL} a_{ON} k_n A_e [NH_3\text{-}N]_2 - f_{OL} SOD A_e - f_{OL} k_{RS} [RS]_2 V_2 + v_t A_i ([DO]_1 - [DO])_2 \tag{25}$$

Model coefficients are summarized below (Table 1). The mass balance expressions presented here as Equations 10-11, 19-20, and 24-25 are solved numerically using an Euler integrator (Chapra and Canale 1988) to obtain time-variable output for CBOD, RS, and DO.

Field Measurements of DO and Related Parameters

Field data used for comparison with model output were derived from samples collected at one meter intervals at a centrally-located station in the south basin of Onondaga Lake. This site is known to be representative of water quality conditions lakewide (Effler 1996). Samples were collected over the May-November periods of 1989 and 1990 and analyzed for a suite of parameters (Table 2). Data from vertical profiles were used to calculate volume-weighted average concentrations for the UML and LML. Concentrations

Table 1.–Model coefficients.

Model Coefficient (symbol)	Value	Unit	Reference
Mass transport process parameters			
Vertical exchange coefficient (v_t)	0.001-5.0	m/d	4
Liquid film transfer (reaeration) coefficient (k_L)	0.22-4.65	m/d	5
Kinetic processes rate constants			
CBOD oxidation (k_d)	0.28	1/d	7
NBOD oxidation (k_n)	0.135	m/d	2, 3
Reduced species oxidation (k_{RS})	0.25	1/d	9
Sediment oxygen demand (SOD)	1.68	$gO_2/m^2/d$	6
Net photosynthesis rate (P_n)	-0.37-0.82	$gO_2/m^3/d$	2
Fraction of measured SOD as reduced sp. flux (f_{RS})	0.78-0.94	*	6
Half saturation constant for DO limitation ($K_{s,DO}$)	3.5	gO_2/m^3	9
Temperature correction coefficients			
CBOD oxidation (θ_{CBOD})	1.047	*	1, 8
NBOD oxidation (θ_{NBOD})	1.085	*	1
Sediment oxygen demand (θ_{SOD})	1.065	*	1, 8

* dimensionless.
1-Bowie et al. (1985); 2-Canale et al. (1996); 3-Canale et al. (1995); 4-Doerr et al. (1996a); 5-Gelda et al. (1996); 6-Gelda et al. (1995); 7-Upstate Freshwater Institute, unpublished data; 8-Thomann and Mueller (1987); 9-Model calibration.

Table 2.–Monitoring and analytical procedures.

Variable	Frequency	Method	Reference
Dissolved Oxygen	Weekly at 1m intervals	Probe; verified by	APHA (1985) Winkler Method
Total Chlorophyll	Weekly at 1m intervals over 0-10m depth	Spectrophotometric	Parsons et al. (1984)
Carbonaceous BOD	Weekly at 1m and 16m Summers of 1990, 1991	Filtered samples	APHA (1985)
Temperature	Weekly at 0.5m intervals	HydroLab	
Wind speed	Hourly	Anemometer with data-logger	
Incident Solar Radiation	Hourly	Pyranometer with data-logger	
Methane	Weekly at 1m intervals in LML	Gas chromatograph	Fendinger and Adams (1985)
Sulfides	Weekly at 1m intervals in LML	Iodometric	APHA (1985)
Ammonium	Weekly at 1m intervals in LML	Spectrophotometric	Solorzano (1969)
Ferrous Iron	Weekly at 1m intervals in LML	Spectrophotometric	Heaney and Davison (1977)

representative of a 1m layer were multiplied by the layer volume to yield a mass. The masses were then summed and divided by the total layer volume to yield the volume-weighted average concentration. This procedure accounts for non-uniform basin geometry not addressed by simple arithmetic averaging. Vertical heterogeneity is illustrated in comparison plots of model output and field data using bars to represent minimum and maximum observed concentrations.

Model Performance

Model performance was evaluated through calculation of the root mean square error (RMSE, units of the parameter being analyzed; Thomann 1982):

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (X_{i,obs} - X_{i,prd})}{N}} \qquad (26)$$

where, N = number of observations, $X_{i,obs}$ = observed value of ith observation of parameter X, and $X_{i,prd}$ = predicted value of ith observation of parameter X. RMSE is statistically well behaved and is an indicator of the average error between observations and predictions. Generally, a lower RMSE implies a better model fit to observations. When evaluating model performance, however, particular care should be paid to the capability of the model in simulating phenomena of management significance, i.e. the onset and duration of anoxia, the period of accumulation of reduced species, and the period of DO recovery following fall turnover.

Reduced Species

Reduced species are rapidly oxidized in the well-aerated waters of the UML and thus measured and model-predicted concentrations remain at or near the limit of detection. Reduced species appear in the LML with the onset of anoxia, progressively increasing in concentration over the thermally-stratified period and subsequently declining during fall mixing. These temporal trends and seasonal dynamics are well-tracked and appropriately described by the model for both the calibration (1989) and verification (1990) years (Figure 3). The average error between observations and predictions, as quantified by RMSE, is 2.22 gO_2^*/m^3 (N = 17) in 1989 and 5.12 gO_2^*/m^3 (N = 17) in 1990.

Dissolved Oxygen - UML

Recurrent features of the observed distribution of DO in the UML, important to water quality, include:

- significant intralayer structure in mid-summer, i.e. strong vertical gradients;
- dramatic fluctuations in the May-August period, often including episodes of supersaturation;
- marked depletion with the approach to turnover in September and October; and
- recovery from depletion in the post-turnover period of October and November.

Strong vertical gradients in DO are observed in the UML (bars in Figures 4a and c), especially in mid-summer. The UML includes waters ranging from those at the surface with a high algal standing crop and a tendency toward supersaturation to those in the metalimnion, coincident with the oxycline. The development of secondary stratification during quiescent periods, with attendant reductions in air-water exchange, further promotes vertical structure in DO. Wide fluctuations in DO, with episodic supersaturation, are observed between sampling dates during the productive summer months (May-August; Figures 4a and c). These dynamics are driven by variation in rates of algal photosynthesis and respiration and their response to changes in light and algal standing crop. Dissimilarities in UML DO between 1989 and 1990, especially in the timing, frequency and magnitude of supersaturation, are largely related to interannual variability in algal standing crop. The resolution required to accommodate these phenomena is not provided by the geometry (two layer segmentation of the DO model) and kinetic structure (phytoplankton growth in the nitrogen model) applied here. Nonetheless, the model succeeds in tracking volume-weighted average DO in the UML quite well (Figures 4a and c). RMSE values for the UML were 1.79 gO_2/m^3 (N = 62) and 1.55 gO_2/m^3 (N = 49) for 1989 (calibration) and 1990 (verification), respectively.

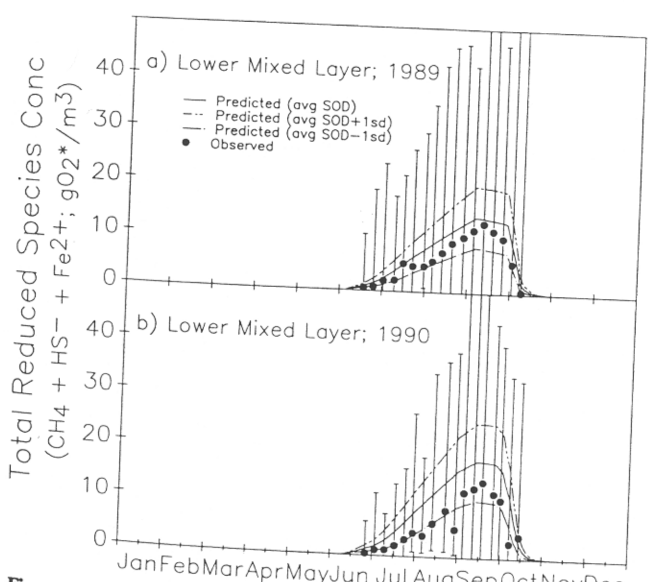

Figure 3.–Comparison of measured and model-predicted reduced species concentrations in Onondaga Lake: a) LML, 1989 and b) LML, 1990. Bars represent ranges of observed concentrations. Band represents model output using ± 1 SD on the mean measured SOD.

From a management perspective, the fall depletion-recovery event is of special significance. Oxygen depletion in the UML with the approach to turnover occurs due to entrainment and oxidation of reduced species and because the conditions of light and temperature which mediate photosynthesis become less favorable during this period. The severity of the fall depletion event is also influenced by the initial UML oxygen concentration, chlorophyll concentrations in the UML and LML, levels of reduced species in the LML, and the duration of the period of thermocline migration (entrainment). During the recovery period there is a return to near-saturated conditions as reduced species are oxidized, algal standing crop declines and atmospheric reaeration replenishes the lake's oxygen supply. The duration of the recovery period, generally 3 - 4 weeks, is determined by the magnitude of the remaining sink terms (e.g., net algal photosynthesis, CBOD, NBOD, and SOD) and wind effects on the rate of reaeration. The model performs well in simulating the fall depletion-recovery event in 1989 (Figure 4a), and the recovery phase in 1990 (Figure 4c), but performs less well for the depletion phase in 1990 (Figure 4c). Although the timing and magnitude of the depletion event (i.e., change in DO over the interval) is well matched, the minimum UML DO is overpredicted. During the fall entrainment period, algae are distributed vertically over the entire water column and encounter a much less favorable light environment. Failure to account for this phenomenon results in an overestimation in photosynthesis and thus DO in the UML (Figure 4c) with the approach to turnover.

Dissolved Oxygen - LML

From a water quality perspective, the key features of the distribution of DO in the LML are:

- the rate of oxygen depletion in late spring-summer; and
- the duration of anoxia.

The rate of summer depletion (AHOD, Wetzel, 1983) displays considerable interannual variation (2.1 $g/m^2/d$ in 1989 versus 1.0 $g/m^2/d$ in 1990) resulting in differences in the onset of complete anoxia in the LML (early July in 1989 versus late July in 1990). Year-to-year differences in the rate of summer oxygen depletion (onset of anoxia and the attendant AHOD) are largely a result of variability in the degree of vertical mixing (meteorological effects) and in the algal standing crop (algal respiration in the LML). Similar results were reported by Nürnberg (1995) in a study quantifying anoxia in several lakes. The total duration of anoxia was about 5 months (mid-May through mid-October) in both years. Wind energy input, particularly, during fall turnover is the key factor influencing the duration of anoxia. The model performs well in simulating both the rapid depletion of DO in the LML following the onset of stratification and the duration of the anoxic period (Figures 4b and 4d). RMSE values for the LML were 1.54 gO_2/m^3 (N=62) in 1989 and 1.74 gO_2/m^3 (N = 49) in 1990.

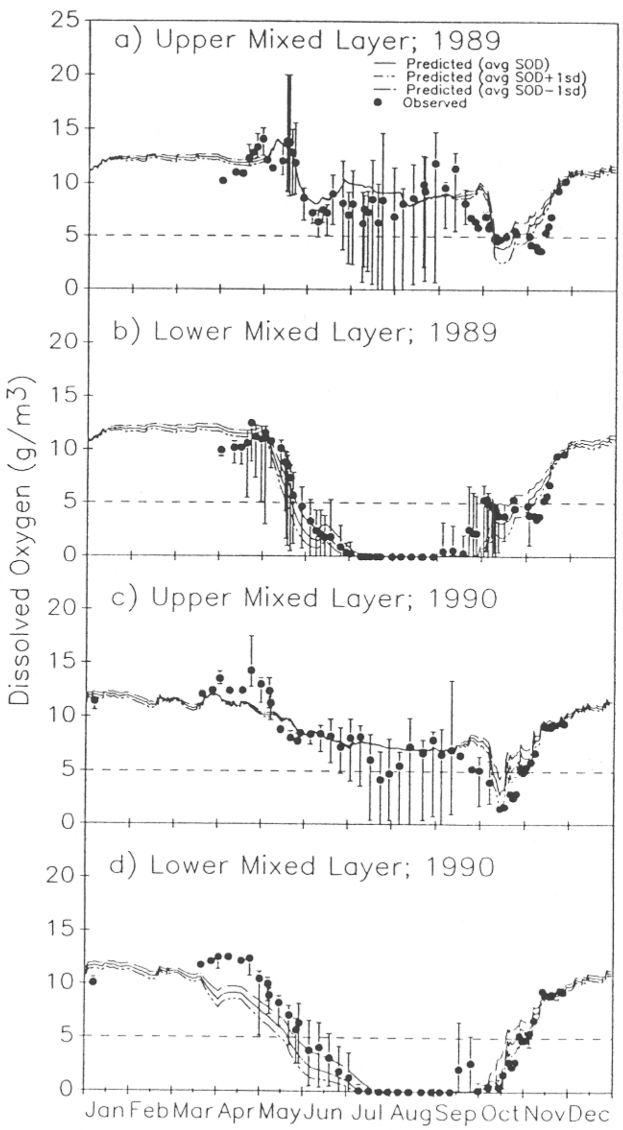

Figure 4.–Comparison of measured and model-predicted DO concentrations in Onondaga Lake: a) UML, 1989; b) LML, 1989; c) UML, 1990; and d) LML, 1990. Bars represent ranges of observed concentrations. Band represents model output using ± 1 SD on the mean measured SOD.

Analysis

From a management perspective, two features of the oxygen resources of Onondaga Lake stand out: DO depletion in the bottom waters following the onset of thermal stratification in spring and DO depletion over the entire water column with the approach to turnover in fall. These two phenomena provide focus for the analysis of model output.

Summer DO depletion in the LML

The model was applied to calculate the relative contribution of the various oxygen sinks to summer DO depletion in the LML (Figure 5). The period of evaluation extends from the onset of stratification until the LML is totally anoxic. During this period, SOD is the largest oxygen sink, accounting for more than 50% of the overall depletion (Figure 5). Oxidation of reduced species accumulating in the LML prior to the onset of anoxia contribute an additional 20%. Thus sediment processes account for more than 70% of the observed oxygen depletion in the LML, with water column processes (CBOD, NBOD and algal respiration) contributing the balance (~30%). This finding is significant from a lake management perspective. It suggests that those water quality constituents likely to exhibit a rapid response to reductions in pollutant load (CBOD, NBOD, and algal standing crop) are of minor importance compared with sediment oxygen demand, a phenomenon which integrates years of pollutant loading and which may be expected to display a "delayed response" to loading changes. The retardation of lake recovery by sediments is well documented for phosphorus (cf. Welch 1992) and estimates of the time course of recovery of polluted sediments have been developed (Penn et al. 1995).

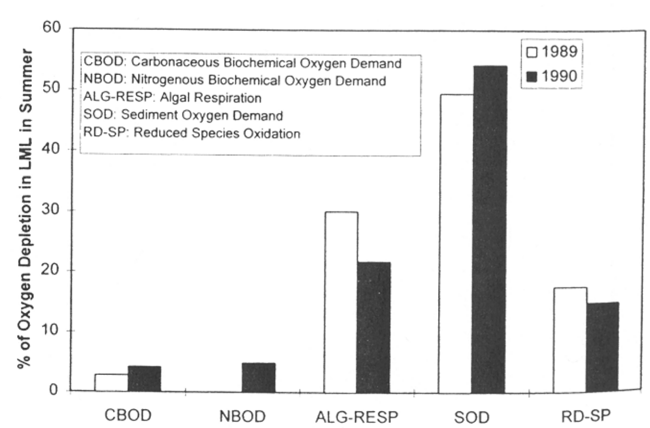

Figure 5.–Relative importance of various DO sinks in the LML in summer, 1989 and 1990.

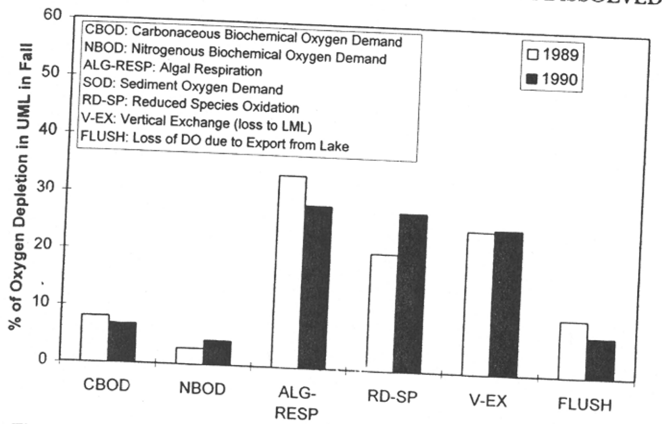

Figure 6.–Relative importance of various DO sinks in the UML in fall, 1989 and 1990.

Fall DO depletion in the UML

The relative contribution of the various oxygen sinks to fall DO depletion in the UML of Onondaga Lake is illustrated in Figure 6. The period of evaluation is essentially the period of entrainment - from the time of maximum reduced chemical species accumulation in the LML (i.e. late summer) until the time of complete turnover. During this period, reduced species oxidation, algal respiration and vertical exchange account for 30%, 25%, and 25% of the oxygen loss from the UML, respectively. The remaining 20% is accounted for by CBOD, NBOD, and hydraulic flushing in essentially equal proportion. Although "fast response" processes (e.g. algal respiration) play a more important role here than in the LML in summer, "slow response", sediment-related phenomena, remain dominant. In this regard, note (Figure 7) that both the oxidation of reduced species in the UML and the vertical transport of oxygen from the UML (consumed in reduced species oxidation in the LML) ultimately satisfy an oxygen demand originating in the sediment.

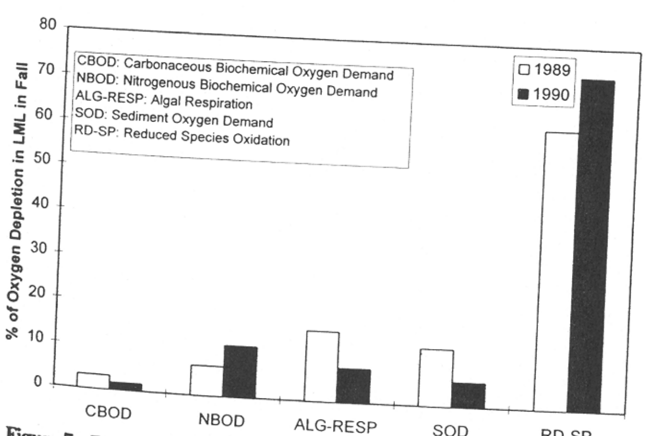

Figure 7.–Relative importance of various DO sinks in the LML in fall, 1989 and 1990.

Management Concerns

Elimination of violations of the surface water quality DO standard associated with the fall depletion event has been identified as an expected first response to remediation efforts. A review of Figures 5-7 makes it clear that "fast response" phenomena (CBOD, NBOD and algal respiration) do not play a dominant role in mediating this phenomenon. It is unlikely, therefore, that management actions aimed at reductions in primary production through control of nutrient loads will engender any significant, immediate improvement in the oxygen resources of the lake. Similar findings were reported for Lake Erie by Charlton et al. (1993) and DiToro and Connolly (1980).

Given that SOD and the attendant accumulation of reduced species is the major factor dictating the minimum DO at fall turnover, it is instructive to investigate the relationship between lake management, SOD, and the fall depletion phenomenon. The DO model was utilized to develop a relationship between SOD and the minimum fall DO (Figure 8). Data added to that figure illustrate the mean minimum DO associated with the present SOD, as well as the natural variability associated with that value. From Figure 8, it may be deduced that an SOD on the order of 1.25 $gO_2/m^2/d$ would be required to insure that the 5 g/m^3 water quality standard is met. Based on reports of annual rates of primary production for lakes of various trophic states (Wetzel 1983), calculations of the fraction of fixed carbon delivered to the sediment (Nedwell, 1984; Baines et al. 1994; N. Urban, unpublished data), and determinations of the fraction of the sediment carbon available for decomposition (Stromquist and Auer 1995), it is estimated that a mesotrophic lake would exhibit an SOD over the range of 0.2-0.7 $gO_2/m^2/d$.

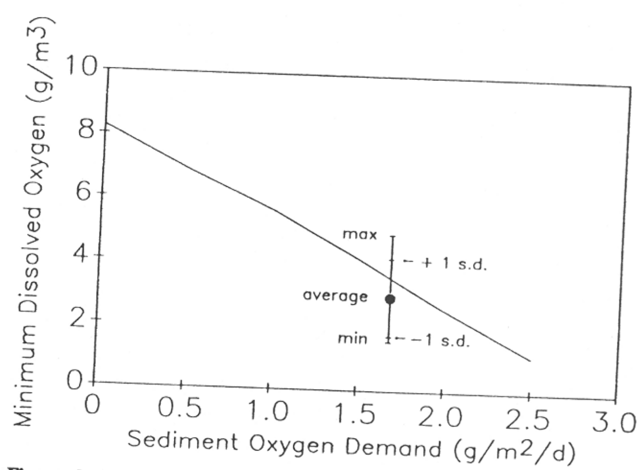

Figure 8.–Relationship between SOD and the minimum UML DO during the approach to turnover as calculated by the Onondaga Lake DO model. Data point and bar show the maximum, minimum, mean and standard deviation for DO under the present SOD.

Thus management strategies seeking the establishment of mesotrophic conditions in Onondaga Lake would be expected to meet the surface water quality standard for dissolved oxygen in fall. Model simulations of the response of the lake's oxygen resources to various management alternatives are presented elsewhere in this issue (Doerr et al. 1996b, Effler and Doerr 1996).

Sensitivity Analysis

Sensitivity analyses may be used to illustrate the reliability of model predictions relative to acknowledged uncertainty in model inputs and coefficients and to natural variability in environmental forcing conditions. For example, sensitivity analysis indicated that uncertainty in several features of the model (e.g. DO inputs from tributary and point sources, carbonaceous BOD, and methane ebullition) has little impact on model performance and therefore does not merit further attention (i.e. additional investigation and quantification).

Sensitivity analyses can also play a vital role in the development of appropriate expectations for the water quality response to management actions. As an example, we present the results of sensitivity analyses focusing on DO in the UML during the fall depletion period, a time when the surface water DO standard is often violated. This phenomenon is a clear reflection of the degraded conditions of the oxygen resources of Onondaga Lake and remediation of the problem is a featured goal of the lake restoration program. Model sensitivity to two kinetic coefficients (k_n, nitrification, and k_{RS}, reduced species oxidation), one model input of management significance (SOD), and one environmental variable (wind speed) is examined. Simulation results for the calibration year (1989) are used as a basis for comparison.

The coefficients k_n and k_{RS} were selected for testing because their values were determined through model calibration rather than by direct measurement. Model sensitivity was examined by setting k_n at one-half and double and k_{RS} at ± 50% of their values as determined by calibration. Results of this analysis (Figures 9a and 9b) suggest that the model is only modestly sensitive to variability in values for these coefficients, with predicted DO deviating from the base case by < ± 1 mg/L.

SOD was selected for testing because it is, through reduced species accumulation and oxidation, the major oxygen sink during the fall depletion period. SOD was varied ± one standard deviation of the experimentally-determined value, yielding departures in DO of ± 2 g/m^3 from the base case (Figure 9c). This analysis serves to confirm and expand upon earlier conclusions (cf. Figures 4b and 4d) that SOD is the management variable of most importance to the oxygen resources of Onondaga Lake. This finding further suggests that additional refinements in estimates of SOD and the development of an improved conceptual understanding of the response of SOD to changes in trophic state are merited.

Wind-driven energy inputs play a major role in determining the reaeration rate, a key player in recovery of the lake's oxygen resources following depletion at turnover. Sensitivity to variability in reaeration (Figure 9d), as governed by wind speed, was examined for wind speed time series corresponding to the lower (average wind = 3.74 m/s; 1971) and upper (average wind = 4.97 m/s; 1960) ten percentile values for a thirty-year data

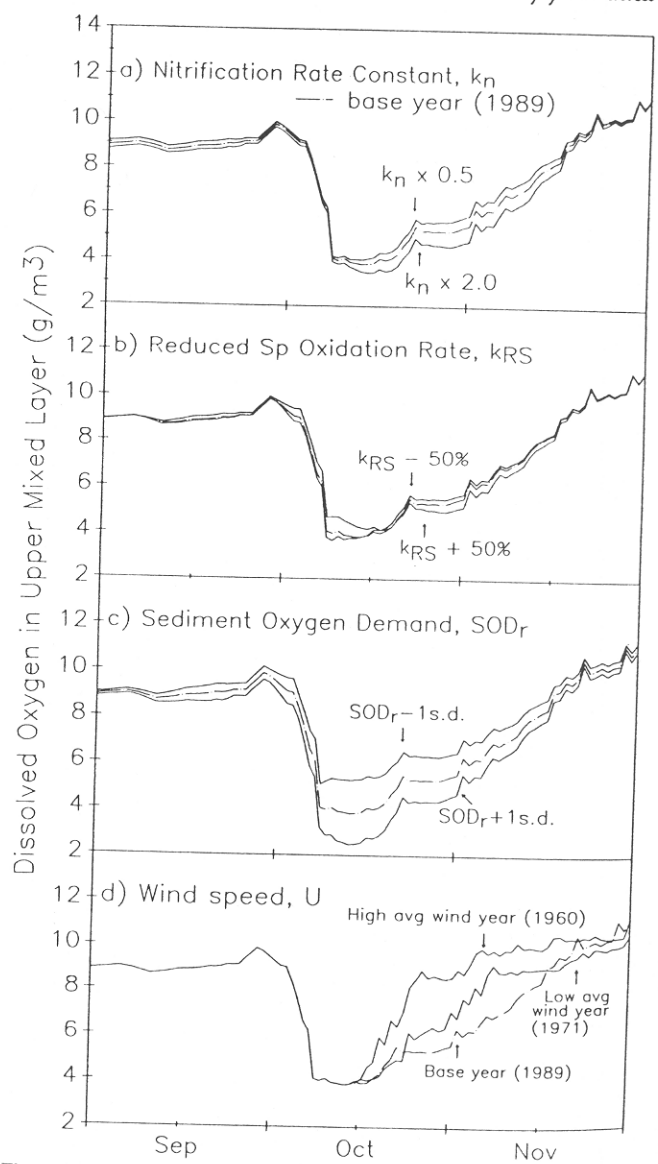

Figure 9.–Sensitivity analysis describing the impact of uncertainty in: a) nitrification rate, b) reduced species oxidation rate, c) SOD, and (d) wind speed on model-calculated DO in the UML of Onondaga Lake for the September to November period.

base (in the period 1958-1990). For this analysis, adjustment of wind speed was limited to the period following complete turnover (mid-October), to isolate the interplay of reaeration and oxygen resources in the recovery period. It is clear that wind speed influences the recovery process and that interannual differences in the rate of response will occur due to natural variability in environmental conditions (see also bar in Figure 8).

Wind conditions also influence the time course of the approach to fall turnover (i.e. the rate of entrainment), a phenomenon which determines the severity of fall DO depletion. For example, a period of high winds (rapid entrainment of RS-rich LML waters) followed by a period of calm conditions (low reaeration) would result in severe DO depletion in the UML. In contrast, extended periods of mild winds at the approach to turnover would provide a sustained oxidation of RS and minimal depletion. The time course of vertical mixing in fall and the associated entrainment of LML waters are subject to wide variation as a result of natural variability in meteorological conditions (Owens and Effler 1989). A mechanistic lake stratification model (e.g., Owens and Effler 1989) would be necessary to address this potentially important source of variability in the timing and severity of the fall depletion event.

Summary and Conclusions

A mechanistic, two-layer mass balance model for dissolved oxygen in a hypereutrophic urban lake has been developed and tested. The model accommodates the processes of reaeration, algal photosynthesis and respiration, CBOD, NBOD, SOD and water column oxidation of reduced species. Most model inputs, including values for many kinetic coefficients, were developed through an extensive program of field monitoring and field and laboratory experimentation.

The model was calibrated using data collected in 1989 and verified using data obtained the following year, 1990. The model adequately describes temporal distributions of DO in the lake. Specifically, the model successfully simulates DO depletion in the LML following the onset of thermal stratification in spring and over the entire water column at fall turnover. In the spring, SOD and the related reduced species oxidation in the water column account for >70% of the overall oxygen depletion. CBOD, NBOD and algal respiration contribute the balance (~30%). Oxygen depletion in the UML in fall occurs largely due to watercolumn reduced species oxidation (~30%), algal respiration (~25%) and vertical exchange (~25%). Oxygen transported from the UML through vertical exchange is consumed in the LML through oxidation of reduced species. Again, sediment-related processes dominate.

Sensitivity analyses suggest that the character of the DO resources of the lake are importantly influenced by meteorological conditions, as well as by those features of pollutant loading and fate considered amenable to management. Application of the model for management purposes will require specification of the trophic state response to management actions (e.g., primary production and algal standing crop), linkage of the rates of sediment oxygen demand and reduced species accumulation to primary production, and a knowledge of the sensitivity of the system to natural variability in environmental conditions impacting DO resources.

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References

Addess, J. M. and S.W. Effler. 1996. Summer methane fluxes and fall oxygen resources of Onondaga Lake. Lake and Reserv. Manage. 12(1):91-101.

American Public Health Association, American Water Works Association and Water Pollution Control Federation. 1985. Standard Methods for the Examination of Water and Wastewater, 16th Ed. American Public Health Association, Washington, DC. 1268 p.

Auer, M. T., M. L. Storey, S. W. Effler, N. A. Auer and P. Sze. 1990. Zooplankton impacts on chlorophyll and transparency in Onondaga Lake, New York, USA. Hydrobiol. 200/201:603-617.

Auer, M. T., N. A. Johnson, M. R. Penn and S.W. Effler. 1996. Pollutant sources, depositional environment, and the surficial sediment of Onondaga Lake, New York. J. Environ. Qual. (in press).

Baines, S. B., M. L. Pace and D. M. Karl. 1994. Why does the relationship between sinking flux and planktonic productivity differ between lakes and oceans? Limnol. Oceanogr. 39:213-226.

Bella, D. A. 1970. Dissolved oxygen variations in stratified lakes. J. Sanitary Eng. Div., ASCE 96:1129-1146.

Biswas, A. K. (ed.). 1981. Models for Water Quality Management. McGraw-Hill International Book Company, NY. 348 p.

Bouldin, D. R. 1968. Models for describing the diffusion of oxygen and other mobile constituents across the mud-water interface. J. Ecol. 56:77-87.

Bowie, G. L., W. B. Mills, D. B. Porcella, C. L. Campbell, J. R. Pagenkopf, G. L. Rupp, K. M. Johnson, P. W. H. Chan, S. A. Gherini and C.E. Chamberlin. 1985. Rates, constants, and kinetic formulations in surface water quality modeling, 2nd Edition. EPA/600/3-85/040, U.S. Environmental Protection Agency, Athens, GA. 455 p.

Bowman, G. T. and J. J. Delfino. 1980. Sediment oxygen demand: a review and comparison of laboratory and in-situ systems. Wat. Res. 14:491-499.

Brown, L. C. and T.O. Barnwell, Jr. 1985. Computer program documentation for the enhanced stream water quality model QUAL2E. EPA/600/3-85/065, U.S. Environmental Protection

Agency, Athens, GA. 141 p.
Canale, R. P., R. K. Gelda and S.W. Effler. 1996. Development and testing of a nitrogen model for Onondaga Lake. Lake and Reserv. Manage. 12(1):151-164.
Canale, R. P., E. M. Owens, M. T. Auer and S. W. Effler. 1995. Validation of water quality model for Seneca River, NY. J. Wat. Resour. Plan. Manage. 121:241-250.
Chapra, S. C. and R.P. Canale. 1988. Numerical Methods for Engineers. 2nd Edition, McGraw Hill Book Company, NY. 812 p.
Charley, R. C., D. G. Hooper and A. G. McLee. 1980. Nitrification kinetics in activated sludge at various temperatures and dissolved oxygen concentrations. Wat. Res. 14:1387-1396.
Charlton, M. N., J. E. Milne, W. G. Booth and F. Chiocchio. 1993. Lake Erie offshore in 1990: Restoration and resilience in the Central Basin. J. Great Lakes Res. 19(2):291-309.
Chiaro, P. S. and D.A. Burke. 1980. Sediment oxygen demand and nutrient release. J. Environ. Eng. Div., ASCE 106:177-195.
DiToro, D. M. and J.P. Connolly. 1980. Mathematical models of water quality in large lakes. Part 2: Lake Erie. EPA-600/3-80-065, U.S. Environmental Protection Agency, Duluth, MN. 231 p.
DiToro, D. M., R. P. Paquin, K. Subburamu and D. A. Gruber. 1990. Sediment oxygen demand model: methane and ammonia oxidation. J. Environ. Eng. Div., ASCE 116:945-986.
Doerr, S. M., R. P. Canale and S.W. Effler. 1996a. Development and testing of a total phosphorus model for Onondaga Lake. Lake and Reserv. Manage. 12(1):141-150.
Doerr, S. M., S. W. Effler and E. M. Owens. 1996b. Forecasting impacts of a hypolimnetic wastewater discharge on lake water quality. Lake and Reserv. Manage. 12(1):207-217.
Effler, S. W. and C.T. Driscoll. 1986. A chloride budget for Onondaga Lake, New York, USA. Wat., Air and Soil Pollut. 27:29-44.
Effler, S. W., M. G. Perkins and C. Brooks. 1986. The oxygen resources of the hypolimnion of ionically enriched Onondaga Lake, NY, USA. Wat., Air, and Soil Pollut. 29:93-108.
Effler, S. W., J. P. Hassett, M. T. Auer and N. Johnson. 1988. Depletion of epilimnetic oxygen and accumulation of hydrogen sulfide in the hypolimnion of Onondaga Lake, NY, USA. Wat., Air, and Soil Pollut. 39:59-74.
Effler, S. W. (ed.). 1996. Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY (in press).
Effler, S.W. and S.M. Doerr. 1996. Water quality model evaluations for scenarios of loading reductions and diversion of domestic waste effluent around Onondaga Lake. Lake and Reserv. Manage. 12(1):181-193.
Effler, S. W. and R. D. Hennigan. 1996. Onondaga Lake, New York: legacy of pollution. Lake and Reserv. Manag. 12(1):1-13.
Fendinger, N. J. and D. D. Adams. 1986. A headspace equilibrium technique for measurement of dissolved gases in sediment pore water. Internat. J. Anal. Chem. 23:253-265.
Gardiner, R. D., M. T. Auer and R. P. Canale. 1984. Sediment oxygen demand in Green Bay (Lake Michigan). Proc. 1984 Specialty Conf., ASCE 514-519.
Gelda, R. K., M. T. Auer, S. W. Effler, S. C. Chapra and M. L. Storey. 1996. Determination of reaeration coefficients: a whole lake approach. J. Environ. Eng. (in press).
Gelda, R. K., M. T. Auer and S. W. Effler. 1995. Determination of sediment oxygen demand by direct measurement and by inference from reduced chemical species accumulation. Mar. Freshwat. Res. 46:81-88.
Gromiec, M. J., D. P. Loucks and G.T. Orlob. 1983. Stream quality modeling, P. 227-273. *In:* G. T. Orlob (ed.). Mathematical modeling of water quality: streams, lakes, and reservoirs. John Wiley and Sons, Chichester, Great Britain.
Hall, G. H. 1986. Nitrification in lakes, P. 127-156. *In:* J. I. Prosser (ed.). Nitrification. IRL Press, Washington, DC.
Hall, E. R. and K. L. Murphy. 1980. Estimation of nitrifying biomass and kinetics in wastewater. Wat. Res. 14:297-304.
Hatcher, K.J. 1986. Introduction to Part 1: Sediment oxygen demand processes. P. 113-138. *In:* K.J. Hatcher (ed.). Sediment oxygen demand. processes, modeling and measurement. Institute of Natural Resources, University of Georgia, Athens, GA.
Heaney, S. I. and W. Davison. 1977. The determination of ferrous iron in natural waters with 2,2' bipyridyl. Limnol. Oceanogr. 22:753-760.
Jannasch, H. W. 1975. Methane oxidation in Lake Kivu (central Africa). Limnol. Oceanogr. 20:860-864.
Jorgensen, B. B., J. G. Kuenen and Y. Cohen. 1979. Microbial transformations of sulfur compounds in a stratified lake (Solar Lake, Sinai). Limnol. Oceanogr. 24:799-822.
Krenkel, P. A. and V. Novotny. 1979. River water quality model construction. P. 18.1-18.40. *In:* H. V. Shen (ed.). Modeling of rivers. John Wiley and Sons, NY.
Lam, D. C. L., W. M. Schertzer and A. S. Fraser. 1984. Modeling the effects of sediment oxygen demand in Lake Erie water quality conditions under the influence of pollution control and weather conditions. P. 281-297. *In:* K. J. Hatcher (ed.). Sediment oxygen demand. Processes, modeling and measurement. Institute of Natural Resources, University of Georgia, Athens, GA.
Lidstrom, M. E. and L. Somers. 1984. Seasonal study of methane oxidation in Lake Washington. Appl. Environ. Microbiol. 47:1255-1260.
Nedwell, D. B. 1984. The input and mineralization of organic carbon in anaerobic aquatic sediments. P. 93-131. *In:* K. C. Marshal (ed.). Advances in microbiology, #7.
Nürnberg, G. K. 1995. Quantifying anoxia in lakes. Limnol. Oceanogr. 40:1100-1111.
O'Connor, D. J. 1983. Wind effects on gas-liquid transfer coefficients. J. Environ. Eng. Div., ASCE 109:731-752.
Onondaga County. 1990. Onondaga Lake Monitoring Program, 1990. Annual Publication. Onondaga County, Syracuse, NY. 75 p.
Owens, E. M. and S.W. Effler. 1989. Changes in stratification in Onondaga Lake, New York. Wat. Resour. Bull. 25:587-597.
Owens, E. M. and S. W. Effler. 1996. Chapter 4. Hydrodynamics. *In:* S. W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY (in press).
Parsons, T. R., Y. Marta and C. M. Lalli. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press, New York, NY. 173 p.
Penn, M. R., J. J. Pauer, R. K. Gelda and M. T. Auer. 1993. Laboratory measurements of chemical exchange at the sediment-water interface of Onondaga Lake. Technical report submitted to the Upstate Freshwater Institute, Syracuse, NY, by the Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI. 40 p.
Penn, M. R., M. T. Auer, E. L. VanOrman and J. J. Korienek. 1995. Phosphorus diagenesis in lake sediments: investigations using fractionation techniques. Mar. Freshwat. Res. 46:89-99.
Snodgrass, W. J. and R. J. Dalrymple. 1985. Lake Ontario oxygen model. 1. Model development and application. Environ. Sci. Tech. 19:173-179.
Snodgrass, W. J. and P. S. Ng. 1985. Biochemical models for hypolimetic oxygen depletion in lakes impacted by wastewater discharges: 1. Alternative models. Arch. Hydrobiol. /Supplement 72. 1:81-109.
Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14:799-801.
Streeter, H. W. and E. B. Phelps. 1925. A study of the pollution and natural purification of the Ohio River. III. Factors concerned in the phenomena of oxidation and reaeration. Public Health Bulletin No. 146, U.S. Public Health Service. 75 p.
Stromquist, V. K. and M. T. Auer. 1995. Organic carbon diagensis in the sediments of Onondaga Lake, Syracuse, NY. Abstract of poster presented at the 15th International Symposium on Lake Reservoir and Watershed Management, Nov., 1995. Toronto.

Stumm, W. and J. J. Morgan. 1981. Aquatic Chemistry, Wiley-Interscience, NY. 780 p.

Symons, J. M., W. H. Irwin, R. M. Clark and G. G. Robeck. 1967. Management and measurement of DO in impoundments. J. Sanitary Eng. Div., ASCE. 93:181-209.

Thomann, R. V. and J. A. Mueller. 1987. Principles of surface water quality modeling and control. Harper and Row Publishers, New York, NY. 644 p.

Walker, R. R. and W. J. Snodgrass. 1986. Models for sediment oxygen demand in lakes. J. Environ. Eng. Div., ASCE 112:25-43.

Welch, E. B. 1992. Ecological effects of wastewater. Applied limnology and pollutant effects. 2nd Edition. Chapman and Hall Publishers, London. 424 p.

Wetzel, R. G. 1983. Limnology. Saunders College Publishing, Philadelphia, PA, 2nd Edition. 767 p.

Wilmot, P. D., K. Cadee, J. J. Katinic and B. V. Kavanagh. 1988. Kinetics of sulfide oxidation by dissolved oxygen. J. Wat. Poll. Contr. Fed. 60:1264-1270.