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# Long-term changes in the areal hypolimnetic oxygen deficit (AHOD) of Onondaga Lake: Evidence of sediment feedback

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## *Abstract*

Long-term trends in the rate of depletion of hypolimnetic dissolved oxygen (DO) are documented for ionically enriched hypereutrophic Onondaga Lake, New York, for the 1978–2002 interval. Depletion rates, represented as areal hypolimnetic oxygen deficits (AHOD, $g\ m^{-2}\ d^{-1}$), are calculated on the basis of weekly DO profiles of 1-m resolution and estimates of coincident inputs of DO from overlying layers driven by vertical mixing. Vertical mixing inputs of DO are important in this system, representing from 15% to 37% (mean 25%) of AHOD. Interannual variations in hypolimnetic temperatures have comparatively minor (±6%) effects on AHOD. AHOD decreased 49%, from an average of 2.12 $g\ m^{-2}\ d^{-1}$ for the 1978–1986 interval, to an average of 1.08 $g\ m^{-2}\ d^{-1}$ for the 1997–2002 interval. This decrease was driven by an abrupt decrease in the deposition of particulate organic carbon into the hypolimnion starting in 1987. The magnitude of the decrease in AHOD closes reasonably well with decreases in both primary production in the trophogenic zone and organic carbon deposition to the tropholytic zone. The time course of the decrease in AHOD is consistent with localization of oxygen-demanding processes within the lake sediments, reflecting the progression of sediment diagenesis.

Dissolved oxygen (DO) is a fundamental resource of lakes that has profound effects on lake chemistry and biology (Wetzel 2001). Most hypolimnia are isolated from the important oxygen source of photosynthesis and potential inputs of DO from atmospheric exchange. Oxygen consumption in hypolimnia and sediments reflects decomposition of settling and deposited particulate organic matter that is formed mostly through primary production in the overlying trophogenic zone (Hutchinson 1957). The rate of hypolimnetic oxygen depletion has long been recognized as an integrator of lake metabolism. The evolution of these concepts and various calculation protocols to quantify the rate of DO depletion as an index, or even an indirect measure (Hutchinson 1938; Mortimer 1941), of primary production has been reviewed by Wetzel (2001). The rate of loss of the mass of DO, normalized for the surface area of the hypolimnion, described as the areal hypolimnetic oxygen deficit (AHOD, $g\ m^{-2}\ d^{-1}$), is recognized as a quantitative representation of this oxygen depletion (Wetzel and Likens 2000). Alternatively, the oxygen depletion rate can be normalized for hypolimnetic volume and represented as a volumetric hypolimnetic oxygen deficit (VHOD, $g\ m^{-3}\ d^{-1}$; Burns 1995).

The AHOD representation has been widely used as an index of the productivity of stratifying lakes, particularly for interlake comparisons (Lasenby 1975; Walker 1979; Beutel 2003). However, the strength of the cause and effect relationship between primary production and AHOD has been questioned (Cornett and Rigler 1979, 1980; Charlton 1980*a*). A number of factors, unaccounted for in the traditional AHOD calculation (Wetzel and Likens 2000), have been identified that could affect hypolimnetic DO concentrations and limit the utility of AHOD as a comparative measure of primary production among lakes, including differences in (1) vertical density gradients within the metalimnion and related effects on the fraction of organic matter decomposed in the hypolimnion (Gliwicz 1979), (2) contributions of allochthonous organic material (Brezonik 1994), (3) thickness of the hypolimnion (Cornett and Rigler 1979, 1980; Charlton 1980*a*), (4) temperature of the hypolimnion (Cornett and Rigler 1979, 1980; Charlton 1980*b*), and (5) DO inputs to the hypolimnion from vertical mixing (Stauffer 1987). Burns (1995) expanded this listing of factors that can affect VHOD (or AHOD) to nine and included the delayed decomposition of organic material in sediments. Despite these issues, AHOD has been found to be correlated with primary production and its surrogates, total phosphorus concentration (TP; Rast and Lee 1978; Chapra and Canale 1991), chlorophyll *a* (Chl *a*) concentration (Vollenweider and Janus 1981), and Secchi disc transparency (Lasenby 1975).

Some of the problems inherent in cross-sectional studies with AHOD are eliminated or ameliorated in the application of this metric to long-term data from a single lake. Such an activity is particularly interesting if there is a documented change in primary production within the record, thereby offering an opportunity to test the coupling between production in the trophogenic zone and oxygen depletion in the tropholytic zone. However, long-term data are rarely available, particularly where changes in primary production have also been documented. For example, a slow progressive decrease in the amount of DO below the metalimnion of Douglas Lake, Michigan, was reported over the 1911–1964 period (Bazin and Saunders 1971), but in the absence of indepen-

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dent measures of primary production. Deterioration of the hypolimnetic DO resources of Lake Washington, Washington from cultural eutrophication (municipal wastewater) was reported by Edmondson (1966) from analysis of temporally limited data. However, subsequent improvements in the lake, driven by reductions in external nutrient loading over a 5-yr interval (Edmondson and Lehman 1981), were documented in detail on the basis of a 21-yr record (1963–1984) of annual assessments of hypolimnetic DO depletion and were supported by 17 yr of annual primary production estimates (Lehman 1988). Rosa and Burns (1987) reported an increase in hypolimnetic DO depletion rates for the central basin of Lake Erie over the 1929–1974 period that was attributed to cultural eutrophication (e.g., a nearly sevenfold increase in external phosphorus loading over the 1900–1970 interval).

It is valuable to partition hypolimnetic DO consumption rates according to demands exerted in the water column (WOD) and by surficial ($SOD_s$) versus deeper sediments ($SOD_d$; DiToro 2001) to support evaluations of changes in AHOD induced in a single system by changes in productivity. Exertions by the first two of these oxygen sinks reflect decomposition of recently deposited organic material. These sinks might, in certain deep systems of modest productivity, be adequate to decompose all (i.e., $SOD_d \approx 0$) but the recalcitrant fraction of the organics deposited from the trophogenic zone. However, in shallower productive systems, deposition inputs are greater than can be satisfied by WOD and $SOD_s$, resulting in accumulation of decomposable sediment and exertion of $SOD_d$ (e.g., oxidation of reduced by-products of anaerobic decomposition diffusing upward through the sediments; Berner 1980; Westrich and Berner 1984; DiToro 2001). Nearly contemporaneous responses to changes in primary production can be anticipated for the WOD and $SOD_s$ components of AHOD. However, substantial delays are to be expected where $SOD_d$ is important, timing that is regulated by the slower processes inherent in sediment diagenesis as the sediments approach a new steady state consistent with a new flux rate of depositing organic material (DiToro 2001).

In this paper, we document the response of the hypolimnetic oxygen resources of an urban hypereutrophic lake, Onondaga Lake, New York, to an abrupt decrease in organic carbon deposition through AHOD calculations for 23 yr of a 25-yr period. Particular attention is given to calculation protocols for AHOD, including year-specific adjustments for vertical mixing inputs of DO and interannual variations in hypolimnetic temperatures. The extent to which the documented changes in AHOD match changes in organic matter deposition and primary production is evaluated. The consistency of the time course of the change in AHOD with regulation by sediment diagenesis is demonstrated and evaluated by an available system-specific model of sediment organic carbon diagenesis.

## Methods

*Site description*—Onondaga Lake is an alkaline, hard-water, dimictic system located north of the City of Syracuse, New York (43°6′54″N, 76°14′34″W). The lake has a surface area of 12.0 km², a volume of $1.31 \times 10^8$ m³, a mean depth of 10.9 m, and a maximum depth of ~19.5 m. The lake flushes about four times a year on a completely mixed basis (Effler 1996) and thus responds rapidly to changes in external loading (Doerr et al. 1994). Ice cover is established in most years, although duration varies greatly; the average and standard deviation for the 1988–2002 interval was 55 ± 24 d (K. M. Stewart unpubl.).

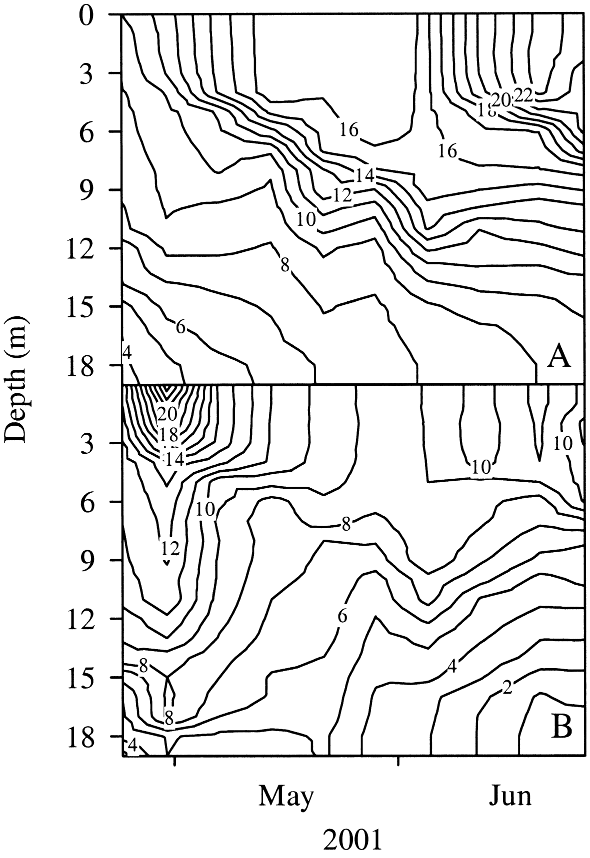

Fig. 1. Temperature and dissolved oxygen (DO) distributions in Onondaga Lake for the interval of the 2001 AHOD calculation: (A) isotherms (°C) and (B) isopleths of DO (mg $L^{-1}$).

Before European settlement in the late 1700s, Onondaga Lake was oligo–mesotrophic (Rowell 1996). The lake has been severely degraded because of inputs of domestic and industrial wastes that accompanied development and urbanization in the watershed (Effler 1996). The Onondaga County Metropolitan Sewage Treatment Plant (Metro) contributes ~20% of the lake's inflow and ~85% of the effective (i.e., can support phytoplankton growth) phosphorus (P) load (Effler et al. 2002) on an annual average basis. Metro's P load causes the lake to be hypereutrophic, which is manifested in the lake's degraded oxygen resources. Oxygen is depleted rapidly from the hypolimnion after the onset of thermal stratification (Fig. 1A,B). Substantial depletion occurs in spring (Fig. 1B) before strong stratification develops (Fig. 1A). Oversaturated DO levels occur commonly in the epilimnion during spring, associated with phytoplankton blooms (Effler 1996). Reduced by-products of anaerobic metabolism subsequently accumulate in the hypolimnion (Gelda et al. 1995).

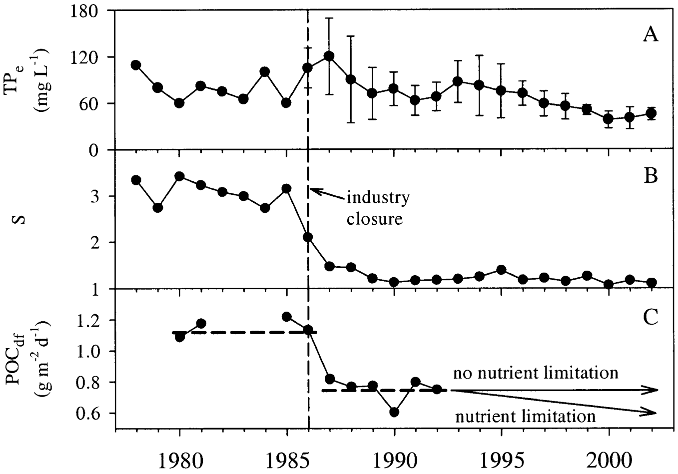

Fig. 2. Time series of summer average values of indicators and drivers of trophic state in Onondaga Lake, 1978–2002: (A) $TP_e$, mean ± 1 SD starting in 1986 (modified from Effler et al. 2005); 1978–1985 data from Onondaga County, 1986–2002 data from authors; (B) *S* (modified from Effler and Matthews 2003); and (C) $POC_{df}$ (from Effler et al. 2001). Dashed vertical line identifies closure of soda ash facility in 1986.

These by-products are oxidized during the fall mixing period, causing severe depletion of DO (e.g., DO $\leq$ 5 mg $L^{-1}$) in the upper waters (Gelda and Auer 1996).

Onondaga Lake is P limited, in that this is the nutrient present in the lowest concentrations relative to the needs of phytoplankton (Effler 1996). However, despite a 30-fold reduction in Metro's P load since the early 1970s (Effler et al. 2005), the lake was described as nearly nutrient saturated through the early 1990s (Connors et al. 1996). Summer average epilimnetic TP concentrations ($TP_e$) continue to exceed 50 $\mu$g $L^{-1}$ in most years (Fig. 2A). Further reductions in external loading of P will occur through mandated treatment upgrades at Metro as part of a rehabilitation program aimed at ameliorating the effects of this discharge (Matthews et al. 2001).

The primary industrial polluter of Onondaga Lake was a soda ash ($Na_2CO_3$) manufacturer that operated on the western shore of the lake from 1884 until 1986. The manufacturing process produced 1.5 kg of ionic ($Cl^-$, $Na^+$, and $Ca^{2+}$) waste for each kilogram of product. The lake was used as a source of cooling water and for disposal of the ionic waste. The facility discharged $>1.0 \times 10^6$ metric tons of ionic waste into the lake annually during the 1940–1986 interval, causing the lake to be unusually saline (Effler and Matthews 2003); $[Ca^{2+}]$ was usually $\geq$500 mg $L^{-1}$ (Effler 1996). Annual average salinity (*S*) decreased precipitously after closure of the facility, from ~3.1 in 1985 to 1.2 in 1989 (Fig. 2B). This 61% decrease in *S* was accompanied by a 65% decrease in $[Ca^{2+}]$ (Effler et al. 2001). The high $[Ca^{2+}]$ promoted coagulation (Weilenmann et al. 1989) and thus increased deposition losses of particles (including phytoplankton) from the trophogenic layers (Effler et al. 2001). The downward flux of particulate organic carbon ($POC_{df}$, g $m^{-2}$ $d^{-1}$) decreased abruptly by 37% following closure of the soda ash facility (Fig. 2C). The leading explanation for the decrease in $POC_{df}$ is reduced coagulation and rate of deposition of phytoplankton associated with the decreased $Ca^{2+}$ concentration (Effler et al. 2001). Under the nutrient-saturated conditions that prevailed before closure of the facility (e.g., Field 1980), the enhancement of phytoplankton deposition from elevated $Ca^{2+}$ levels fostered increased primary production in the lake (Effler et al. 2001). In addition, this facility's ionic discharge caused chemical stratification in the lake and in some years prevented complete spring turnover (Effler and Matthews 2003).

Closure of the soda ash facility caused substantial changes in the composition of the phytoplankton community of Onondaga Lake. In the decade before closure (1978–1986), the community was characterized by dominance of diatoms and cryptomonads during the spring and chlorococealean green algae during summer (Sze 1980; Effler 1996). Starting in 1987, nuisance filamentous cyanobacteria replaced chlorococealean green algae as the dominant form during summer, driven by selective feeding by large daphnids (Siegfried et al. 1996). These native salinity-intolerant, efficient-grazing daphnids were absent from the lake before 1987 because of high salinity levels (Siegfried et al. 1996). However, diatoms and cryptomonads have remained dominant during spring, although the spring diatom blooms and the frequency of their occurrence in summer and fall have diminished (Effler 1996).

*Monitoring*—Onondaga Lake was monitored at its deepest location (~19.5 m) over the April–July interval of 1978–1982 and 1985–2002. This site is generally representative of lakewide conditions (Effler 1996). Monitoring was conducted two to three times per week in 1978, 1980, 1981, 1987, and 1989 and weekly in the other years. Field measurements of DO and temperature (*T*) were made at 1-m depth intervals with calibrated probes between 0900 and 1000 h, when daily average DO concentrations are approached in the upper waters (Gelda and Effler 2002*b*). Before 1991, DO measurements were made with a YSI (model 54) DO meter, and temperature measurements were made with a Montedoro-Whitney (model TC-5C) underwater thermistor. During the 1991–2000 interval, DO and *T* profiles were collected with a Hydrolab Surveyor 3, and in 2001 and 2002, measurements were made with a YSI 6562 sonde attached to a robotic monitoring platform (RUSS, Apprise Technologies).

*Data analysis*—The average upper bound of the hypolimnion was determined to be 10.5 m on the basis of *T* and DO profiles. The volume-weighted DO concentration and total DO mass in the hypolimnion were calculated from each profile and the volumes of corresponding 1-m layers (Wetzel and Likens 2000) from the hypsographic data presented by Effler (1996). Rates of areal hypolimnetic oxygen depletion ($AHOD_{obs}$, g $m^{-2}$ $d^{-1}$) were calculated from the slopes (g $d^{-1}$) of hypolimnetic DO mass versus time, during the period of near linearity, divided by the area of the upper bound of the hypolimnion ($6.75 \times 10^6$ $m^2$). $AHOD_{obs}$ was adjusted for two factors: (1) vertical mixing inputs of DO from overlying layers into the hypolimnion and (2) temperature of the hypolimnion. Depletion rates for 1978–1981 were presented previously by Effler et al. (1986) but were not adjusted for these factors.

Downward fluxes of DO into the hypolimnion ($\mathrm{DO_{flux}}$, g $\mathrm{m^{-2}\ d^{-1}}$) were estimated for each sampling interval as the product of the vertical heat exchange coefficient ($v_t$, m $\mathrm{d^{-1}}$) and the DO concentration difference between the epilimnion and hypolimnion ($\mathrm{DO_e} - \mathrm{DO_h}$, mg $\mathrm{L^{-1}}$).

$$\mathrm{DO_{flux}} = v_t(\mathrm{DO_e} - \mathrm{DO_h})$$

Values of $v_t$ were estimated according to Chapra (1997),

$$v_t = \frac{V_\mathrm{h}}{A_t t_\mathrm{s}} \ln \frac{T_\mathrm{h,i} - \overline{T}_\mathrm{e}}{T_\mathrm{h,s} - \overline{T}_\mathrm{e}} \tag{2}$$

where $V_\mathrm{h}$ ($\mathrm{m^3}$) is the volume of the hypolimnion, $A_t$ ($\mathrm{m^2}$) is the area of the upper bound of the hypolimnion, $t_\mathrm{s}$ is the calculation interval (days), $\overline{T}_\mathrm{e}$ is the average volume-weighted temperature of the epilimnion over the calculation interval, and $T_\mathrm{h,i}$ and $T_\mathrm{h,s}$ are the volume-weighted temperatures of the hypolimnion at the beginning and end of the calculation interval, respectively. Values of $\mathrm{DO_{flux}}$ for individual sampling intervals were summed and added to $\mathrm{AHOD_{obs}}$ to obtain $\mathrm{AHOD_{vm}}$, a depletion rate adjusted for vertical mixing inputs.

This two-layer approach to accommodate vertical mixing (e.g., Chapra 1997) is conceptually consistent with the constant dimensions of the hypolimnion invoked in AHOD calculations (Wetzel and Likens 2000). An alternative approach instead considers ''local'' vertical mixing conditions at the depth(s) limiting vertical transport (e.g., depths of maximum density gradients; Jassby and Powell 1975). Accordingly, downward flux is quantified by (e.g., Wodka et al. 1983),

$$\mathrm{DO_{flux}} = K_z \times \frac{\Delta\mathrm{DO}}{\Delta z} \tag{3}$$

where $K_z$ ($\mathrm{m^2\ d^{-1}}$) is the thermal diffusivity coefficient at depth $z$ and $\Delta\mathrm{DO}/\Delta z$ is the local vertical DO gradient (g $\mathrm{m^{-4}}$). Values of $K_z$ are calculated for multiple depths according to the following expression, referred to as the flux gradient method (Jassby and Powell 1975).

$$K_z = \frac{H}{\rho c \dfrac{\Delta T}{\Delta z}} \tag{4}$$

$H$ is the vertical heat flux (J $\mathrm{m^{-2}\ d^{-1}}$), $\rho$ is the density of water, $c$ is the specific heat capacity of water (J $\mathrm{g^{-1}\ {}^\circ C^{-1}}$), and $\Delta T/\Delta z$ is the local vertical $T$ gradient (°C $\mathrm{m^{-1}}$). Commonly, time-averaging procedures and expanded depth intervals are used (Jassby and Powell 1975; Wodka et al. 1983) to reduce ''noise'' in estimates. Temporal deviations in the depth limiting vertical transport from that established as the boundary for AHOD calculations, as encountered in Onondaga Lake (Fig. 1A), represent an inconsistency for application of this approach. Two versions of the flux gradient approach were considered here in preliminary analyses: application at the fixed boundary of the AHOD calculations and application at the depth of the maximum density gradient, arguably the position at which vertical transport is limited. Estimates of the contribution of DO flux to AHOD on the basis of the latter alternative generally approached (average difference of 5%) those from the two-layer approach. However, estimates calculated according to the vertical boundary of the AHOD calculation were much higher than those from the two-layer approach in a number of years (>20% in 4 yr, 9% on average). This reflects the varying depths of maximum density gradients often encountered in the lake in spring (Fig. 1A) when substantial hypolimnetic DO depletion is underway (Fig. 1B). On the basis of these observations, the above two-layer framework (Eqs. 1, 2) was adopted to represent the effects of vertical mixing on AHOD.

Values of $\mathrm{AHOD_{vm}}$ were normalized to 10°C (average $T_\mathrm{h}$ during the intervals of AHOD calculations was 9.4°C), to accommodate the effects of interannual differences in $T_\mathrm{h}$ on hypolimnetic metabolism, with the use of a modified Arrhenius expression (Chapra 1997).

$$\mathrm{AHOD_{10}} = \frac{\mathrm{AHOD}_T}{\theta^{T-10}} \tag{5}$$

$\mathrm{AHOD_{10}}$ and $\mathrm{AHOD}_T$ are values of AHOD at temperatures of 10°C and $T$°C, respectively, and $\theta$ is the temperature coefficient. A value of 1.0718 was used for the temperature coefficient $\theta$ ($Q_{10} = 2$; e.g., Burns 1995). Values of $\mathrm{AHOD_{obs}}$ adjusted for vertical mixing inputs and temperature effects are referred to as $\mathrm{AHOD_{adj}}$.

## Results

The time course of hypolimnetic oxygen depletion was highly linear in 21 of the 23 study years (Fig. 3). Coefficients of determination ($r^2$), obtained from least squares linear regression, exceeded 0.89 and 0.94 for 20 and 15 years, respectively (Table 1). The rate of oxygen depletion decreased modestly with the approach to complete hypolimnetic anoxia in some years (e.g., 1989, 1990, and 1995) and increased in others (e.g., 1998, 2000, and 2002). Inclusion of these nonlinearities was avoided in the determination of depletion rates. Depletion rates were not estimated for 1980 or 1993 because of low initial DO content and nonlinearities associated with the failure of complete spring turnover (Fig. 3C, N). The initial low oxygen content of the hypolimnion observed in 1978, 1979, 1980, 1986, 1993, and 1994 was a consequence of incomplete or abbreviated spring turnover.

Transport of DO from the upper layers into the hypolimnion is driven by both the magnitude of turbulent mixing and the attendant concentration gradient (expressed by the heat exchange coefficient and the DO concentration difference, respectively, in Eq. 1). Temporal details of these drivers and temperatures and DO concentrations embedded in these estimates are illustrated (Fig. 4) for the April–June interval of 1998. Epilimnetic and hypolimnetic temperatures increased in a generally progressive manner during the April–June interval, with the exception of epilimnetic cooling and pronounced hypolimnetic heating during the first week of June (Fig. 4A). The temperature difference between the epilimnion and hypolimnion decreased from 7.4°C on 1 June to 2.7°C on 8 June, suggesting an interval of substantial vertical mixing. This observation is consistent with wind speed data, which depict a period of high winds over the 3–6 June interval (Fig. 4B). During this period, winds were

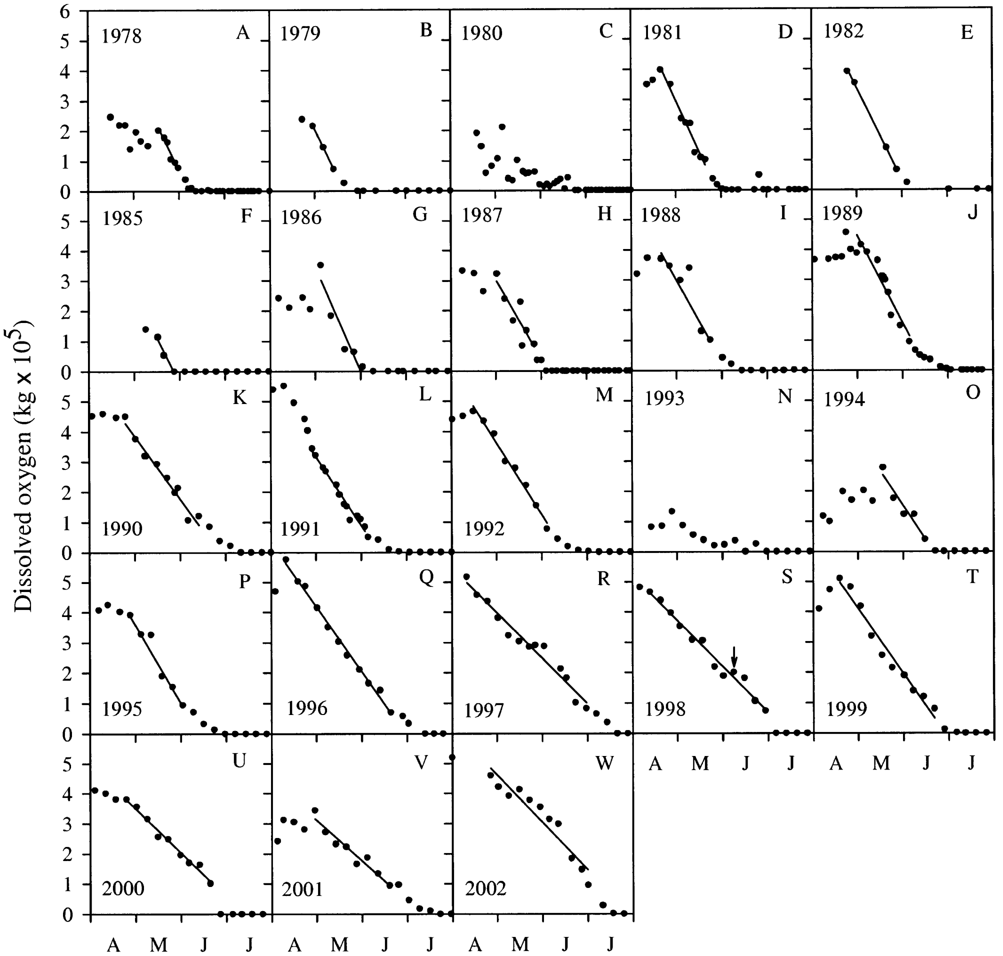

Fig. 3. Time series of the mass of DO in the hypolimnion of Onondaga Lake, 1978–2002. Regression lines used to calculate AHOD are included for reference.

generally along the lake's main axis, and hourly average wind speeds >8 m s$^{-1}$ were common. The calculated value of $v_t$ increased over two orders of magnitude during the interval (note log scale, Fig. 4C). Calculated values of $v_t$ were high during April, when the lake was weakly stratified, and again during the first week of June, which included the wind event. The high $v_t$ values calculated for early June were a result of wind-induced turbulent mixing. Hypolimnetic DO concentrations decreased progressively, except for a modest increase (5.1–5.5 mg L$^{-1}$) during the windy interval of early June (Fig. 4D). The DO difference between the epilimnion and hypolimnion generally increased after mid-May. The estimated transport of DO into the hypolimnion from the upper layers was greatest during April and early June (Fig. 4E). Vertical mixing inputs accounted for a major portion of AHOD$_{\mathrm{vm}}$ during these intervals (Fig. 4F). The adjustment was particularly important for the June wind event, as evidenced by the large difference between AHOD$_{\mathrm{obs}}$ ($-0.26$ g m$^{-2}$ d$^{-1}$) and AHOD$_{\mathrm{vm}}$ (1.42 g m$^{-2}$ d$^{-1}$) for that interval (Fig. 4F).

Time series of AHOD estimates for the 25-yr period depict the relative importance and temporal patterns of the vertical mixing and temperature adjustments (Fig. 5). Vertical mixing inputs increased AHOD$_{\mathrm{obs}}$ substantially for each of the study years, accounting for 15–37% of AHOD$_{\mathrm{vm}}$ (average 25%; Fig. 5A; Table 1). Temperature effects were relatively less important, resulting in increases and decreases to AHOD$_{\mathrm{vm}}$ (Fig. 5B) ranging from 0% to 17% (average 6%; Table 1). The average value of $T_{\mathrm{h}}$ for the intervals of AHOD calculations ranged from 7.6°C (1992) to 11.5°C (1978). The magnitude of the correction for vertical mixing (DO$_{\mathrm{flux}}$) appears to have decreased over the 1978–2002 interval (Fig. 5A). In order to test this hypothesis, the study years were divided a priori into two periods: 1978–1986, before, and 1987–2002, after closure of the soda ash facility. DO$_{\mathrm{flux}}$ decreased significantly ($t$-test; $p_8 = 0.02$) from the preclosure period (0.51 g m$^{-2}$ d$^{-1}$) to the postclosure period (0.35 g m$^{-2}$ d$^{-1}$). The primary reason for the decrease in DO$_{\mathrm{flux}}$ was lower DO differences (DO$_{\mathrm{e}}$ $-$ DO$_{\mathrm{h}}$) during the postclosure period, rather than lower levels of $v_t$ (Fig. 6). Distributions of $v_t$ for the two periods were similar (Fig. 6A), and median values were not significantly different (Mann–Whitney $U$-test, $p = 0.94$). Distributions of DO$_{\mathrm{e}}$ $-$ DO$_{\mathrm{h}}$, however, were shifted lower for the postclosure period (Fig. 6B), and median values were significantly different (Mann–Whitney $U$-test, $p < 0.001$). The shift in DO$_{\mathrm{e}}$ $-$ DO$_{\mathrm{h}}$ was due to both lower epi-

Table 1. Summary data for areal hypolimnetic oxygen deficits (AHOD) estimated annually over the 1978–2002 interval. *n*, Number of observations used for the regression; $\mathrm{AHOD_{obs}}$, uncorrected AHOD; $\mathrm{AHOD_{vm}}$, $\mathrm{AHOD_{obs}}$ adjusted for vertical mixing inputs; $\mathrm{AHOD_{adj}}$, $\mathrm{AHOD_{vm}}$ normalized for temperature; % vm, percent increase between $\mathrm{AHOD_{obs}}$ and $\mathrm{AHOD_{vm}}$; % t, percent change between $\mathrm{AHOD_{vm}}$ and $\mathrm{AHOD_{adj}}$.

| Year | $n$ | $r^2$ | $\mathrm{AHOD_{obs}}$ (g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$) | $\mathrm{AHOD_{vm}}$ (g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$) | $\mathrm{AHOD_{adj}}$ (g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$) | % vm | % t |
|---|---|---|---|---|---|---|---|
| 1978 | 6 | 0.93 | 1.53 | 2.25 | 2.04 | 32 | 9 |
| 1979 | 3 | 0.99 | 1.52 | 2.00 | 2.20 | 24 | 10 |
| 1981 | 8 | 0.96 | 1.59 | 2.26 | 2.35 | 30 | 4 |
| 1982 | 4 | 0.99 | 1.48 | 1.81 | 1.87 | 18 | 3 |
| 1985 | 3 | 0.97 | 1.49 | 1.99 | 1.92 | 25 | 4 |
| 1986 | 5 | 0.90 | 1.68 | 2.05 | 2.31 | 18 | 13 |
| 1987 | 7 | 0.75 | 1.29 | 1.86 | 1.94 | 31 | 4 |
| 1988 | 5 | 0.98 | 1.32 | 1.58 | 1.80 | 16 | 14 |
| 1989 | 11 | 0.89 | 1.41 | 1.72 | 1.81 | 18 | 5 |
| 1990 | 9 | 0.97 | 1.02 | 1.52 | 1.50 | 33 | 2 |
| 1991 | 12 | 0.97 | 1.12 | 1.57 | 1.57 | 29 | 0 |
| 1992 | 8 | 0.99 | 1.18 | 1.39 | 1.62 | 15 | 17 |
| 1994 | 5 | 0.91 | 1.12 | 1.66 | 1.62 | 33 | 2 |
| 1995 | 5 | 0.99 | 1.26 | 1.69 | 1.71 | 25 | 1 |
| 1996 | 11 | 0.99 | 1.05 | 1.31 | 1.51 | 20 | 15 |
| 1997 | 13 | 0.96 | 0.73 | 1.15 | 1.17 | 37 | 2 |
| 1998 | 12 | 0.98 | 0.74 | 1.10 | 1.06 | 33 | 3 |
| 1999 | 10 | 0.97 | 1.05 | 1.23 | 1.31 | 15 | 7 |
| 2000 | 9 | 0.98 | 0.72 | 0.97 | 1.03 | 26 | 6 |
| 2001 | 8 | 0.94 | 0.66 | 0.94 | 1.01 | 30 | 7 |
| 2002 | 11 | 0.91 | 0.77 | 0.93 | 0.86 | 17 | 8 |

limnetic DO concentrations and higher hypolimnetic DO concentrations during the postclosure interval (Fig. 6C,D). Values of DO percent saturation for the lake's upper waters were significantly higher during the preclosure period (Fig. 6C; Mann–Whitney *U*-test, $p < 0.001$) and hypolimnetic DO concentrations were significantly higher during the postclosure period (Fig. 6D; *t*-test; $p_{45} < 0.001$).

Hypolimnetic oxygen depletion rates have decreased in a generally progressive fashion since closure of the soda ash facility in 1986 (Fig. 5). The decreasing trend is manifested with ($\mathrm{AHOD_{adj}}$) or without ($\mathrm{AHOD_{obs}}$) adjustments for vertical mixing and temperature effects (Fig. 5). $\mathrm{AHOD_{adj}}$ decreased at an average rate of 0.07 ± 0.02 g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$ (95% CI) per year over the 1986–2002 interval, as determined by linear regression ($r^2 = 0.84$, $p_{20} < 0.001$). Alternatively, these data can be grouped according to three time periods: (1) 1978–1986, preclosure conditions, (2) 1987–1996, a transition interval, and (3) 1997–2002, an interval of yet lower and more uniform values (Fig. 5B). ANOVA followed by individual contrasts revealed that means for the three time periods were significantly different from one another ($p_2 < 0.001$). $\mathrm{AHOD_{adj}}$ decreased 49% from the 1978–1986 interval (mean 2.12 ± 0.21 g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$) to the 1997–2002 interval (mean 1.08 ± 0.26 g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$). The values of AHOD presented here for Onondaga Lake are among the highest reported in the literature. The recent lower values of this long-term record continue to exceed, by a wide margin, limits for eutrophy of 0.55 and 0.33 g $\mathrm{m^{-2}}$ $\mathrm{d^{-1}}$ proposed by Mortimer (1942) and Hutchinson (1957), respectively.

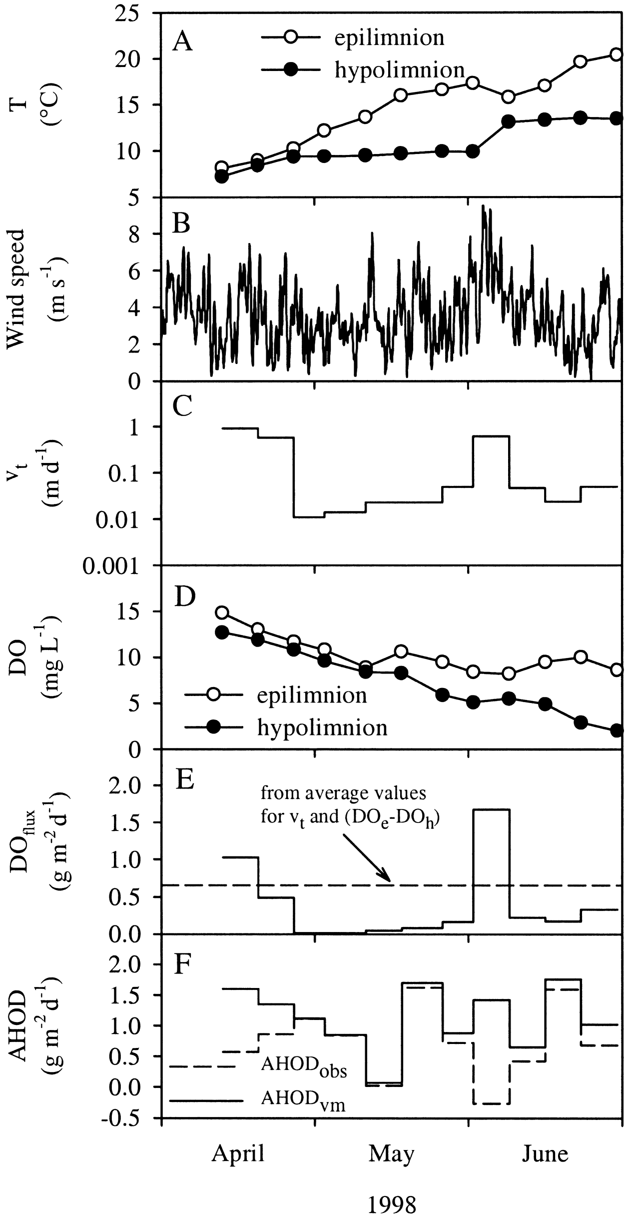

Fig. 4. Time series of parameter values for Onondaga Lake over the April–June interval of 1998: (A) volume-weighted temperatures of the epilimnion and hypolimnion; (B) wind speed, presented as an 8-h moving average; (C) $v_t$; (D) volume-weighted DO concentrations of the epilimnion and hypolimnion; (E) $\mathrm{DO_{flux}}$; and (F) AHOD.

Decreasing rates of hypolimnetic oxygen depletion over the 1978–2002 interval (Fig. 5; Table 1) have resulted in improvements in the lake's oxygen resources. For example, the onset of complete hypolimnetic anoxia has shifted to later in the year by >1 month since closure of the soda ash facility in 1986. The average date of complete hypolimnetic anoxia for the preclosure interval (1978–1986) was 2 June, compared with 11 July for 1997–2002. Despite this improvement, the entire hypolimnion (11–19 m) was devoid of ox-

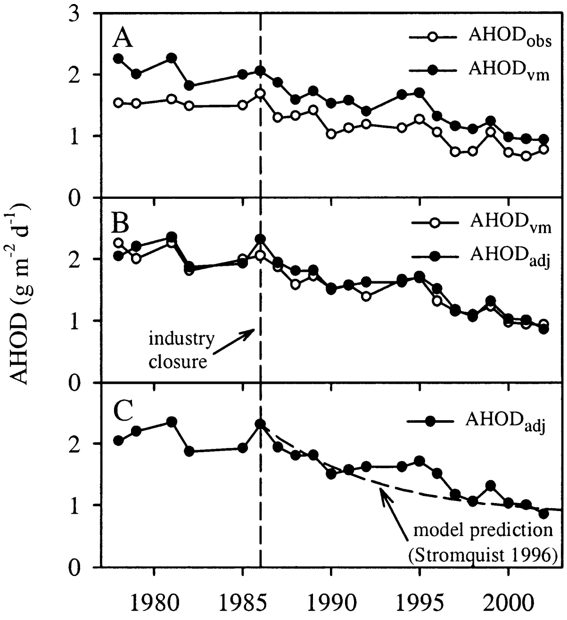

Fig. 5. Time series of annual AHOD values for Onondaga Lake, 1978–2002: (A) with (AHOD$_{vm}$) and without (AHOD$_{obs}$) adjustments for vertical mixing, (B) with (AHOD$_{adj}$) and without (AHOD$_{vm}$) adjustments for hypolimnetic temperature, and (C) AHOD$_{adj}$ and SOD from model predictions. Dashed vertical line identifies closure of soda ash facility in 1986.

ygen by the end of July in each of the monitored years (Fig. 3).

## Discussion

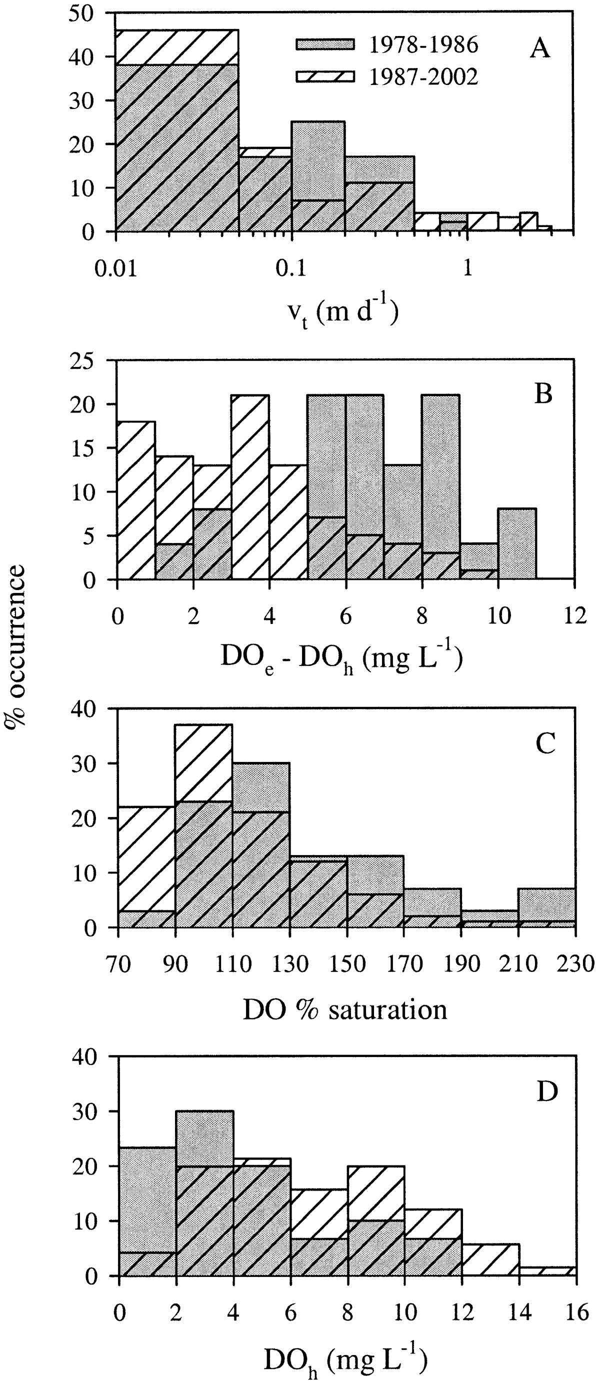

Fig. 6 Distributions of observations during intervals of AHOD calculations for study years before (1978–1986) and after (1987–2002) closure of the soda ash facility: (A) $v_t$, (B) DO$_e$ − DO$_h$, (C) DO percent saturation for the upper waters, and (D) DO$_h$.

*Adjustments in AHOD calculations and other potential effects*—A number of factors other than the magnitudes of primary production and organic matter deposition can potentially influence the rate of hypolimnetic DO depletion. If not considered and quantified, these factors could compromise the linkage between AHOD and metabolism of the trophogenic zone and the record presented here for Onondaga Lake. The nine factors identified by Burns (1995) as potentially influencing depletion rates guided our critical evaluation of this record: (1) downward transport of oxygen; (2) temperature effects on oxygen uptake; (3) effects of ambient DO concentrations; (4) relative roles of WOD, SOD$_s$, and SOD$_d$ and effect of hypolimnion thickness; (5) delayed decomposition of organic matter; (6) variations in the fraction of production reaching the hypolimnion; (7) within-season variation in depletion rates; (8) photosynthesis in the hypolimnion; and (9) effects of inflows. The first two of these factors have been quantified for Onondaga Lake in the presented calculations of AHOD$_{adj}$. The other seven were critically evaluated within the context of the observations presented here and available system-specific limnologic information. Three of the factors are coupled to the stratification regime of the lake: vertical mixing, temperature of the hypolimnion, and dimensions of the hypolimnion. These features are widely observed to vary year-to-year in response to natural variations in meteorological drivers, as demonstrated specifically for Onondaga Lake by long-term simulation with a validated mechanistic hydrothermal stratification model (Owens and Effler 1989).

Adjustments in AHOD for vertical mixing were found to be important for Onondaga Lake (Table 1; Fig. 5A). Furthermore, the substantial difference in the magnitude of the adjustment between years establishes the need to represent year-specific conditions in the calculations. This should be expected to be the case for other highly productive systems with high hypolimnetic depletion rates. These systems will require the largest adjustments in absolute (but not necessarily relative) terms (i.e., high $DO_{flux}$ values) for inputs driven by vertical mixing. There are two contributing features. First, $v_t$ values are generally systematically higher early in the stratification interval, associated with weak water column stability (Wodka et al. 1983; Chapra 1997). Thus, hypolimnia of productive lakes that experience DO depletion before the onset of strong thermal stratification will also likely receive substantial DO inputs as a result of intense vertical mixing during this period of weak stability (Fig. 4C,D). Second, the vertical DO gradient tends to be greater in highly productive systems associated with higher (e.g., supersaturated) epilimnetic oxygen concentrations (Fig. 6C) driven by elevated photosynthetic activity and with lower hypolimnetic oxygen concentrations driven by decomposition of organic matter (Fig. 6D). The higher degree of oversaturation for epilimnetic DO concentrations in Onondaga Lake before closure of the industry (Fig. 6C) has been attributed to higher levels of primary production in that interval (Effler 1996). The shift to lower $DO_{flux}$ as primary production decreases, which was observed in Onondaga Lake, should be expected to be recurring. Although the change in Onondaga to date is attributable largely to the decrease in the vertical DO gradient (Fig. 6), further decreases in production are expected to also be accompanied by a shift to lower $v_t$ as a result of the inclusion of more stably stratified intervals (Wodka et al. 1983; Owens and Effler 1989) within the period of the AHOD calculation.

Potential issues for the vertical mixing adjustments are related to time segmentation, the form of the calculations adopted, and the reliability of the supporting measurements. The episodic nature of wind events and their importance to the vertical transport of DO (Fig. 4B,C,E), together with the nonlinear nature of this coupling (Eq. 2), results in a dependence of $DO_{flux}$ on the interval of the adjustment calculation. For example, if average values for the April–June interval of 1998 were used for $v_t$ ($0.215\ m\ d^{-1}$) and the DO gradient ($3.0\ mg\ L^{-1}$), the resulting $DO_{flux}$ would be $0.65\ g\ m^{-2}\ d^{-1}$, nearly twice the flux estimated from weekly calculations ($0.36\ g\ m^{-2}\ d^{-1}$). More frequent measurements (e.g., daily) could further alter best estimates of $DO_{flux}$. Thus, monitoring frequency represents a largely inescapable source of error in $AHOD_{adj}$, although the magnitude is expected to decrease with the use of shorter time segments.

Despite acknowledgments of the entry of oxygen from overlying layers and the potential importance of this source in AHOD or VHOD calculations (Burns 1995; Chapra 1997), actual implementation of related adjustments have been rare. Lehman (1988) reported an adjustment of $<5\%$ in hypolimnetic DO depletion rates over the May–October interval in the much deeper (maximum and mean depths of 65 and 33 m) and less productive Lake Washington, in which the hypolimnion remained oxic. In contrast, Stauffer (1987) reported substantial adjustments for the shallower and more eutrophic Wisconsin lakes Mendota (mean depth 12.7 m; 34% adjustment) and Delavan (mean depth 6.4 m; 43% adjustment) for the May–July interval of 1972. Rosa and Burns (1987) reported an average adjustment of 12% for DO inputs driven by vertical mixing for Lake Erie's central basin for 18 yr of the 1929–1980 interval, with substantial year-to-year differences (range 0–22%).

Accurate $T$ profiles might not always be representative of the time scale of the calculations if collected during substantial oscillations caused by internal waves. This is not expected to be a noteworthy source of uncertainty in the Onondaga Lake results because profiles were collected at a position not far from the probable node for such oscillations. The form of the vertical mixing adjustment used here (Eqs. 1, 2) is similar to those used by Rosa and Burns (1987) and recommended by Chapra (1997). Accordingly, representation of the lake as two completely mixed layers separated by an infinitely sharp metalimnion artificially eliminates the potential effects of $T$ and DO gradients within the epilimnion or hypolimnion. Actual vertical patterns of both $T$ and DO commonly deviate from these idealizations in Onondaga (Fig. 1) and other lakes. However, the approximate convergence of $DO_{flux}$ estimates from the two-layer approach with those from the flux gradient approach (with time variation of the depth at which vertical transport is limited) serves to support the appropriateness of the general magnitude of the presented AHOD adjustments (Fig. 5A). In addition, the consistency of the two-layer framework with the fixed hypolimnetic volume of the AHOD calculations makes it conceptually attractive.

Despite widespread recognition that DO depletion rates should be adjusted for differences in hypolimnetic temperatures (Charlton 1980*a*; Burns 1995; Chapra 1997), examples of such corrections in the literature are also rare. The magnitude of this adjustment for Onondaga Lake (0–17%, average 6%) was remarkably similar to that calculated for Lake Erie's central basin (0–19%, average 8%; Rosa and Burns 1987). An analysis was conducted to investigate the sensitivity of the temperature adjustment to the range of $\theta$ values (1.04–1.13) reported by Zison et al. (1978). The average adjustment to AHOD for the 1978–2002 interval was 4% with $\theta = 1.04$ and 13% with $\theta = 1.13$, indicating only a modest degree of sensitivity to the selection of the temperature coefficient $\theta$ relative to the effects of vertical mixing. Specification of different reference temperatures represents a potential source of differences in AHOD for systems in which a temperature adjustment is made.

Conflicting evidence exists regarding the dependence of DO depletion rates on ambient DO concentrations (Burns 1995). In multilake studies of oxygen depletion, Lasenby (1975) and Cornett and Rigler (1984) observed that hypolimnetic DO concentrations decreased linearly with time, suggesting that the process of hypolimnetic oxygen depletion is independent of the ambient DO concentration. However, evidence also exists that DO concentrations $<2$–$3\ mg\ L^{-1}$ cause lower depletion rates (Cornett and Rigler 1984; Campbell and Rigler 1986). Burns (1995) recommends that hypolimnetic oxygen depletion rates should not be calculated for hypolimnia with DO concentrations $<2$–$3\ mg\ L^{-1}$. Although annual DO depletion rates for Onondaga Lake were generally highly linear, the rate of depletion decreased with the approach to complete hypolimnetic anoxia in 1989, 1990, and 1995 (Fig. 3), deviations that remain unexplained.

Thus, observations in which the volume-weighted DO concentration of the hypolimnion was $<3$ mg $L^{-1}$ were usually avoided in the calculation of AHOD (1985 and 1986 are exceptions; Fig. 3F,G). Trimbee and Prepas (1988) found that AHOD for a partially meromictic lake was positively correlated with the magnitude of the DO pool at the onset of summer thermal stratification. In contrast, AHOD for Onondaga Lake was negatively correlated with the initial DO mass of the hypolimnion (linear regression, $p_{20} = 0.02$). However, this is an artifact of the frequent failure of complete spring turnover coincident with higher DO depletion rates during the interval before closure of the industry (1978–1986; Fig. 3).

Concerns regarding the location of DO consumption within the hypolimnion and its thickness (Burns 1995) are related largely to the effects of different decomposition rates for WOD and SOD. Some authors reported that decomposition of organic material occurs more efficiently in the water column than at the sediment–water interface (Cornett and Rigler 1979; Charlton 1980*b*). This may contribute to the observation of Cornett and Rigler (1979) that lakes with thick hypolimnia have relatively high DO depletion rates, which is more of a concern in cross-sectional studies with lakes of widely different depths or when tracking a single system in which large differences in the volume of the hypolimnion occur one year to the next. It is not a noteworthy issue for Onondaga Lake because the thickness of the hypolimnion exhibited only modest variation during the 1978–2002 interval (mean 9.8 m, C.V. 0.14). Furthermore, oxygen depletion was manifested throughout the designated vertical limits of the hypolimnion in all the years included in this analysis.

Gelda et al. (1995) reported SOD was the dominant DO sink for the hypolimnion of Onondaga Lake in the late 1980s, responsible for 72–100% of AHOD. They reported good closure between laboratory determinations of SOD ($=\mathrm{SOD}_s + \mathrm{SOD}_d$) from sediment cores with intact sediment–water interfaces and calculations from accumulation rates of oxygen-demanding reduced species following the onset of anoxia. A mechanistic mass balance model for DO that incorporated these results performed well in simulating hypolimnetic DO depletion in the lake (Gelda and Auer 1996). The dominance of SOD in Onondaga is also consistent with the findings of Cornett and Rigler (1987), who reported that ~60–75% of the hypolimnetic DO consumption in shallow productive lakes included in their study occurred in the sediments. The progressive, rather than abrupt, decrease in AHOD (Fig. 5B) following the abrupt decrease in $\mathrm{POC}_{df}$ (Fig. 2C) is consistent with the dominance of SOD, reflecting a ''memory'' of the earlier higher rates of organic deposition (DiToro 2001). This delayed character needs to be taken into account when considering the AHOD response (Burns 1995) to such a systematic change in the primary driver of hypolimnetic oxygen depletion (subsequently).

Changes in phytoplankton composition can affect the fraction of produced biomass that settles into the hypolimnion (Burns 1995). In particular, colonial cyanobacteria (including filamentous forms), which reemerged in Onondaga Lake (Effler 1996) following closure of the industry (Siegfried et al. 1996), often have lower settling velocities (Burns and Rosa 1980) and thus are more likely to undergo substantial decomposition in the epilimnion than other forms of phytoplankton. However, colonial cyanobacteria do not become important in Onondaga Lake until midsummer (Effler 1996; Matthews et al. 2001), after the period of the AHOD calculation (Fig. 3). Furthermore, no substantial shift in the seasonality of $\mathrm{POC}_{df}$ has been observed since the reemergence of colonial cyanobacteria as a prominent component of the phytoplankton assemblage (Effler et al. 2001), suggesting the absence of major shifts in settling velocity. This could be associated in part with the nitrogen-saturated state of this assemblage (Matthews et al. 2001; i.e., gas vacuoles absent).

Lehman (1988) suggested that an increase in the depth interval of primary production, along with a reduction in the extent of decomposition in the upper layers, might have contributed to the reported shift in the ratio of hypolimnetic DO depletion to primary production in Lake Washington following the major reductions in external loading of nutrients. Despite systematic improvements in light penetration (Perkins and Effler 1996) that resulted from increased zooplankton grazing following the closure of the industry (Siegfried et al. 1996), the photic zone (1% of photosynthetically active radiation penetrating the surface) only rarely has reached the specified upper boundary of the hypolimnion. Furthermore, no manifestations of photosynthetic activity have been observed within the hypolimnion in time-intensive profiling of DO (Gelda and Effler 2002*a*). Thus, there is no noteworthy complication from photosynthetic inputs in the AHOD record presented here.

Potential shortcomings in AHOD estimates because of temporally limited observations, which could reflect short-term changes in metabolism in the trophogenic zone (Burns 1995), were avoided by performing calculations over almost the entire interval of depletion (Fig. 3). This approach is further supported for Onondaga Lake by the dominance of SOD, which has a time-integrated (i.e., more temporally uniform than WOD) effect on the water column. Finally, plunging inflows have occurred in the lake both before (Owens and Effler 1989) and after closure (Effler et al. 2002) of the soda ash facility associated with the industry's ionic waste. This phenomenon, manifested as an interflow, is not considered to substantively influence hypolimnetic DO depletion rates because interflows enter the lake at depths of $\leq 10$ m (i.e., above the hypolimnion; Effler et al. 2002) and are manifested during late summer and early fall, after the period of the AHOD calculation (Owens and Effler 1989; Effler et al. 2002). Furthermore, a mechanistic, two-layer mass balance model for DO in Onondaga Lake that did not accommodate inflows to the hypolimnion was able to simulate accurately the time course of hypolimnetic oxygen depletion (Gelda and Auer 1996).

*Closure of* $\mathrm{AHOD}_{adj}$ *calculations with related metrics and a sediment model*—Three forms of system-specific metabolic information are available to test the consistency of the presented temporal pattern of $\mathrm{AHOD}_{adj}$ and its linkages to changes in primary production and deposition of organic matter. First, reasonably comprehensive (two to three times per week) measurements of primary production were made over the spring to late summer interval of selected years before (1978; Field 1980) and after (2000–2002; Gelda and

Effler 2002*a*; Effler et al. in press) closure of the industry. This temporal coverage is rather modest compared with the detailed estimates of annual primary production for the 17 yr available to support interpretation of the long-term oxygen depletion data for Lake Washington (Lehman 1988).

In contrast, the availability of attendant $POC_{df}$ data, particularly bracketing the major perturbation (Fig. 2C), is rare, if not unique. The downward flux of POC is an acknowledged metric of primary production (Molongoski and Klug 1980; Kelly and Chynoweth 1981), and it is the link connecting metabolism between the trophogenic and tropholytic zones. The abrupt, steplike, decrease in $POC_{df}$ following industry closure has provided a rare opportunity to resolve and characterize the effects on hypolimnetic DO resources. Changes in drivers for other long-term investigations have been more gradual by comparison (Rosa and Burns 1987; Lehman 1988). The $POC_{df}$ data have two temporal limitations in evaluating the extent of closure with the $AHOD_{adj}$ estimates. First, these represent conditions for the productive April–October interval, rather than annual conditions. Second, the record is limited to a 12-yr interval, although the most critical portion with regards to the perturbation is included (Fig. 2C). The incomplete record before closure of the industry is not a noteworthy limitation because there is little question concerning the nutrient-saturated state of the lake over that interval (Field and Effler 1983). The lack of $POC_{df}$ data after 1992 is more problematic because the extent of nutrient limitation, and thus the time trajectory of $POC_{df}$, is less certain (Fig. 2C).

Finally, the system-specific carbon diagenesis model for the lake sediments (Stromquist 1996) supports an evaluation of the consistency of the temporal pattern of the $AHOD_{adj}$ response to the step decrease in $POC_{df}$. The model for Onondaga Lake partitions the organic carbon in the lake sediments into two labile fractions (2-G) and a refractory fraction, representing fractions of different composition and reactivity, as described by the G model of Berner (1980). Model coefficients were determined through laboratory experiments (Stromquist 1996). The model predicts a steady-state SOD from POC deposition according to Eq. 6,

$$\mathrm{SOD} = a \times \left( \sum_{j}^{m} f_{\mathrm{L}j} \right) \times \mathrm{POC}_{\mathrm{df}} \tag{6}$$

where $a$ is the stoichiometric coefficient to convert carbon to oxygen units ($a = 32/12$ g $O_2$ g $C^{-1}$) and $f_L$ is the fraction of labile organic carbon at the time of deposition ($0.40 \pm 0.17$), as determined by Stromquist (1996). A steady-state SOD value of 0.8 g $m^{-2}$ $d^{-1}$ is predicted (Eq. 6), assuming $POC_{df}$ has remained at 0.75 g $m^{-2}$ $d^{-1}$ since closure of the industry. The temporal response of the sediments in the approach to a new steady-state SOD following a decrease in $POC_{df}$ is represented by Eq. 7,

$$t_{f_{ss}} = \frac{-\ln(1 - f_{ss})}{\sum_{j}^{m} k_j} \tag{7}$$

where $k_j$ are organic carbon diagenesis coefficients for the fast ($k_1 = 0.7 \pm 0.6$ $yr^{-1}$) and slow ($k_2 = 0.01$ $yr^{-1}$) fractions of labile organic carbon, as determined by Stromquist (1996), and $f_{ss}$ is the fraction of the change in steady-state values reached in time $t_{f_{ss}}$. Operationally, the time to steady-state is often represented by $f_{ss} = 0.99$ (99% of steady-state SOD reached). With the use of the reported best estimates of the model coefficients (Stromquist 1996), the predicted $t_{f_{ss}}$ is 12 yr. An alternative estimate of $k_1$ was obtained here through calibration of the diagenesis model to match the trajectory of the reported $AHOD_{adj}$ (Fig. 5C), assuming SOD dominates AHOD (Gelda and Auer 1996). This estimate ($k_1 = 0.15$ $yr^{-1}$) corresponds to a slower temporal response, but it remains within the reported experimental bounds of uncertainty (0.10–1.3 $yr^{-1}$; Stromquist 1996) and is comparable with estimates from several other lakes (Berner 1980; Klump et al. 1989; Carignan and Lean 1991). The corresponding $t_{f_{ss}}$ value (30 yr) is also comparable to estimates from other lakes (Berner 1980; Klump et al. 1989; Carignan and Lean 1991). Accordingly, the AHOD and SOD have not fully reached steady-state following the reduction in $POC_{df}$, but rather ~90% of the steady-state value(s).

The delayed temporal character of the $AHOD_{adj}$ response (Fig. 5C) to the steplike decrease in $POC_{df}$ (Fig. 2C) is consistent with the dominant role of $SOD_d$ and the response of this areal process to such a decrease (DiToro 2001). This form of sediment response is a widely acknowledged problem for the recovery of culturally eutrophic systems (Larsen et al. 1981; Chapra and Canale 1991), whereby response is delayed by feedback from sediments deposited during earlier more productive years. The observed progression of $AHOD_{adj}$ since the abrupt decrease in $POC_{df}$ is tracked reasonably well by the simulated trajectory (Fig. 5C), generally supporting the delayed character of $AHOD_{adj}$ as attributable to regulation by sediment diagenesis. However, the possibility that the trajectory reflects somewhat more complicated dynamics in forcing conditions cannot be eliminated. For example, further decreases in $POC_{df}$ could have occurred beyond the time of reported measurements (Fig. 2C). Such decreases could have been driven by the observed additional decreases in P concentration in the productive layers (Fig. 2A) that resulted from further decreases in loading from Metro (Effler et al. 2005) by achieving some degree of nutrient limitation of phytoplankton growth (Fig. 2C). It is highly likely that such an effect would be modest compared with the abrupt reduction in $POC_{df}$ following closure of the industry. Connors et al. (1996) concluded that phytoplankton of the lake remained nearly nutrient saturated over the 1989–1992 interval on the basis of detailed P data and analyses with multiple kinetic frameworks. Distinctly lower $TP_e$ values than reported through 1992 were not observed until the late 1990s (Fig. 2A). The most recent observations of concentrations of TP in Onondaga Lake continue to exceed levels found to be essentially saturating in Green Bay, Lake Michigan (Auer et al. 1986). Regardless of this potential complication, it is clear that this $AHOD_{adj}$ time series has supported the general resolution of the effects of delayed response of the hypolimnetic oxygen resources of this productive lake associated with sediment diagenesis processes.

The temporal features of the response of Onondaga Lake's hypolimnetic oxygen resources stand in sharp contrast to those reported for Lake Washington after major reductions in nutrient loading. The decreases in hypolimnetic depletion rates in Lake Washington occurred nearly coincidently with the decrease in primary production (Lehman 1988), without substantial subsequent further (i.e., delayed) decreases. This indicates sediment feedback associated with earlier deposition inputs (i.e., deeper sediments) from the trophogenic zone was not an important DO sink for the lake's lower layers (e.g., $SOD_d \approx 0$). This suggests that oxygen demand from these inputs was satisfied annually through WOD or SOD exerted by the most recently deposited sediments (i.e., $SOD_s$). These different characteristics for Lake Washington are conceptually consistent with its greater depth, and thus greater opportunity for exertion of WOD, and the much lower level of primary production that prevailed when it was most eutrophic (e.g., <20% of daily average gross primary production reported for Onondaga; Lehman 1988; Effler et al. 2005).

A causal relationship between primary production and $AHOD_{adj}$ is predicated on the more direct linkages ($n = 2$) between primary production and $POC_{df}$ and between $POC_{df}$ and $AHOD_{adj}$. The 49% decrease observed for $AHOD_{adj}$ (Fig. 5B) compares reasonably well with the decrease reported for $POC_{df}$ (37%; Fig. 2C), particularly in light of uncertainties associated with these measures. In fact, percent decreases calculated from 95% confidence intervals (30%–65% for $AHOD_{adj}$, 22%–46% for $POC_{df}$) exhibit considerable overlap, suggesting that the decreases are not only coupled but also are approximately equal. The extent of closure might be better than indicated by the above comparisons, associated with the potential further decreases in $POC_{df}$ after 1992 (Fig. 2C) described previously. Assuming the same relative decrease in $POC_{df}$ over the 1992–2002 interval as observed for $TP_e$ (34%), the overall reduction in $POC_{df}$ from before closure of the industry to 2002 would be 50% (i.e., an additional 13% since 1992). Regardless of these considerations and related uncertainties, this closure analysis remains imperfect because of the differences in the monitoring coverage (within years and long term) for $POC_{df}$ and $AHOD_{adj}$.

The reported (Effler et al. 2005) decreases in primary production since closure of the industry are also generally consistent with the decrease in $AHOD_{adj}$, although the extent of this closure is less compelling because of the temporal limitations of the production measurements. The average daily gross primary production (9.6 g $O_2$ $m^{-2}$ $d^{-1}$) in 2002 was 32% lower than in 1978 (14.0 g $O_2$ $m^{-2}$ $d^{-1}$), over the mid-May to mid-August interval (Effler et al. 2005). The average for this interval observed in 2000 and 2001 (8.5 g $O_2$ $m^{-2}$ $d^{-1}$; results from the 2 yr combined to cover the interval) was 39% lower than in 1978 (Effler et al. 2005).

*Implications*—Estimates of AHOD for highly productive shallow lakes without adjustments for oxygen inputs from overlying layers could substantially underestimate DO depletion rates. Adjustments for the effect of vertical transport need to be conducted annually and for multiple time intervals during the DO depletion period to accommodate the effects of variability in meteorological drivers over long-term records. Although less important in Onondaga Lake, adjustments for interannual differences in hypolimnetic temperatures were noteworthy and are recommended for the analysis of long-term data sets and to support comparisons among systems.

The delayed response of $AHOD_{adj}$ reflects the importance of the $SOD_d$ component in this system and the inherently slower reactions of sediment diagenesis (DiToro 2001) compared with the response time of the overlying trophogenic zone to perturbations in inputs to those layers. The dominance of sediment–water exchange in regulating the hypolimnetic pools of various critical constituents prevails in many shallow eutrophic lakes. The time necessary to reach a new lower steady-state sediment flux is an important management issue where reductions in anthropogenic loading are under consideration. The $AHOD_{adj}$ record has provided a signature of the progression of diagenesis in Onondaga Lake and an excellent opportunity to support testing of a mechanistic sediment diagenesis model. However, the delayed nature of the AHOD response compromises it as a trophic state indicator for this lake over the interval that $SOD_d$ approaches a new steady state. Interestingly, $AHOD_{adj}$ remains a more reliable, albeit delayed, metric of trophogenic zone metabolism in this system than the widely adopted trophic state indicators of Chl *a* concentration and Secchi disc transparency. The abrupt changes in these two indicators observed with the closure of the industry have been driven largely by a coincident change in top-down pressure, rather than the reduction in primary production (Effler et al. 2005). The integrating character of $AHOD_{adj}$ continues to offer certain advantages in tracking long-term patterns in primary production.

An ongoing rehabilitation program of this lake will offer additional opportunities to test the coupling between primary production and AHOD in the future. Treatment upgrades will abruptly reduce phosphorus loads discharged by Metro in 2005 (~4.5-fold) and again in 2012 (an additional sixfold; i.e., 27-fold overall). These decreases should result in abrupt reductions in primary production in both cases and impart temporal signals of diagenesis-mediated decreases in AHOD. Quantitative coupling with trophogenic zone metabolism through these perturbations will benefit from continuation of the records of primary production and $POC_{df}$ measurements.

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