

Improved Modeling of Sediment Oxygen Kinetics and Fluxes in Lakes and Reservoirs

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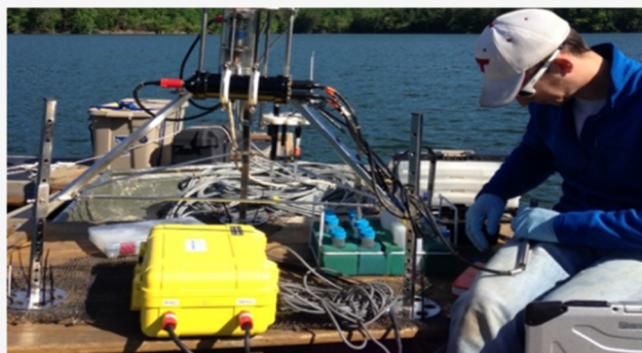


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ABSTRACT: To understand water quality degradation during hypoxia, we need to understand sediment oxygen fluxes, the main oxygen sink in shallow hypolimnia. Kinetic models, which integrate diffusion and consumption of dissolved oxygen (DO) in sediments, usually assume a downward flux of DO from the sediment–water interface (SWI) with a zero-flux condition at the lower boundary of the oxic sediment layer. In this paper, we separately account for the oxidation of an upward flux of reduced compounds by introducing a negative flux of DO as a lower boundary condition. Using in situ measurements in two lakes, kinetic models were fit to DO microprofiles using zero-order and first-order kinetics with both zero and non-zero lower boundary conditions. Based on visual inspection and goodness-of-fit criteria, the negative-flux lower boundary condition, $-0.25 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$, was found to more accurately describe DO consumption kinetics. Fitted zero-order rate constants ranged from 50 to 510 $\text{mg L}^{-1} \text{ d}^{-1}$, and first-order rate constants ranged from 60 to 400 d^{-1} , which agree well with prior laboratory studies. DO fluxes at the SWI calculated from the simulated profiles with the negative-flux lower boundary condition also showed better agreement with the observed DO fluxes than the simulated profiles with the zero-flux lower boundary condition.



1. INTRODUCTION

Hypoxia, often defined as dissolved oxygen (DO) $< 2 \text{ mg L}^{-1}$, commonly occurs in the deep waters of marine and freshwater systems during seasonal stratification.¹ In lakes and reservoirs, hypoxia usually leads to a lower redox potential in the sediments,² which can result in the reduction and dissolution of ferric and manganese oxides, decreasing their capacity to adsorb and retain nutrients. As a result, the concentration of nutrients (e.g., phosphorus and nitrogen) in the overlying water column increases,^{3–5} which may exacerbate blooms of nuisance algae and cyanobacteria.^{6–8} Algal and cyanobacterial blooms are significant concerns for lake and reservoir management because they stimulate eutrophication,⁹ complicate water treatment processes, and increase water treatment costs.¹⁰ To make matters worse, some algae and cyanobacteria can be toxic¹¹ (e.g., *Karenia brevis*), causing fish mortalities⁹ and restricting tourism in coastal areas.¹²

In the 1960s and 1970s, eutrophication stimulated by biologically available phosphorus was recognized as the primary cause of hypolimnetic hypoxia¹³ in lakes and reservoirs. However, it was later discovered that simply preventing the release of phosphorus from the sediment by artificial aeration or oxygenation^{10,14} did not eliminate hypolimnetic hypoxia as expected.^{15,16} In some artificially oxygenated lakes, hypoxia was unaffected or even worsened¹⁷ because DO was added to the water column but did not

penetrate into the sediment, where reduced substances (e.g., methane and ammonium) impacting hypolimnetic DO consumption are released.¹⁸ Hypolimnetic DO demand and corresponding hypoxia are also influenced by DO consumption in the water column resulting from various chemical reactions and biological processes,¹⁹ such as settling of organic matter.²⁰ To better understand the processes governing hypolimnetic DO consumption, more attention should be paid to DO consuming processes in upper lacustrine sediment.

Sediment oxygen flux (J_{O_2}) is usually the dominant sink for DO in the hypolimnion and usually comprises a majority of the DO demand in shallow water bodies. Processes on both sides of the sediment–water interface (SWI) influence J_{O_2} .²¹ On the water side, J_{O_2} is controlled by the presence of a diffusive boundary layer (DBL) immediately above the SWI. Molecular diffusion is the primary transport mechanism for DO through this thin, millimeter-scale layer, limiting the rate of DO transport to the SWI. Turbulent flow in the bottom boundary layer generally controls the thickness of the DBL (δ_{DBL}) and is therefore an important factor controlling J_{O_2} from the water

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side of the SWI.²² The concentration gradient of DO across the DBL also plays an important role as it provides the driving force for diffusive transport. On the sediment side of the SWI, DO may be transported deeper into the sediment porewater via diffusion or interstitial flow and is consumed within the sediments by aerobic microbial respiration and chemical oxidation of reduced species (i.e., manganese, iron, ammonium, and methane). Müller et al.²³ studied areal hypolimnetic mineralization (AHM) rates in 21 lakes in Switzerland and France and found that rates varied based on both sediment composition, depth of the hypolimnion, and artificial oxygenation conditions. Under quiescent near-sediment flows, water-side processes typically limit J_{O_2} .²⁴ Alternatively, sediment-side chemical and biological processes requiring DO can limit J_{O_2} under turbulent conditions when the supply of DO from the water column to the SWI exceeds the rate at which it can be consumed or transported deeper into the sediment.²⁴ In the hypolimnion of most lakes, turbulence near the SWI is low, meaning J_{O_2} is primarily controlled on the water side and DO is readily consumed within the upper few millimeters of the sediment. In artificially oxygenated lakes and reservoirs, the oxygenation systems can enhance J_{O_2} by increasing both turbulent mixing and DO concentrations near the SWI.^{25,26}

DO is consumed within the sediment by a broad range of processes driven by chemical and biological reactions. When simulating DO consumption within the sediment, these processes are usually lumped together into an apparent overall reaction rate following zero-order, first-order, or Monod kinetics.^{19,22} Prior studies have investigated the transport of DO in the sediment by fitting these kinetic models to DO microprofiles or by measuring DO depletion rates in the water column above the sediment in different types of aquatic systems to calculate J_{O_2} and estimate a rate constant. Brewer et al.²⁷ tracked DO concentrations in water above a dredged sediment sample in laboratory incubations, assuming that DO consumption in the sediment followed first-order kinetics. Likewise, Beutel et al.²⁸ monitored DO depletion in sediment core incubations to calculate J_{O_2} , also assuming first-order kinetics. Hall et al.²⁹ measured DO depletion rates using in situ flux chambers deployed in a Swedish fjord. They assumed zero-order kinetics, reporting a rate constant of $1750 \text{ mg L}^{-1} \text{ d}^{-1}$ (L refers to 1 L of porewater in the sediment) at an in situ temperature of 10°C . Rasmussen and Jørgensen²² incubated sediment cores collected from Aarhus Bay, Denmark, and measured DO microprofiles across the SWI using microsensors. They considered zero-order and first-order kinetic models, finding zero-order kinetics to fit the microprofiles better than first-order kinetics. At an incubated temperature of 4°C , they reported a fitted zero-order rate constant of $83 \text{ mg L}^{-1} \text{ d}^{-1}$. House³⁰ used dredged riverine sediments in a laboratory flume to measure factors affecting DO penetration into the sediment, including flow velocity above the sediment, sediment grain size, and organic matter content. DO was measured in water and the sediment using microsensors, similar to the study of Rasmussen and Jørgensen.²² House³⁰ considered several kinetic models, including zero-order, first-order, and Monod kinetics. The study showed that the simple zero-order model fits the data equally well or better than the more complex models. Depending on the flow conditions above the SWI and the characteristics of the sediment, House reported fitted zero-order rate constants ranging from 9.7 to $44 \text{ mg L}^{-1} \text{ d}^{-1}$ at an average temperature of 18.4°C .

These studies, while informative and worthwhile, are all somewhat limited by their methods or assumptions. A common approach is to only monitor DO in water above the SWI.^{19,27,28} However, this does not capture the behavior of DO within the sediment and does not capture processes driving the kinetics and actual DO consumption within the sediment. Studies performed on sediment in laboratory incubations^{22,27,28,30} may disturb the sediment and SWI during the dredging or coring process. Furthermore, laboratory conditions may not always be representative of in situ conditions, particularly with respect to the critical control of turbulent flow in water overlying the sediment. The studies using microsensor measurements^{22,30} assumed that DO profiles were at a steady state when fitting kinetic models to the data, which is appropriate for a laboratory study under controlled conditions that allow the incubated sediment to reach a steady state. However, Bryant et al.³¹ measured in situ DO microprofiles in a seiche lake and observed large changes in the vertical DO distribution above the SWI and within the sediment on an hourly timescale, highlighting the fact that ambient conditions in the field are typically quite variable and that DO profiles in the sediment may never actually reach a steady state.

Another key point is that almost all previous studies assumed zero-flux lower boundary conditions, where the lower boundary was assumed to exist at the location where measurement terminated. Interpretation of measured DO concentration profiles by Berg et al.³² addresses this by accounting for increased DO consumption in the upper sediment zone due to bioturbation; however, the specific contribution of the reduced species flux was not considered.

A recent study that provides an innovative approach for upper sediment research is by Müller et al.²³ Combining water-column, sediment, and porewater chemistry analyses and sediment-to-water flux estimates in 11 eutrophic lakes, their study suggested a new method of describing sediment DO consumption close to the lower boundary. One main outcome of their research is to demonstrate that the estimated AHM rate ($0.25\text{--}0.49 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$) in eutrophic lakes is induced by both mineralization of the organic material and a flux of reduced species propagating from the sediment toward the SWI including methane, ammonium, nitrate (NO_2^-), manganese (Mn(II)), and iron (Fe(II)). Their study is simplified compared to existing and more comprehensive models for sediment diagenesis,³³ where the sediment is divided into an upper aerobic layer and a lower anaerobic layer. More comprehensive models simulate organic matter mineralization, nitrification, denitrification, partitioning of hydrogen sulfide (H_2S), and oxidation, while the estimated AHM rate only considers the two most essential hypolimnetic DO depletion processes. Despite the simplification, the agreement between estimations and measurements of the AHM rates is striking. Although their study did not directly focus on sediment DO microprofiles, this has significant implications for the validity of the traditional sediment profile interpretation with the zero-flux boundary condition and also shows the potential to simplify the modeling of sediment DO kinetics by considering only the most essential biogeochemical processes impacting DO concentrations in the upper sediment.

This paper focuses on how to better describe DO consumption close to the lower boundary of theoxic freshwater sediments. Transient DO profiles are modeled under two different lower boundary conditions but using the

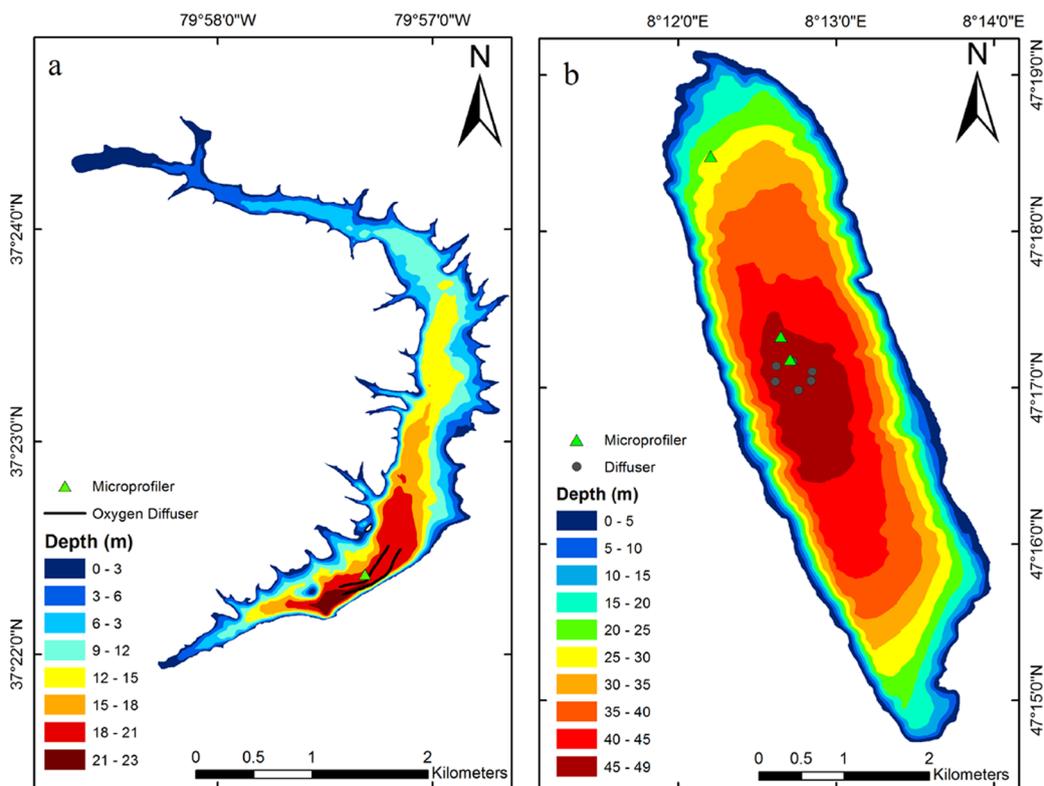


Figure 1. Bathymetric maps of (a) Carvins Cove Reservoir (CCR) and (b) Lake Hallwil (LH). Locations of the linear diffusers in CCR and the circular diffusers in LH are shown, as well as the deployed positions of the microprofiler. Note that one of the six diffuser symbols in LH is partially obscured by a symbol for the microprofiler.

same governing equations. Simulated profiles with two lower boundary conditions are then compared to determine which lower boundary condition is more appropriate. Simulated sediment DO fluxes are also compared as they are critical parameters needed for defining the water quality and ecosystem health for lake and reservoir management. To our knowledge, the current study is the first to fit kinetic models to obtain rate constants using DO microprofiles measured in situ rather than using laboratory incubations. It is also the first kinetic study to consider the reaction of DO at the lower boundary with reduced species propagating upward from deeper within the sediments, inspired by Müller et al.²³ In this study, the oxidation of the reduced species is assumed to be instantaneous at the bottom of the oxic sediment layer. Although DO consumption within the oxic sediment layer is partially related to reduced species penetrating upward, there is evidence that the gradient of reduced species close to the bottom of the oxic layer is higher than in other regions of the upper sediment.^{34,35}

2. METHODS

2.1. Study Sites. DO microprofiles were measured in situ in two oxygenated lakes: Lake Hallwil and Carvins Cove Reservoir (Figure 1). Lake Hallwil (LH) is located north of Lucerne, Switzerland, on the Swiss Plateau, and is primarily used for recreational purposes. It has a maximum depth of 48 m, a surface area of 9.95 km², and a volume of 285 × 10⁶ m³ and is at an elevation of 449 m above the mean sea level. Carvins Cove Reservoir (CCR) is a water-supply reservoir for the City of Roanoke in southwest Virginia, USA. CCR has a maximum depth of 22 m, a surface area of 2.5 km², and a

volume of 24 × 10⁶ m³ and is at an elevation of 357 m above the mean sea level.

2.2. Microprofile Data Collection. A microprofiler (MP4; Unisense A/S) was deployed for periods of ~2 to ~5 days at three locations along the main axis of LH (as shown in Figure 1) from 24 May to 1 June 2012. The microprofiler was deployed at one location in CCR (also shown in Figure 1) from 26 May to 2 June 2013. While deployed, the microprofiler was equipped with a Clark-type oxygen microsensor (Unisense OX-100) and a thermocouple temperature sensor (Unisense TP-200). Measurements were made in triplicate at a sampling rate of 1 Hz at the following vertical resolution: 10 mm resolution from 100 to 10 mm above the SWI, 1 mm resolution from 10 to 5 mm above the SWI, and 0.1 mm resolution from 5 mm above the SWI to 5 mm below the SWI. The single oxygen microsensor was used to obtain three measurements in rapid succession at each vertical depth position; these triplicate measurements were averaged prior to modeling the data. This protocol resulted in complete microprofiles of both DO and temperature measured across the SWI every ~55 min.

The SWI location was visually determined by examining each microprofile to identify the linear region in the DBL and the slope change associated with the porosity difference between water and the sediment. The standard deviation of the triplicate DO measurements taken at each point in the microprofiles was used to further identify and confirm the correct location of the SWI as standard deviation of DO measurements should decrease as the microsensor approaches the SWI.²¹

2.3. Sediment Kinetics. Sediment DO kinetics is typically described using zero-order, first-order, or Monod (sometimes

referred to as Michaelis–Menten) kinetic models. Zero-order and first-order kinetic models are shown below in eqs 1 and 2.³⁰ These model formulations account for molecular diffusion of DO through the sediment porewater and consumption of DO within the sediment. Rather than trying to account for the numerous chemical and biological processes that consume DO in the sediment, DO consumption is assumed to be adequately represented using an all-encompassing rate constant or, in the case of the Monod model, two constants. Monod kinetics has the effect of becoming zero-order or first-order depending on DO concentrations.

The study by House³⁰ showed that zero-order and Monod models described DO kinetics within the sediment equally well, although zero-order models often agreed slightly better. Olinde³⁶ also showed that despite the additional fitting parameter offered by Monod kinetics, it does not result in a substantially improved fit to DO microprofiles measured during sediment core incubations. Given these observations and to minimize model complexity, the Monod kinetic model was not employed in this study. By applying a finite shift to the zero-order and first-order kinetic models (eqs 1 and 2), the transient numerical solutions can be obtained (eqs 3 and 4) as

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - k_0 \quad (1)$$

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - k_1 C \quad (2)$$

$$\frac{C_n^i - C_{n-1}^{i-1}}{\Delta t} = \frac{D_s}{\Delta z^2} (C_{n+1}^{i-1} - 2C_n^{i-1} + C_{n-1}^{i-1}) - k_0 \quad (3)$$

$$\frac{C_n^i - C_{n-1}^{i-1}}{\Delta t} = \frac{D_s}{\Delta z^2} (C_{n+1}^{i-1} - 2C_n^{i-1} + C_{n-1}^{i-1}) - k_1 C_n^{i-1} \quad (4)$$

where C represents the DO concentration, t is the time, D_s is the effective diffusion coefficient of DO in the sediment (where $D_s = \varphi D_m$, φ is the sediment porosity and D_m is the molecular diffusion coefficient of DO in water), z is the depth below the SWI, k_0 is a zero-order rate constant, and k_1 is a first-order rate constant. The superscript i denotes the profile number in the time series of profiles, and the subscript n represents depth in the porewater DO profile, where the positive upward direction is toward the sediment.

The models were coded using Matlab.³⁷ They were initialized with the first profile in the series of microprofiles measured at each deployment using only the portion of the profile at and below the SWI. Measured DO concentrations below 3 μM were forced to zero as concentrations below this level become difficult to discern from zero due to microsensor capabilities; furthermore, the depth at which DO is <3 μM (0.096 mg L^{-1}) has been defined as the depth of maximum DO penetration in previous studies (e.g., Bryant et al.^{35,38}). The model assumes constant temperature over the series of profiles and constant φ with the sediment depth. This results in a constant value of D_s for a given series of profiles. Measurements of φ were obtained from sediment cores collected from both CCR and LH during field studies conducted prior to the current study following Dalsgaard et al.³⁹ The φ values in the sediment of CCR and LH were 0.96 and 0.94, respectively.²¹ The upper boundary condition is the measured DO concentration at the SWI. This study adopts four methods of characterizing boundary conditions, denoted

by ZOZF, ZONF, FOZF, and FONF. ZOZF (zero-order, zero-flux) and ZONF (zero-order, negative-flux) adopt zero-order kinetics, while FOZF (first-order, zero-flux) and FONF (first-order, negative-flux) adopt first-order kinetics. The lower boundary condition for ZOZF and FOZF is the traditional zero-flux boundary condition (eq 5) with the lower boundary located where the measurement terminates (5 mm):

$$D_s \frac{\partial C}{\partial z} = 0 \text{ g m}^{-2} \text{ d}^{-1} \quad (5)$$

The lower boundary condition for ZONF and FONF is a negative-flux boundary condition (eq 6) with the lower boundary located where the DO concentration goes to zero in each profile, representing a fixed value of reduced species flux based on the general value Müller et al.²³ obtained for 11 eutrophic lakes:

$$D_s \frac{\partial C}{\partial z} = -0.25 \text{ g m}^{-2} \text{ d}^{-1} \quad (6)$$

The benthic flux of reduced substance is set to a fixed value rather than being treated as a second fitting parameter to ensure the stability of the kinetic model and to keep the model simple. Because eqs 1 and 2 are expressed in terms of DO, we assume that the upward flux of reduced compounds is rapidly oxidized by DO and that the result could be reasonably expressed as an upward “negative” flux of DO at the depth where the DO concentration becomes zero for each profile. To ensure a stable solution that does not oscillate, the time step (Δt) is made sufficiently small so that the diffusion number (λ , eq 7) is less than 0.25.⁴⁰

$$\lambda = \frac{D_m \Delta t}{\Delta z^2} \quad (7)$$

Since the Δt necessary to achieve $\lambda < 0.25$ is much smaller than the time interval between two consecutive microprofiles measured in the field ($\Delta t = 1$ s in the model vs $\Delta t \approx 55$ min in field measurements), the DO concentration at the SWI used as the upper boundary condition for the modeled profiles is determined by linearly interpolating between measured DO concentrations at the SWI as needed. After the DO concentrations for every Δt (1 s) have been simulated, the DO concentration for the time between two microprofiles ($\frac{t^i + t^{i+1}}{2}$) is used as the simulated result of profile i , where t^i is the time when profile i starts being measured, and t^{i+1} is the time when profile $i+1$ starts being measured.

The models were evaluated using rate constants from 1 to 2000 ($\text{mg L}^{-1} \text{ d}^{-1}$ for zero-order kinetic models and d^{-1} for first-order kinetic models), whose range was selected based on reported values from previous studies.^{21,22,28,30} The best-fit value for the kinetic rate constant is the value that minimizes the root mean square error (RMSE)

$$\text{RMSE} = \sqrt{\frac{\sum (C_{\text{Obs}} - C_{\text{Sim}})^2}{p}} \quad (8)$$

for each microprofile, where C_{Obs} is the observed DO concentration, C_{Sim} is the simulated DO concentration, and p is the total number of microprofile data points among all depths and profiles. After calculating the best-fit k_0 or k_1 for all profiles in one series, the average values of the best-fit k_0 and k_1 were applied as the best-fit kinetic rate constants for the full series of microprofiles; these globally averaged values were

deemed most suitable due to the high variability in the profile-specific rate constants (as shown in Figures S5–S8). The averaged best-fit k_0 and k_1 are used for additional analysis described in section 2.4.

2.4. Model versus Field Data Comparisons. Using the fitted k_0 and k_1 from each series of profiles, the sediment-side DO flux is calculated from the simulated profiles and compared to the sediment-side DO flux calculated from the measured microprofiles. DO flux (J_{O_2}) was estimated as

$$J_{O_2} = D_s \frac{\Delta C}{\Delta z} \quad (9)$$

where $\Delta C/\Delta z$ is the DO concentration gradient immediately below the SWI. To compare how well the modeled data agree with the field data, the relative error and the normalized RMSE are calculated using eqs 10 and 11, where N is the number of profiles, $J_{O_2, Sim}$ is the simulated DO flux, $J_{O_2, Obs}$ is the observed DO flux, and the subscript i denotes the profile number in the time series of profiles:

$$\text{relative error} = \frac{J_{O_2, Sim_i} - J_{O_2, Obs_i}}{J_{O_2, Obs_i}} \quad (10)$$

$$\text{normalized RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{J_{O_2, Sim_i} - J_{O_2, Obs_i}}{J_{O_2, Obs_i}} \right)^2} \quad (11)$$

3. RESULTS AND DISCUSSION

3.1. Fitted Rate Constants. The fitted values of k_0 for ZOZF and ZONF, the fitted values of k_1 for FOZF and FONF, and the corresponding average RMSE values for each series of microprofiles are displayed in Table 1. Values for k_0 and k_1 range from 120 to 510 $\text{mg L}^{-1} \text{d}^{-1}$ and 90 to 400 d^{-1} in LH, while values for CCR are lower at 50–60 $\text{mg L}^{-1} \text{d}^{-1}$ and 60–80 d^{-1} . Differences in the fitted rate constants between the two study sites are likely attributable to differences in the sediment

composition between the two lakes, including the amount of labile organic matter and mineral composition. Labile carbon, reduced metals, and other chemical species exert a demand for DO within the sediment, and larger quantities of any of these oxygen-consuming species would result in an increase in the observed rate constant. The large range in fitted rate constants within LH is likewise attributable to spatial variability in the sediment composition within LH itself. The first and third deployments were both in the central, deepest portion of LH (~42 m depth and ~300 m apart) and yielded similar best-fit rate constants. The second deployment, though still in the hypolimnion, was at a shallower location (~25 m depth) and has higher fitted rate constants. Sediment in the shallower portions of LH is likely to have more labile carbon in the sediment than deeper portions of the lake²¹ since settling the organic matter has less time to be oxidized in the water column before reaching the sediment. A similar observation was made in a study of Lake Gevena,⁴¹ a Swiss lake where sediment DO uptake declines with increasing lake depth due to decreased rates of organic matter settling and sediment surface mineralization with greater depth. Additionally, the LH bubble-plume oxygenation system is located in the deepest portion of the lake, within 300 m of the first and third microprofiler deployments (LH-1 and LH-3, respectively). This oxygenation system, which has been in operation for roughly 30 years, would further enhance oxidation of settling organic matter in the water column by increasing the availability of DO in the water column and by satisfying oxygen demand exerted by the nearby sediment. It has been shown that the organic content of the sediment in LH has been significantly decreased by oxygenation.^{23,42} Thus, it seems reasonable that the fitted rate constant should be higher in the shallower regions of the lake, which are also farther from the oxygenation system. Temperature may play a minor role in the increased best-fit rate constants at the shallower site as temperatures measured near the SWI were only about 1 °C warmer at this shallower location.

In both the CCR data set and the LH data sets, ZONF and FONF (with a negative-flux lower boundary condition) appear to fit much better than ZOZF or FOZF (zero-flux lower boundary condition) as evidenced by the distinctly lower RMSE values (Table 1). Most of the observed profiles also agree much better visually with the simulated profiles of ZONF and FONF than with those of ZOZF or FOZF in all data sets, as shown in Figures 2 and 3. It should be noted that, in CCR, some profiles simulated by FOZF fit the field profiles very well, while other profiles simulated by FOZF have rather high RMSEs, which is the reason why FOZF outperforms FONF in Table 2, but not Table 1. Considering this visual comparison and the relatively lower RMSE values, the negative-flux lower boundary condition appears to be more appropriate for describing DO consumption close to the lower boundary of the sediment for both LH and CCR. This provides strong evidence supporting the description of hypolimnetic DO consumption in the model of Müller et al.²³ Moreover, these new results indicate that it is possible to simulate DO consumption in the upper sediment by modeling the lumped zero-order or first-order reaction and the reduced species fluxes.

Differences between the simulated and observed profiles are likely a result of adopting the globally averaged rate constants and also the interpolation necessary to force the model. Since the field data only has direct DO measurements at the SWI

Table 1. Summary of Fitted Kinetic Rate Constants and Average Root Mean Square Error (RMSE) with Lower RMSEs between ZOZF/ZONF and Lower RMSEs between FOZF/FONF Shown in Bold

site	parameter	zero-order		first-order	
		ZOZF k_0 ($\text{mg L}^{-1} \text{d}^{-1}$)	ZONF k_0 ($\text{mg L}^{-1} \text{d}^{-1}$)	FOZF k_1 (d^{-1})	FONF k_1 (d^{-1})
CCR	rate constant	50	60	60	80
	RMSE (mg L^{-1})	0.32	0.08	0.30	0.10
LH-1	rate constant	150	170	90	130
	RMSE (mg L^{-1})	0.86	0.37	0.53	0.38
LH-2	rate constant	510	390	400	380
	RMSE (mg L^{-1})	0.58	0.33	0.54	0.22
LH-3	rate constant	200	120	190	120
	RMSE (mg L^{-1})	0.45	0.14	0.52	0.13
	RMSE average ^a (mg L^{-1})	0.46	0.17	0.41	0.16

^aWeighted by number of profiles in each data set.

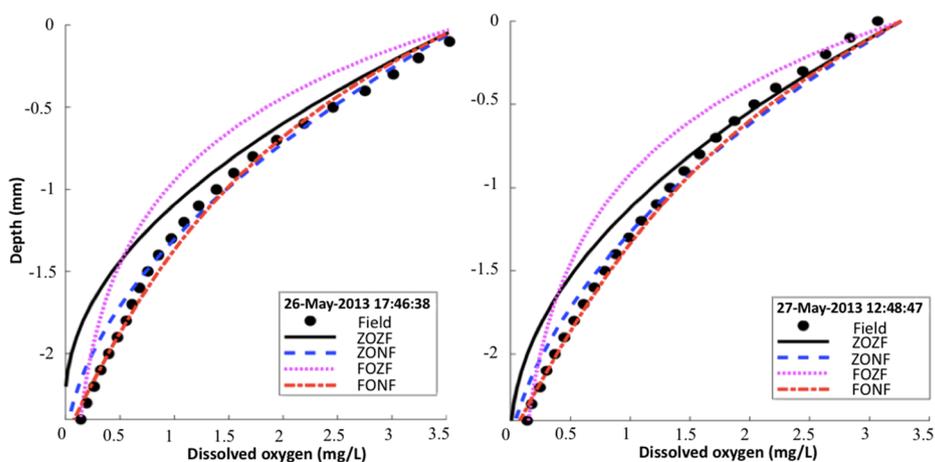


Figure 2. Characteristic DO microprofiles comparing field data to simulations by the four methods (ZOZF, ZONF, FOZF, and FONF) in Carvins Cove Reservoir (CCR).

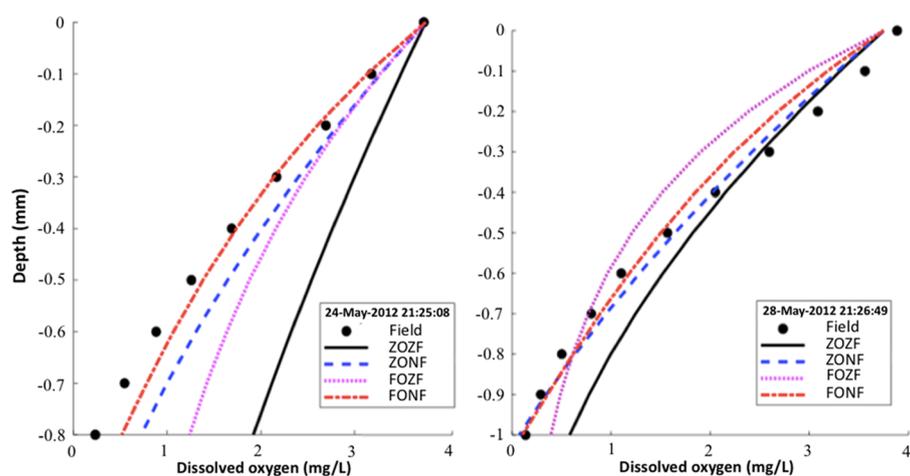


Figure 3. Characteristic DO microprofiles comparing field data to simulations by the four methods (ZOZF, ZONF, FOZF, and FONF) in Lake Hallwil (LH).

Table 2. Percentage of Each Fitting Method with the Best Performance among All 320 Profiles (Combined Total for LH and CCR) Based on RMSE Value for Each Individual Profile (Higher Percentages between ZOZF/ZONF and Higher Percentages between FOZF/FONF Are Shown in Bold)

site	ZOZF (%)	ZONF (%)	FOZF (%)	FONF (%)
CCR	13	57	16	14
LH-1	9	23	23	45
LH-2	13	33	11	43
LH-3	8	47	6	39

roughly every 55 min, any fluctuation in DO concentrations at the SWI occurring on a shorter time scale are not represented in the model forcing. As mentioned in section 2, the model time step is 1 s ($\Delta t = 1$ s) to ensure stable solutions, which is much shorter than the ~ 55 min period between two consecutive in situ microprofiles. If higher frequency data were available to force the model, the agreement between the simulated and observed profiles would likely improve. In some microprofiles (e.g., the profiles in Figure 2), the simulated DO concentration at depth = 0 mm is not equal to that of the observations. This is also related to interpolation of field

profiles and reflects the time-consuming microprofile measurement process.

Despite some differences in the methods used for determining the best-fit rate constants, the fitted values generally compare quite well with the preliminary CCR study by Olinde.³⁶ Olinde found the best-fit k_0 to be 36 ± 10 mg L⁻¹ d⁻¹ at 4 °C and 130 ± 66 mg L⁻¹ d⁻¹ at 20 °C, while the best-fit k_1 were 34 ± 12 d⁻¹ at 4 °C and 170 ± 68 d⁻¹ at 20 °C. The fitted CCR values obtained in the current study (Table 2), measured at an in situ temperature of ~ 7.5 °C, agree nicely with the range from this preliminary study by Olinde.³⁶

Given the differences in methods and variable sediment composition and microbial community structure,⁴² the magnitude of the optimized zero-order rate constant for CCR agrees with k_0 values reported by Rasmussen and Jørgensen²² (83 mg L⁻¹ d⁻¹) and House²⁸ (9.7–44 mg L⁻¹ d⁻¹). The fitted k_0 values for LH are higher than those reported by Rasmussen and Jørgensen²² or House²⁸ but are still within a reasonable range; in comparison, Hall et al.²⁹ reported a k_0 that is an order of magnitude higher than those from LH (1750 mg L⁻¹ d⁻¹ vs 120–510 mg L⁻¹ d⁻¹). It should also be taken into consideration that the negative-flux lower boundary condition in ZONF and FONF assumes an

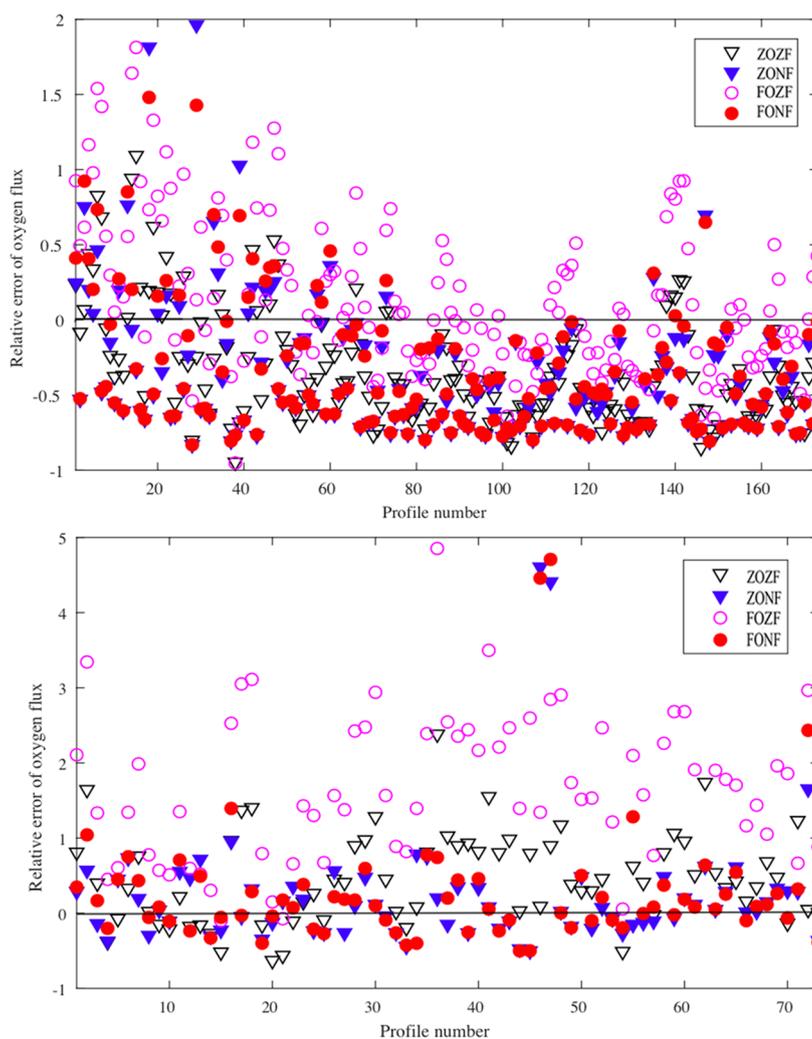


Figure 4. Relative error of the sediment-side DO fluxes at the sediment–water interface (SWI) in the CCR microprofiler deployment between May 26 and June 02 2013 (upper plot) and the third microprofiler deployment in LH (LH- 3) between May 28 and June 01 2012 (lower plot).

instantaneous reaction, while in natural water bodies, the oxidation of reduced species is clearly not instantaneous but only gradually reduces the concentrations of reduced species over the distance of diffusion. Since the concentration gradient of reduced species in the upper sediments is extremely complex to characterize, the proposed simplification is reasonable but may lead to larger k_0 and k_1 estimates.

3.2. DO Flux Comparisons. Sediment-side DO fluxes at the SWI calculated from the simulated DO profiles were used to estimate J_{O_2} , which were then compared to field measurements. The first-order kinetics with the zero-flux boundary condition (FOZF) typically overestimates the DO flux. The sediment-side DO flux calculated by negative-flux lower boundary conditions (ZONF and FONF) agrees better than zero-flux lower boundary conditions (ZOZF and FOZF) with the field data based on both visual inspection and the normalized RMSE values weighted by the number of profiles in each data set as shown in Figure 4 (and also Tables S2 and S3). Due to the overestimation of FOZF, the normalized RMSE of DO flux calculated by FOZF is around twice the normalized RMSE of the negative-flux lower boundary condition (ZONF and FONF) for both CCR and LH. This increased RMSE, along with results in section 3.1, lend more support to using the negative-flux lower boundary condition

over the zero-flux lower boundary condition when modeling DO flux on the sediment side of the SWI in LH and CCR. In addition, ZONF seems to be the best method for LH, yielding the lowest RMSE. Another aspect to be considered is that Monod kinetics, a rate expression that is often used to describe microbial growth and single substrate degradation, has the effect of being zero-order when the concentration is much greater than the Monod half-saturation constant while being first-order when the concentration is much less than the half-saturation constant.⁴³ Because virtually all microbial DO consumption processes have a half-saturation constant near or below the detection limit of the microsensors⁴⁴ ($3 \mu\text{M}$), it is not surprising that zero-order kinetics yields more reliable results.

DO fluxes at the SWI of some profiles have a normalized RMSE of more than 200%, which indicates that fluxes calculated from these simulated microprofiles, primarily by FOZF, do not adequately reproduce the actual measured fluxes. Müller et al.²⁵ assumed the reaction of DO with the organic matter to be a first-order kinetic reaction, which indicates that the negative-flux lower boundary condition has only been studied and verified with first-order sediment kinetics. This may explain why FONF performs much better than FOZF, while ZONF does not outperform ZOZF in DO

flux comparison such as those discussed in section 3.1. Additional sources of discrepancy may be due to the measured DO fluxes being subject to measurement errors at the SWI, especially related to the determination of the exact SWI depth level, and the simulated DO fluxes being influenced by errors arising from the model and numerical solutions.

Both the simulated and observed sets of DO fluxes have significant implications for lake and reservoir management. The sediment-side DO fluxes are closely related to the water-side DO fluxes, which can also be derived from the kinetic rate constants based on empirical equations.^{19,25} The comparison of the simulated and observed DO fluxes indicates that the simulated ones are more reliable than the observed ones because the simulated ones make use of all measured microprofiles. For these reasons, comprehensive microprofiling time series paired with the model described in this study can provide a useful new tool in monitoring sediment DO fluxes for managing the water quality and ecosystem health in lakes and reservoirs.

3.3. Limitation of the Approach. A model of DO transport and consumption in freshwater sediments has been fit to DO microprofiles measured in situ using zero-order and first-order kinetic models with zero-flux and negative-flux lower boundary conditions to determine the appropriate kinetic order and the appropriate bottom boundary condition. While the results support the inclusion of a flux of reduced species propagating upward from deeper within the sediments and thereby contributing to part of the overall sediment DO consumption and corresponding DO flux estimates, additional work is necessary. An even longer time series of microprofiles may be obtained to make the analysis more robust. The overestimation of DO flux in some microprofiles is also likely to be a result of the interpolation necessary to force the model. With a higher-frequency data set to force the model, the agreement between observed and simulated microprofiles is expected to improve, which should, in turn, improve the fluxes calculated from the simulated profiles. If possible, placing focus on profiling immediately across the SWI and into the upper sediment (thereby excluding a majority of the overlying water column) would allow for considerably decreased profiling times, thereby minimizing the difference between actual measurements and model time steps. In addition, the negative-flux value is fixed in this study; however, Müller et al.²³ suggested that values may vary among different lakes and even across different seasons and/or locations within the same lake. Further research is needed to better characterize the value of sediment DO fluxes in these complex aquatic systems using simplified yet accurate models.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b04831>.

Additional details on previous studies investigating DO kinetics in sediment porewater (Table S1), comparison between normalized RMSE values of DO flux using the four methods (ZOZF, ZONF, FOZF, and FONF; Table S2), percentage of profiles whose sediment-side DO flux has relative errors less than ± 0.5 and ± 1.0 (Table S3), DO concentration at the SWI for each site (Figures S1–S4), kinetic rate constants of each profile for each site (Figures S5–S8), and in situ and simulated DO profiles

by ZOZF, ZONF, FOZF, and FONF in CCR and LH (Figures S9–S169) (PDF)

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Notes

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