

Effect of the diffusive boundary layer on benthic mineralization and O₂ distribution: A theoretical model analysis

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Abstract

On the basis of a dynamic diagenetic model, we evaluate and discuss the effect of the diffusive boundary layer (DBL) on benthic O₂ exchange and O₂ consuming pathways. The analysis documents that the DBL has only minor importance for the annual O₂ uptake of coastal cohesive sediments. Imposing static DBL thicknesses of 300–900 μm decreased the annual O₂ uptake by only 2–10% in comparison to a situation without any DBL. Lower O₂ availability as imposed by a thicker DBL, however, markedly reduced the aerobic heterotrophic respiration but enhanced aerobic reoxidation of solutes released by the stimulated anaerobic respiration. The 2–10% decrease in the annual O₂ uptake was caused mainly by higher benthic release rates of NH₄⁺ and Mn²⁺. The overall carbon degradation rate—and thus the carbon preservation—remained unaffected by the DBL thickness. Dynamic modeling revealed that abrupt changes in the DBL thickness caused an instantaneous change in the interstitial O₂ distribution and in the benthic O₂ uptake rate. However, conditions quickly reversed as the pore-water profiles of reduced solutes and distribution of reduced solids readjusted even though full steady state was obtained only after several months. In nature the DBL is constantly changing, and thus in situ O₂ microprofiles are transient by nature. Dynamic modeling showed that the benthic O₂ concentration and the O₂ uptake in Aarhus Bay could vary by 30% or more on time scales of a few hours or days solely because of changes in the DBL thickness. The integrated annual O₂ uptake remained unaffected by these fluctuations.

Solute transport in the water column is dominated by turbulent mixing. Close to the sediment–water interface, however, eddy transport is impeded by friction and viscous forces. The so-called viscous sublayer is defined as the height at which the turbulent mixing, expressed as eddy diffusivity, becomes smaller than the kinematic viscosity of $\sim 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, which usually happens 5–10 mm above the sediment surface (Caldwell and Chriss 1979; Boudreau 2001). In this layer, viscous forces dominate, and in the lower part of this layer, the eddy diffusivity falls below the molecular diffusivity (D_0) of $\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. For cohesive sediments this shift defines the upper boundary of the diffusive boundary layer (DBL). The DBL thickness typically accounts for one-tenth of the viscous sublayer thickness, but as it is defined by the molecular diffusion coefficient, it is solute dependent. Within the DBL, vertical

solute transport is mediated mainly by molecular diffusion. The transport rate across the DBL can influence the rate of important biogeochemical processes such as calcite dissolution, growth of ferromanganese nodules, benthic contaminant release, and benthic O₂ uptake (e.g., Boudreau and Scott 1978; Jørgensen and Revsbech 1985). The in situ DBL thickness is regulated by the dissipation rate of turbulent energy in the benthic boundary layer (Higashino et al. 2003; Lorke et al. 2003). In laboratory flow systems using moderate water heights and approximating laminar flow conditions, it has been shown that the DBL thickness of a given solute at a given salinity and temperature relates primarily to the free-flow velocity and the sediment roughness (Jørgensen and Des Marais 1990; Steinberger and Hondzo 1999).

On the introduction of O₂ microelectrodes in aquatic ecology, the existence of the DBL could be directly documented (Jørgensen and Revsbech 1985; Archer et al. 1989a), and a series of detailed studies of the short-term O₂ dynamics within the DBL followed (e.g., Gundersen and Jørgensen 1990; Jørgensen and Des Marais 1990; Røy et al. 2004). From high-resolution O₂ microprofiles based on averaged O₂ concentrations measured at different positions within the DBL, it is possible to infer the effective DBL

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thickness. By this approach the upper DBL boundary is determined as the intersection between the extrapolated linear concentration gradient in the DBL and the constant O_2 concentration of the overlying mixed water (Jørgensen and Des Marais 1990). Typically, the relative position of the sediment surface in microprofiles can be identified by a distinct change in the slope of the concentration profile due to a change in molecular diffusivity between free water and sediment (Rasmussen and Jørgensen 1992). Data on O_2 microsensor-derived effective DBL thicknesses (δ_{O_2}) are still limited, but in situ values for typical marine settings range between 0.2 and 1.0 mm (e.g., Glud et al. 2003, 2005; Roberts and McMinn 2004).

The average diffusion-mediated transport time for O_2 molecules across the DBL, (t_{DBL}), can be calculated as $t_{DBL} = \pi(\delta_{O_2})^2/4D_0$ (Sten-Knudsen 2002). The δ_{O_2} range of 0.2–1.0 mm thus corresponds to DBL transport times of 21–526 s (at 10°C and a salinity of 30). To the extent that the turnover time of O_2 within the sediment is in the same time range, the DBL thickness can potentially impede the benthic O_2 uptake. The resistance that DBL exerts on the O_2 uptake (i.e., the DBL impedance) is thus expected to be of importance only in diagenetically active sediments with relatively fast turnover of the internal O_2 pool. The impedance exerted by the DBL has been estimated by assuming a constant, depth-independent O_2 consumption rate driven by O_2 respiration within the sediment (Archer et al. 1989a,b). It was concluded that the DBL thickness was important for the benthic O_2 uptake of marine sediments and indirectly affected the carbon preservation rate.

We consider this conclusion not to be generally valid because the assumptions do not apply to the metabolically active sediments that occur along the ocean margins. Such sediments are typically characterized by a depth-dependent aerobic activity with enhanced O_2 consumption at the sediment surface and at the oxic–anoxic interface (e.g., Rasmussen and Jørgensen 1992). A large fraction of the O_2 consumption is related to the oxidation of reduced products from anaerobic mineralization, either in the form of solutes like NH_4^+ , H_2S , Fe^{2+} , and Mn^{2+} or in the form of solids like FeS_x (iron sulfides, pyrite). The distribution of each of these compounds and their oxidation kinetics must respond to changes in the O_2 availability. Thus, each process responsible for the benthic O_2 consumption and their kinetic has to be accounted for when evaluating the quantitative importance of the DBL thickness for the benthic O_2 uptake. From a relative simple steady-state model, Jørgensen and Boudreau (2001) concluded that if O_2 is consumed by oxidation of reduced solutes from the anaerobic mineralization, then the O_2 uptake would remain independent of the DBL thickness (or the O_2 concentration at the sediment–water interface), as the interfacial solute distribution would readjust to maintain the same flux.

In order to distinguish the key processes responsible for the consumption of oxygen in the sediment, we will in the following use the terms “ O_2 respiration” for the aerobic heterotrophic respiration by benthic microorganisms that leads to a direct mineralization of organic matter with oxygen and “ O_2 oxidation” for the combined aerobic lithotrophic oxidation of microorganisms that oxidize

reduced inorganic species and the oxygen consumption by the nonbiologically catalyzed oxidation of reduced inorganic species (the inorganic pool is divided into solutes and solids). The total flux of O_2 across the sediment–water interface is always referred to as “ O_2 uptake.” The present conceptual study quantifies the impact of changing DBL thicknesses on the benthic mineralization processes using a previously described dynamic diagenetic model calibrated to Aarhus Bay sediment (Denmark) (Berg et al. 2003, in press). It is evaluated to what extent variations in the DBL thickness impact the benthic O_2 uptake and the O_2 distribution in the sediment on time scales from minutes to months.

Materials and methods

Study site—Aarhus Bay is a semienclosed 320-km² mesotrophic embayment on the Baltic Sea–North Sea transition, Denmark. During 1990–1992, a large interdisciplinary research program on coastal element cycling was carried out in the central part of the Bay (56°9.1'N, 10°19.2'E; water depth 16 m) providing a detailed biogeochemical data set on pore-water and solid-phase chemistry, volume-specific process rates, and benthic fluxes (Jørgensen 1996 and references therein).

The water column in Aarhus Bay is stratified by a halocline during most of the year, and the study site is characterized by a strong seasonality in primary production, typically dominated by distinct spring and autumn blooms (Jørgensen 1996). The annual net carbon deposition rate is ~ 120 g C m⁻². The sediment is muddy silt with a surface porosity of 0.87 and an organic matter content of 9.9% dry weight (Rasmussen and Jørgensen 1992; Valeur et al. 1992). The benthic mineralization rates reflect the variable input of organic material. On an annual scale, the bottom water O_2 concentration, the benthic O_2 penetration depth, and the in situ total O_2 consumption rate typically vary by a factor of ~ 6 , ~ 9 , and ~ 3 , respectively, with average values of ~ 230 $\mu\text{mol L}^{-1}$, ~ 2.5 mm, and ~ 25 mmol m⁻² d⁻¹, respectively (Glud et al. 2003).

Model description and validation against Aarhus Bay data—A full description of the dynamic diagenetic model, its numerical formulation, and the procedure for its application and validation to specific sites is given by Berg et al. (2003, in press). In short, the model is based on a mass-balance approach expressed for each chemical species, and it includes the vertical transport, by molecular diffusion, bioturbation, irrigation, and burial (Berg et al. 2003). The present exercise will, however, focus only on the effects of variable DBL thickness and will not evaluate the importance of fauna for the benthic biogeochemistry. In typical model applications the DBL and the upper 20 cm of the sediment column are divided into 100–150 control layers that increase in thickness with depth. The latter ensures a high depth resolution, usually ~ 300 μm , right below the sediment–water interface where the concentration gradients are steepest.

The model was recently applied to the Aarhus Bay sediment (Berg et al. unpubl. data). The applied version of the model includes 18 dissolved or solid chemical species, some represented by several pools, and 23 redox equations, including eight oxygen-consuming processes that link the O_2 consumption to the carbon, nitrogen, manganese, iron, and sulfur cycles (Table 1). A crucial element in this model application was the extensive biogeochemical database for Aarhus Bay (Jørgensen 1996). The dynamic model input parameters comprise bottom water temperature, bottom water concentrations of relevant solutes, and sediment–water fluxes of solids and organic matter. Solute diffusion coefficients are expressed as functions of bottom water temperature according to Li and Gregory (1974) and Broecker and Peng (1974) along with the biogeochemical rate constants expressed through a series of Q_{10} values (i.e., rate increase following a 10°C temperature increase). The organic matter flux to the sediment surface is a key parameter driving the model. Below the sediment surface the kinetics of organic matter mineralization are described through a multi-G model that includes fast, slow, and nondegradable pools of organic matter (Jørgensen 1978; Berner 1980; Westrich and Berner 1984), the two former with rate constants of $9.6 \cdot 10^{-6} \text{ s}^{-1}$ and $1.2 \cdot 10^{-8} \text{ s}^{-1}$ (at 9°C), respectively.

The validated model successfully simulated observed concentration profiles of (1) pore-water species: O_2 , dissolved inorganic carbon (CO_2 , NH_4^+ , Mn^{2+} , Fe^{2+} , SO_4^{2-} , H_2S , and PO_4^{3-}); (2) solid species: organic matter (OM), $FeOOH$, MnO_2 , S^0 , FeS , and FeS_2 ; (3) measured sulfate reduction rates; and (4) sediment–water exchange rates of O_2 , CO_2 , NH_4^+ , and NO_3^- (Berg et al. 2003, unpubl. data). In the previous model applications a fixed DBL thickness was imposed for the entire simulated time, and the impact of changing the DBL thickness was not evaluated. This is done in the present work first in a static mode and then by imposing a dynamic DBL thickness derived from high-resolution current measurements from Aarhus Bay.

Results

Effects of DBL on seasonal and annual O_2 consumption rates—In situ microelectrode measurements performed during 1990–1992 showed that the DBL thickness (δ_{O_2}) at the investigated site varied between 299 and $706 \mu\text{m}$ with an average value of $451 \mu\text{m}$ ($n = 98$) (Glud et al. 2003). Even though these measurements do not include periods of rough weather, they provide a good impression of the typical microsensor derived DBL thicknesses for central Aarhus Bay. Microelectrode measurements affect the boundary layer flow, however, and the data typically underestimate the real DBL thickness by 25–35% (Glud et al. 1994). The prevailing in situ DBL thickness at the investigated site during the study period was thus presumably in the order of $600\text{--}700 \mu\text{m}$. To evaluate the impact of DBL thickness on seasonal O_2 uptake, we first ran the model with four different static δ_{O_2} values, while all other input parameters follow the measured and estimated seasonal variability of the area.

Table 1. Oxygen-consuming processes included in the applied dynamic diagenetic model. The production of NH_4^+ and PO_4^{3-} in (R1) is stoichiometrically balanced to the N and P content of the organic matter (OM).

$OM + O_2$	\rightarrow	$CO_2 + NH_4^+ + PO_4^{3-} + H_2O$	(R1)
$NH_4^+ + 2O_2$	\rightarrow	$NO_3^- + H_2O + 2H^+$	(R2)
$2Mn^{2+} + O_2 + 2H_2O$	\rightarrow	$2MnO_2 + 4H^+$	(R3)
$4Fe^{2+} + O_2 + 6H_2O$	\rightarrow	$4FeOOH + 8H^+$	(R4)
$H_2S + 2O_2$	\rightarrow	$SO_4^{2-} + 2H^+$	(R5)
$FeS + 2O_2$	\rightarrow	$Fe^{2+} + SO_4^{2-}$	(R6)
$2FeS_2 + 7O_2 + 2H_2O$	\rightarrow	$2Fe^{2+} + 4SO_4^{2-} + 4H^+$	(R7)
$CH_4 + 2O_2$	\rightarrow	$CO_2 + 2H_2O$	(R8)

The independent modeled O_2 uptake in large captured the seasonal variability of the O_2 uptake as measured in recovered sediment cores incubated at in situ conditions in the laboratory at an average δ_{O_2} value of $457 \mu\text{m}$ (Fig. 1). Previous experimental work has shown that the annual variability in the benthic O_2 uptake at this site is controlled primarily by changes in the sedimentation rate of organic material, bottom water temperature, and O_2 concentration (Rasmussen and Jørgensen 1992; Glud et al. 2003). The model results showed that the presence of a static $900\text{-}\mu\text{m}$ -thick DBL reduced the benthic O_2 uptake during most of the year (from days 60 to 341), with a maximum reduction of $\sim 25\%$ during late autumn (day numbers 250–280) as compared to a situation without any DBL (Fig. 1). However, during the winter (from days 1 to 59 and days 342 to 365), the model demonstrated an opposite effect with enhanced O_2 uptake rates in the presence of the $900\text{-}\mu\text{m}$ -thick DBL (Fig. 1). The presence of a static DBL thus dampened the seasonal fluctuations in the benthic O_2 uptake, an effect that increased with the imposed DBL thickness (Fig. 1). The reason for this response is that during summer the DBL impedes the O_2 uptake of the very active sediment, which is enriched with labile organic material. This stimulates the anaerobic activity and leads to an accumulation of a larger pool of reduced iron sulfides. This “ O_2 debt” is subsequently “repaid” during the winter, leading to an elevated O_2 oxidation during this period. Without any DBL, the O_2 uptake during the summer months is higher, and therefore the accumulation of iron sulfides is correspondingly less. This means that the iron sulfide reoxidation during winter months is reduced as compared to a situation with a DBL. Integrated over the entire year, the presence of a $900\text{-}\mu\text{m}$ -thick DBL reduced the modeled benthic O_2 uptake by 10% (from 8.8 to $7.9 \text{ mol m}^{-2} \text{ yr}^{-1}$) as compared to a situation without a DBL (Fig. 2). An average DBL thickness of $900 \mu\text{m}$ is, however, extreme. When imposing a more realistic value of $600 \mu\text{m}$, the annual O_2 uptake was reduced by 5%, while the reduction with a $300\text{-}\mu\text{m}$ -thick DBL was only 2%.

The presence of a DBL thus had only a modest effect on the annual O_2 uptake even in this diagenetically relatively active sediment (a factor of 1.02–1.10 for δ_{O_2} values of $300\text{--}900 \mu\text{m}$). Yet the DBL had a major impact on the relative contributions of the O_2 -consuming processes (Fig. 2). The model results showed that imposition of a $900\text{-}\mu\text{m}$ -thick DBL reduced the O_2 respiration by 54% (from 2.6 to

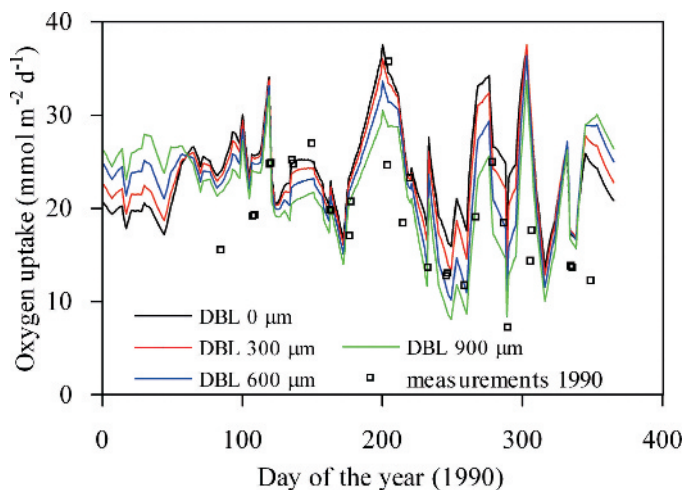


Fig. 1. Dynamics of the benthic O_2 uptake rate throughout a year as modeled at four different static DBL thicknesses. Actual laboratory measurements are extracted from Glud et al. (2003) and are included for comparison (open squares).

$1.2 \text{ mol m}^{-2} \text{ yr}^{-1}$) and increased the O_2 oxidation by 8% (from 6.2 to $6.7 \text{ mol m}^{-2} \text{ d}^{-1}$), both relative to a situation without the presence of a DBL (Fig. 2). The two effects thus counteracted each other, and the overall mineralization rate of organic material was not affected by the presence or absence of a DBL. The minor decrease in the total O_2 uptake following DBL imposition was caused by higher release rates of reduced inorganic components that now were oxidized in the overlying water rather than in the sediment (not shown).

Transition in the O_2 -consuming processes following changes in the DBL thickness—The dynamics of O_2 consumption following a sudden change in DBL thickness were investigated at three different sedimentation rates of 2, 1, and 0.5 times the estimated organic loading experienced in 1990, $9.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Jørgensen 1996). To best illustrate the effects of these changes, all other input parameters were kept constant at their annual mean values.

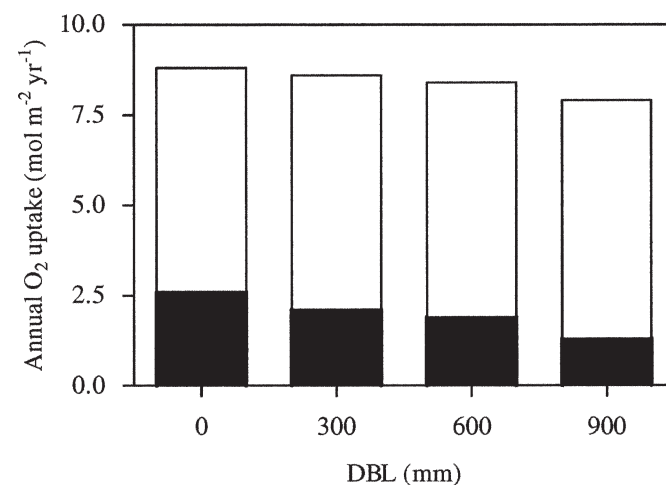


Fig. 2. The annual O_2 uptake as derived from the described model at four different static DBL thicknesses. Closed bars reflect O_2 being consumed by heterotrophic activity (O_2 respiration), while open bars reflect O_2 being used for oxidation of reduced constituents from the anaerobic degradation (O_2 oxidation).

The model was at steady state before the $600\text{-}\mu\text{m}$ -thick DBL was eliminated by setting the O_2 concentration at the sediment surface equal to the value of the mixed water phase. The dynamic response in the O_2 distribution and in selected diagenetic processes was then followed. The steady-state O_2 consumption rate prior to DBL elimination at the three respective carbon loadings equaled 30, 24, and $13 \text{ mmol m}^{-2} \text{ d}^{-1}$. The corresponding O_2 penetration depths, defined at the sediment depth where the O_2 penetration was below $10 \mu\text{mol L}^{-1}$, were 0.7, 1.3, and 4.5 mm, respectively (Figs. 3, 4). These ranges cover conditions in most investigated coastal areas with cohesive sediments. The removal of the DBL immediately resulted in increasing O_2 penetration depths, but the rate of increase gradually leveled off as the new steady-state value was approached (Figs. 3, 4). In accordance with this, the benthic O_2 uptake for the three respective sedimentation rates increased shortly after DBL elimination to maximum

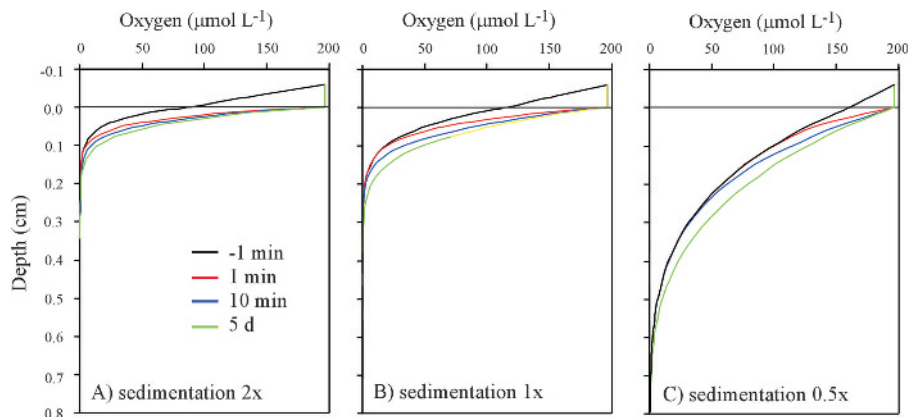


Fig. 3. Benthic O_2 microprofiles as modeled before and 1 min, 10 min, and 5 d after eliminating a $600\text{-}\mu\text{m}$ -thick DBL in sediment exposed to three different sedimentation regimes (2, 1, and 0.5 times the loading experienced in 1990). The horizontal lines indicate the position of the sediment–water interface.

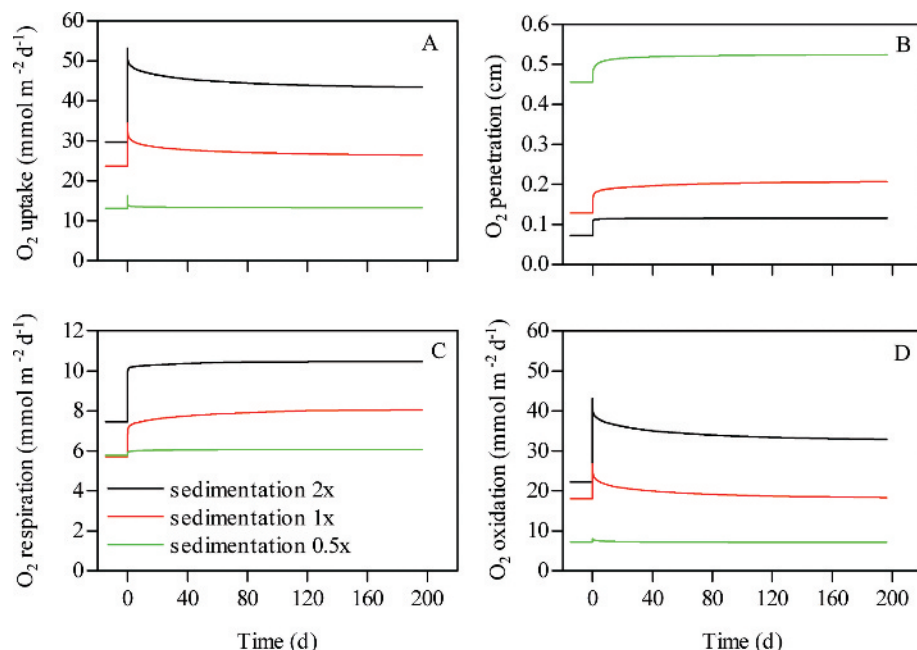


Fig. 4. (A) Total O₂ uptake, (B) O₂ penetration depth, (C) amount of O₂ consumed by aerobic respiration (O₂ respiration), and (D) reoxidation processes (O₂ oxidation) before and after the elimination of a 600- μ m DBL at time 0. The dynamic response is followed for three different sedimentation regimes of 2, 1, and 0.5 times the loading of 1990.

values of 54, 35, and 16 mmol m⁻² d⁻¹. However, the O₂ uptake subsequently decreased at a gradually slower pace, slowly approaching the new elevated steady-state values, which were reached only many months after DBL elimination (Fig. 4).

The overall increase in the O₂ uptake following DBL elimination was the net result of changes in three O₂-consuming processes, each showing different kinetics: O₂ respiration, O₂ oxidation of reduced solutes, and O₂ oxidation of reduced solids. After DBL elimination, the O₂ respiration increased gradually along with the increasing O₂ penetration depth (Fig. 4B,C). However, the O₂ oxidation declined after the initial stimulation as the reduced pools of solutes (Fe²⁺ and Mn²⁺) and solids (FeS and FeS₂) gradually were oxidized (Figs. 4D, 5A,B). The nitrification rate increased with the gradual expansion of the oxic zone (Fig. 5B), while sulfide and methane oxidation accounted for <<1% of the total O₂ uptake (not shown). The oxidation of the solid pool was slow, and the oxidation rate of the solids roughly declined with a half-life value of ~600 h; the corresponding value of the reduced solutes was only in the order of ~4 h (Fig. 5C). Eventually, the oxidation rate of reduced compounds fell below the rate experienced during the presence of a DBL, as also reflected in Figure 2. After the simulations had reached steady state without the presence of a DBL, the respective DBL thicknesses were reintroduced. As was the case for the DBL elimination, the DBL imposition caused an instantaneous response followed by a slow gradual reversion to the original O₂ distribution as the concentration profiles of reduced solutes and solids reestablished (data not shown).

In nature the hydrodynamic forcing constantly changes following variations in tidal currents, wind forcing, seiche, and wave actions, and thus the DBL thickness does not have a constant, static value. The simulations presented here thus demonstrate only the principles of changing the DBL thickness. The overall conclusion is that the combined impact of DBL variations on the long-term O₂ uptake is minor, as changes in the O₂ respiration following changes in O₂ availability are counterbalanced largely by corresponding changes in O₂ oxidation rate, adjusting both in time (seasonally) and in space (sediments depth) to the DBL variations.

Effects of variable flow velocity on the O₂ exchange dynamics—The free-flow velocity at 1 m above the sediment in central Aarhus Bay was monitored continuously by an Aanderaa RCM 7 Current Meter during 18 December 1990–12 January 1991 and 19 February 1991–15 April 1991 (Valeur et al. 1992). On five occasions during that period, the DBL thickness was simultaneously measured by in situ microprofiling (Gundersen et al. 1995; Glud et al. 2003). The in situ measurements of the DBL thickness reflect average conditions during a measuring period of roughly 10–15 min, and the average standard deviation of three to six parallel measurements was in the order of 10%. The in situ flow velocities represent average values of 2-h intervals, and thus the time scales were not completely aligned. Nevertheless, the data showed that an increase in flow velocity from 5.0 to 10.5 cm s⁻¹ reduced the δ_{O_2} by ~50% from 620 to 300 μ m (Fig. 6). There exist only very few simultaneous recordings of the in situ flow velocity and the DBL thickness, but several combined data

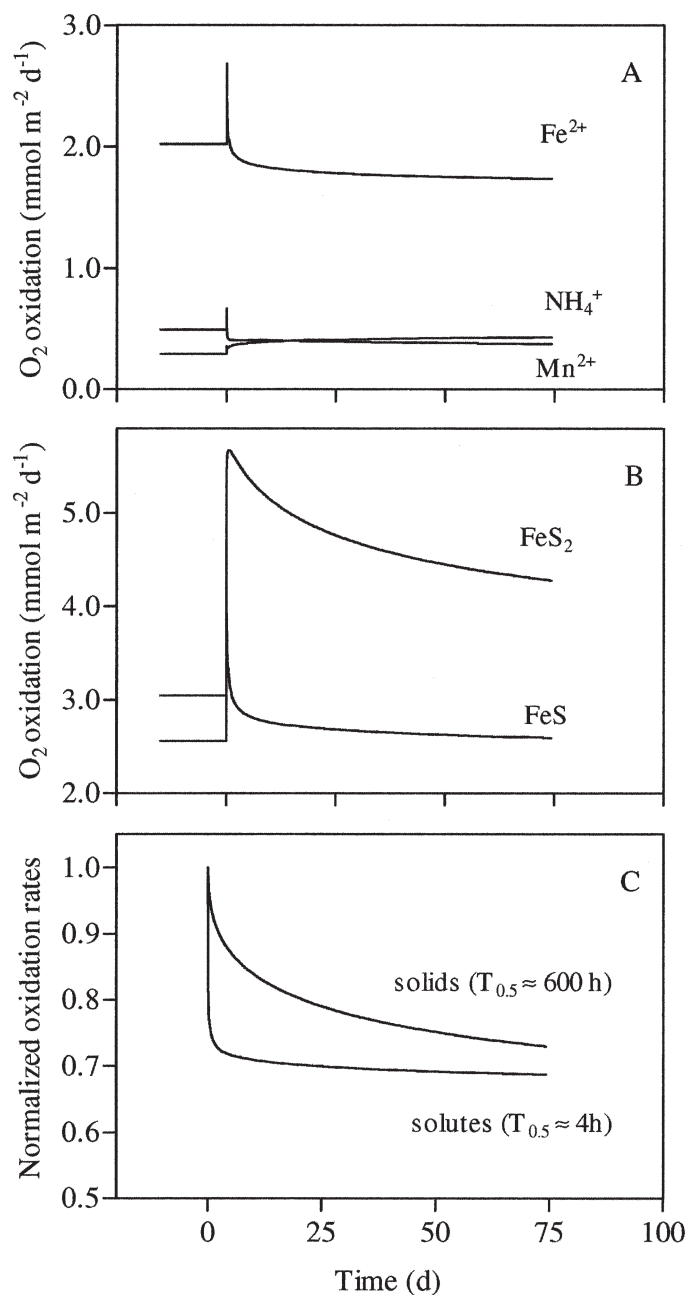


Fig. 5. (A,B) The O₂ oxidation rate related to oxidation of NH₄⁺, Fe²⁺, Mn²⁺, FeS and FeS₂ according to the redox equations of Table 1 before and after elimination of a 600- μ m-thick DBL at time 0. (C) Normalized oxidation rates as a function of time for all reduced solutes and solids after removal of a 600- μ m-thick DBL. The rates at time 0 are set to 1, and the half-life value as estimated from the decline in the oxidation rates are indicated.

sets from laboratory-based investigations have been presented (e.g., Jørgensen and Des Marais 1990). Despite quite different hydrodynamic conditions, the in situ data from Aarhus Bay match measurements from a laboratory-based flume study by Steinberger and Hondzo (1999) remarkably well (Fig. 6). The alignment between the two data sets in no way implies that the hydrodynamic forcing in the two situations can be compared, but it provides us with

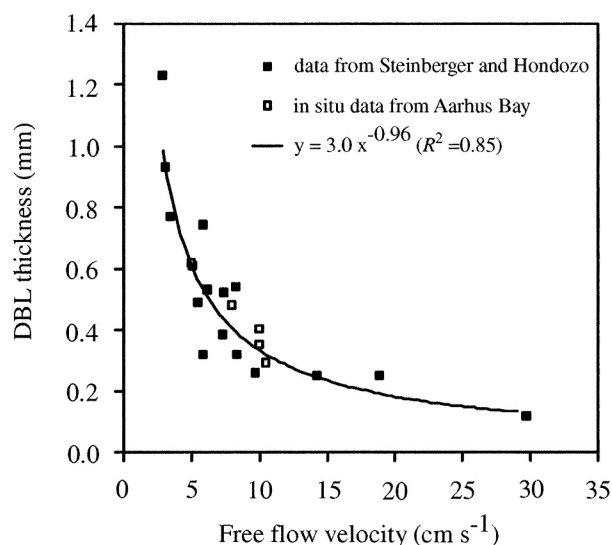


Fig. 6. Closed symbols show the DBL thickness versus free-flow velocity as measured by an oxygen microelectrode in a laboratory flume (Steinberger and Hondzo 1999). Open symbols show measurements made in situ by an autonomous profiling instrument deployed in central Aarhus Bay (Gundersen et al. 1995; Glud et al. 2003). The line represents the fitted relation, where y is the DBL thickness in cm.

a reasonable relation between the flow velocity and the DBL thickness that we can apply in our theoretical exercise for Aarhus Bay. By using a power-function fit to the compiled data in Fig. 6, we derived δ_{O_2} values from the recorded in situ flow velocity data measured in Aarhus Bay. The relation was poorly defined around the end points, so to avoid unrealistic extrapolations in the δ_{O_2} estimates, we did not allow δ_{O_2} to vary outside the range given by the observed data ($120 \mu\text{m} < \delta_{O_2} < 1,230 \mu\text{m}$) (Fig. 6). Assuming that the flow velocities of the 3-month measuring period realistically represented the annual flow dynamics, we extrapolated the data set to cover an entire year by repeating the data set four consecutive times. The average DBL thickness of the constructed data set was $790 \mu\text{m}$, which was only slightly above the estimated annual average at the investigated site ($\sim 600\text{--}700 \mu\text{m}$; see above discussion). The constructed data set on DBL variability was subsequently imposed in the model instead of the static δ_{O_2} values of the previous analysis.

The result expressed extensive short-term variability in the instantaneous benthic O₂ uptake, in the O₂ concentration at the sediment surface, and, to lesser extent, in the O₂ penetration depth (Fig. 7). On time scales of a few hours, the benthic O₂ uptake could vary by 10–30% of the O₂ uptake modeled using a static annual mean DBL thickness of $790 \mu\text{m}$. However, the modeled annually O₂ uptake was identical during the two DBL scenarios. These findings strongly suggest that the in situ O₂ dynamics are much more extensive than previously anticipated. This is most clearly seen by focusing in on some specific periods with nearly constant O₂ concentration in the bottom water (Fig. 8). Despite the relatively stable O₂ concentration in the overlying water, the O₂ concentration at the sediment

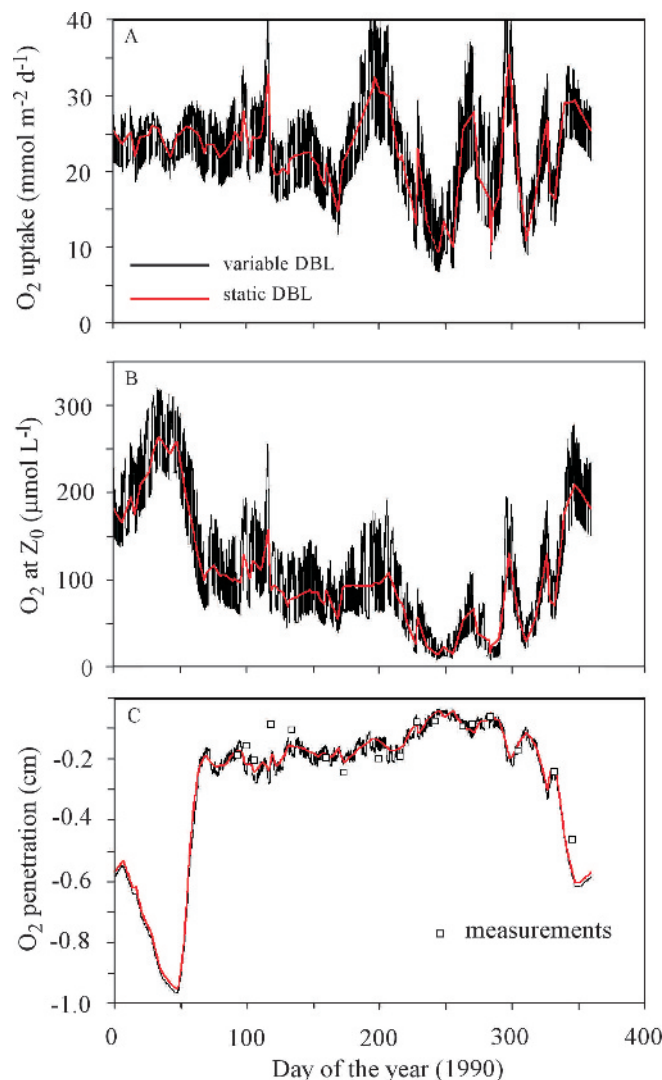


Fig. 7. (A) O_2 uptake, (B) O_2 concentration at the sediment surface, and (C) O_2 penetration depth. All modeled with a variable (black line) and a static (red line) DBL thickness ($790\ \mu\text{m}$).

surface varied by almost $100\ \mu\text{mol L}^{-1}$ on time scales of a few hours to days because of the variable DBL thickness. The O_2 concentration within the sediment fluctuated correspondingly, but with a gradual dampening of the amplitude with increasing sediment depth.

Discussion

DBL impedance of marine sediments—The first attempts to quantify the DBL impedance of marine sediments assumed depth-independent O_2 consumption rates and that the O_2 was used solely for heterotrophic activity “ O_2 respiration” (Archer et al. 1989a). From this it follows that the removal of a DBL would enhance the benthic O_2 uptake by a factor of $(C_0/C_v)^{0.5}$, where C_0 and C_v represent the O_2 concentration at the sediment surface and in the mixed water column, respectively (Archer et al. 1989a; Reimers and Glud 2000). Calculations show that this approach would predict that the removal of a $900\text{-}\mu\text{m}$ -thick

DBL from the eutrophic sediments of Aarhus Bay on average would enhance the annual benthic O_2 uptake by 58%. While the assumptions behind such a calculation may be partly fulfilled in deep-sea sediments with a much deeper oxic zone, they do not represent coastal, shelf, or slope sediments. The present theoretical study, which accounted for the complex O_2 consumption kinetics of diagenetically active marine sediments, estimated only a minor increase of $\sim 11\%$ in the annual O_2 uptake (Fig. 2) following the removal of a $900\text{-}\mu\text{m}$ -thick DBL. The increased O_2 uptake was related to elevated benthic O_2 oxidation of reduced solutes from the anaerobic mineralization (mainly NH_4^+ , Mn^{2+}) that during DBL imposition had been oxidized in the overlying water column rather than in the sediment. The model results also showed that the higher O_2 availability on DBL removal caused a 13% lower pyrite burial rate.

The long-term impedance exerted by the DBL on the benthic O_2 uptake was thus of minor importance for the total O_2 uptake and the carbon mineralization even in this meso- to eutrophic setting. The main reason is that in such areas the benthic mineralization is dominated by anaerobic degradation processes, and the model allowed the oxidation zone for reduced metal and sulfur compounds to gradually migrate closer to the sediment surface as the O_2 availability decreased with increasing DBL thickness. The O_2 oxidation of solids tends to move seasonally toward periods with low input of organic material, and the DBL presence thereby dampens the seasonal variability in the benthic O_2 uptake (Fig. 1). However, the total organic carbon degradation rate remained unaltered. This result aligns well with the conclusion of Jørgensen and Boudreau (2001), who predicted that if O_2 consumption were dominated by oxidation processes, the steady-state O_2 uptake would remain independent of the O_2 concentration at the sediment surface.

The present model does not account for possible differences in the efficiency of aerobic versus anaerobic carbon degradation. It has been suggested that carbon preservation in the absence of O_2 is higher because of less efficient degradation of refractory material (and lack of oxygen radicals) but that long-term oxygen exposure time (OET) is required to make any marked difference (Hedges et al. 1999). In environments with high deposition rates (typically rich in bioturbating fauna), the impact of DBL thickness on the OET must be marginal. It is, however, important to emphasize that the DBL thickness strongly influences the relative importance of the processes responsible for the benthic O_2 consumption: the O_2 respiration versus the O_2 oxidation of reduced solutes and solids (Fig. 2).

In a recent nondynamic model study by Kelly-Gerreyn et al. (2005), the maximum increase in the benthic O_2 uptake following the elimination of a 1-mm -thick DBL was estimated to be 22%. This, however, was for sediments that were dominated by aerobic mineralization, with high lability of the entire organic carbon pool, relatively shallow O_2 penetration depth ($2\text{--}4\text{ mm}$), no metal cycling, and sulfate reduction fueled mainly by sulfate from the benthic sulfide oxidation. Such environments are not very representative for marine settings, and even under circumstances

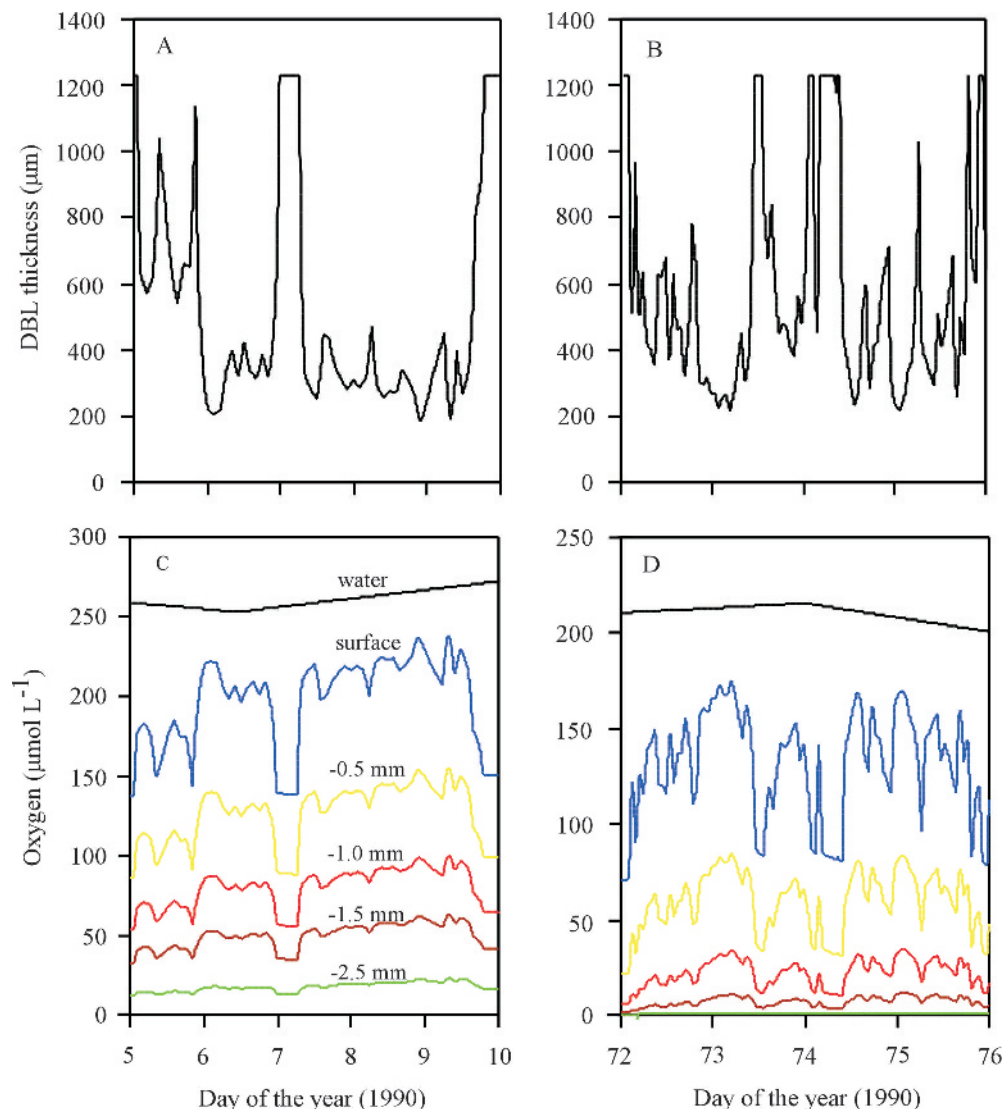


Fig. 8. (A,B) The DBL thickness calculated from the regression curve in Fig. 6 and in situ flow velocities measured in central Aarhus Bay (Valeur et al. 1992) for two 4–5-d periods in mid- and late winter of 1990. Panels (C) and (D) show the modeled O₂ concentration in the water column and at five depths between the sediment surface (0.0 mm) and 2.5-mm subsurface for the two periods. Periods where the DBL thickness was truncated as it reached the maximum thickness permitted are apparent. The minimum value was not reached within the selected time frame.

that would favor potential DBL impedance, theoretical DBL elimination enhanced the O₂ uptake only by roughly 20–25%. For typical coastal sediments, variations in the DBL should be of minor importance for the long-term benthic O₂ uptake according to our model results.

In deep-sea sediments with low organic carbon input, the oxygen uptake is dominated by aerobic heterotrophic respiration (Thamdrup 2000). Here the O₂ penetration depth is measured in centimeters, however, and the large interstitial O₂ pool has a lifetime of several hours or days (Wenzhöfer and Glud 2002). Thus, the diffusion time for O₂ across the DBL (i.e., 5–10 min) is short compared to the transport time down through the oxic zone, and DBL variations cannot be expected to have any major impact on

the benthic O₂ uptake rate (e.g., Reimers et al. 2001). This trend is also reflected in the modeling results assuming reduced carbon loading to the sediment of Aarhus Bay (Fig. 4).

Microbial mats of aerobic chemolithotrophic bacteria represent the other extreme. In such mats the average turnover time of O₂ is in the order of seconds, and the O₂ transport time across the DBL is long compared to the interstitial transport times. Consequently, the DBL strongly regulates fluxes and process rates in the mat, including the rate of aerobic sulfide oxidation (e.g., Jørgensen and Revsbech 1983). Increasing the DBL thickness would in this case reduce the O₂ uptake rate, as a correspondingly larger fraction of the H₂S oxidation would occur in the

overlying water. The benthic carbon mineralization, which in such a system is driven entirely by sulfate reduction, would hardly be affected since the SO_4^{2-} supply to the sulfate reducers is controlled by interstitial diffusion rather than by transport through the DBL.

In conclusion, the steady-state modeling results predict that the DBL thickness has only a minor importance for the long-term benthic O_2 uptake or carbon mineralization in most marine sediments. The dynamic modeling also documented that instantaneous O_2 exchange rates were significantly affected by changes in the DBL thickness. The changes in O_2 uptake rates following a DBL perturbation were significant and quickly dissipated before gradually approaching a new steady state that within the model was achieved only after several months because of a relatively large and slowly reacting pool of metal sulfides.

DBL and short-term interstitial O_2 dynamics—Microsensor studies of the sediment–water interface have documented that eddies from the overlying water induce stochastic O_2 fluctuations within the DBL (Gundersen and Jørgensen 1990; Jørgensen and Des Marais 1990). The fluctuations reflect the eddy characteristics and become smaller and faster at increasing flow velocities. The variations are dampened down through the DBL and vanish just below the sediment surface, where the O_2 concentration remain stable (Røy et al. 2004). The theoretical analysis presented here predicts that the in situ O_2 distribution within sediments is dynamic but on a somewhat longer time scale of minutes, hours, or days as a consequence of continuous variations in the DBL thickness.

To analyze the effect of DBL variations on the instantaneous O_2 uptake, we constructed a time series of the in situ DBL thickness. Obviously, the modeling result depends very much on the characteristics of this constructed data set. Although there is a good agreement between the data of Steinberger and Hondzo (1999) and the in situ DBL measurements in Aarhus Bay (Fig. 6), it does not imply that the hydrodynamic conditions can be compared. However, the trend of the data aligns with the few other experimental data sets relating flow velocity to the DBL thickness (Gundersen and Jørgensen 1990; Jørgensen and Des Marais 1990). The flow velocity was measured 1 m above the seafloor, and it may not be the best proxy for the turbulent energy dissipation of the benthic boundary layer, which represents the hydrodynamic forcing regulating the DBL thickness (Higashino et al. 2003). The fact that we truncated potentially large DBL thicknesses beyond the range of 120–1,230 μm also biased the analysis, as can be seen in Fig. 8. However, without this boundary condition, the fluctuations in the O_2 concentration and the O_2 uptake rates would have been even larger, and the revealed fluctuations can in that respect be regarded as conservative estimates. A more realistic modeling approach will await a complete data set on in situ variations in hydrodynamic forcing and DBL thicknesses from coastal sediments. As a sensitivity test of our modeling results, we also applied another DBL–current

relationship (Jørgensen and Des Marais 1990) that did not change our overall conclusions.

The modeled sediment O_2 dynamics align with direct in situ measurements by microsensors positioned at the sediment surface in a lake at 32-m water depth (Lorke et al. 2003). Here, repetitive recordings at different sediment depths indicated a 10–20% variation in the O_2 concentration in the upper 1–2 mm of the sediment. Further, the microsensor measurements documented that the δO_2 varied by a factor of 5 (from 160 to 840 μm) on a diel scale, and hydrodynamic analysis indicated that internal seicheing was responsible for the variations in the DBL thickness and thereby the interstitial O_2 distribution (Lorke et al. 2003). Even though in situ microsenesing provides high-quality data on the benthic O_2 distribution, it does represent an invasive approach since the placement of microsensors and instrumentation on the seafloor will affect the local hydrodynamic and the interstitial O_2 distribution of diagenetically active sediments (Glud et al. 1994; Parker et al. 2002). The quantitative impact of this is difficult to evaluate, but it does bias in situ DBL observations.

Measurements performed in a small flume channel filled with coastal sediment very similar to the sediments of central Aarhus Bay were performed to evaluate changes in the interstitial O_2 concentration following changes in the DBL thickness (data not shown). We inserted microelectrodes from below through small agar-filled holes and penetrated through the sediment up into the oxic zone and the DBL (for setup, see Glud et al. 1994). The average flow velocity of the channel was varied between 1.5 and 7.7 cm s^{-1} , which resulted in a range of δO_2 values between 800 and 343 μm ($\pm 24 \mu\text{m}$ [$n = 7$]) as measured with the microelectrode. Increasing the flow velocity clearly induced a gradual increase in the O_2 concentrations within the sediment. A shift in the DBL thickness from the maximum to the minimum caused the O_2 concentration at the sediment surface to increase by 42 $\mu\text{mol L}^{-1}$ (from 157 to 199 $\mu\text{mol L}^{-1}$) within 1 min, while the O_2 concentration 0.5 mm below the surface increased by 25 $\mu\text{mol L}^{-1}$ on the same time scale. The O_2 penetration depth concurrently increased from 1.1 to 1.4 mm (data not shown). Obviously, these values do not represent a new steady-state situation but merely reflect that the interstitial O_2 concentration does respond on a short temporal scale to changes in the DBL thickness and that the response can be quite extensive.

The model results presented here, combined with laboratory measurements, suggest that the interstitial O_2 concentration and O_2 microprofiles measured at the seabed are more transient by nature than generally believed. The O_2 uptake rate of coastal sediments varies on time scales of days, hours, and even minutes as a result of changes in hydrodynamic forcing due to tidal currents, seicheing, wind, and wave-induced water movements that affect the DBL thickness. One serious implication is that resolving representative in situ O_2 microprofiles (or O_2 exchange rates derived by chamber incubations) is not trivial, as the O_2 distribution and the O_2 exchange rate change along with variations in the hydrodynamic forcing. The O_2 variability following changes in the DBL thickness overlay other

factors that affect the interstitial O_2 distribution, such as fauna activity and sediment microtopography.

The DBL variability probably has no major effect on the integrated long-term benthic mineralization rates, but the impact on the microbial ecology and specific biogeochemical pathways still need to be investigated. It can be speculated that the metabolic versatility and the chemosensory behavior of bacteria and meiofauna must reflect such O_2 variations and that benthic nitrogen cycling (i.e., nitrification, denitrification, and anammox) are affected by DBL-induced changes in the O_2 , NO_3^- , NO_2^- , and NH_4^+ concentration. Another open question is to what extent in situ-chamber derived O_2 uptake rates in nearshore cohesive sediments are affected by the phenomena studied here. Indeed, significant alternations of the DBL thickness may be imposed when chambers are deployed.

References

- ARCHER, D., S. EMERSON, AND C. R. SMITH. 1989a. Direct measurements of the diffusive sublayer at the deep sea floor using oxygen microelectrodes. *Nature* **340**: 623–626.
- , ———, AND C. E. REIMERS. 1989b. Dissolution of calcite in deep-sea sediments: pH and O_2 microelectrode results. *Geochim. Cosmochim. Acta* **53**: 2831–2845.
- BERG, P., S. RYSGAARD, AND B. THAMDRUP. 2003. Dynamic modelling of early diagenesis and nutrient cycling: A case study in an Arctic marine sediment. *Am. J. Sci.* **303**: 905–955.
- , D. SWANEY, S. RYSGAARD, B. THAMDRUP, AND H. FOSSING. In press. A fast numerical solution to the general mass-conservation equation for solutes and solids in aquatic sediments. *J. Mar. Res.*
- BERNER, R. A. 1980. A rate model for organic matter decomposition during bacterial sulfate reduction in marine sediments, p. 35–44. In R. Dumas [ed.], *Biogeochemistry of organic matter at the sediment-water interface*. CNRS International Colloquium. CNRS Marseille.
- BOUDREAU, B. P. 2001. Solute transport above the sediment-water interface, p. 104–143. In B. P. Boudreau and B. B. Jørgensen [eds.], *The benthic boundary layer*. Oxford Univ Press.
- , AND M. R. SCOTT. 1978. A model for the diffusion controlled growth of deep-sea manganese nodules. *Am. J. Sci.* **278**: 903–929.
- BROECKER, W. S., AND T.-H. PENG. 1974. Gas exchange rates between air and sea. *Tellus* **26**: 21–35.
- CALDWELL, D. R., AND T. M. CHRISS. 1979. The viscous sublayer at the seafloor. *Science* **205**: 1131–1132.
- GLUD, R. N., J. K. GUNDERSEN, N. P. REVSBECH, AND B. B. JØRGENSEN. 1994. Effects on the diffusive boundary layer imposed by microelectrodes. *Limnol. Oceanogr.* **39**: 462–467.
- , H. RØY, AND B. B. JØRGENSEN. 2003. Seasonal dynamics of benthic O_2 uptake in a semi-enclosed bay: Importance of diffusion and fauna activity. *Limnol. Oceanogr.* **48**: 1265–1276.
- , F. WENZHÖFER, A. TENGBERG, M. MIDDELBOE, K. OGURI, AND H. KITASATO. 2005. Distribution of oxygen in surface sediments from central Sagami Bay, Japan: In situ measurements by microelectrodes and planar optodes. *Deep-Sea Res.* **52**: 1974–1987.
- GUNDERSEN, J. K., R. N. GLUD, AND B. B. JØRGENSEN. 1995. Oxygen turnover in the seabed. Havforskning fra Miljøstyrelsen—Hav-90 rapport 14, Miljøstyrelsen, Copenhagen. [In Danish.]
- , AND B. B. JØRGENSEN. 1990. Microstructure of diffusive boundary layers and the oxygen uptake of the sea floor. *Nature* **345**: 604–607.
- HEDGES, J. I., F. S. HU, A. H. DEVOL, H. E. HARTNETT, E. TASAMAKIS, AND R. G. KEIL. 1999. Sedimentary organic matter preservation: A test for selective degradation under oxic conditions. *Am. J. Sci.* **299**: 529–555.
- HIGASHINO, M., H. G. STEFAN, AND C. J. GANTZER. 2003. Periodic diffusional mass-transfer near sediment-water interface. *Theor. J. Environ. Eng.* **129**: 447–455.
- JØRGENSEN, B. B. 1978. A comparison of methods for quantification of bacterial sulfate reduction in coastal marine sediments. 2. Calculation from mathematical models. *Geomicrob. J.* **1**: 29–47.
- 1996. Case study—Aarhus Bay, p.137–154. In B. B. Jørgensen and K. Richardson [eds.], *Eutrophication in coastal marine ecosystems*. American Geophysical Union.
- , AND B. P. BOUDREAU. 2001. Diagenesis and sediment-water exchange, p. 211–238. In B. P. Boudreau and B. B. Jørgensen [eds.], *The benthic boundary layer*. Oxford Univ Press.
- , AND D. J. DES MARAIS. 1990. The diffusive boundary layer of sediments: Oxygen microgradients over a microbial mat. *Limnol. Oceanogr.* **35**: 1343–1355.
- , AND N. P. REVSBECH. 1983. Colorless sulphur bacteria, *Beggiatoa* spp. and *Thiovulum* spp. in O_2 and H_2S microgradients. *Appl. Environ. Microb.* **45**: 1261–1270.
- , AND ———. 1985. Diffusive boundary layers and the oxygen uptake of sediments and detritus. *Limnol. Oceanogr.* **30**: 111–122.
- KELLY-GERREYN, B. A., D. J. HYDES, AND J. J. WANIEK. 2005. Control of the diffusive boundary layer on benthic fluxes: A model study. *Mar. Ecol. Prog. Ser.* **292**: 61–74.
- LI, Y. H., AND S. GREGORY. 1974. Diffusion of ions in seawater and deep sea sediments. *Geochim. Cosmochim. Acta* **38**: 703–714.
- LORKE, A., B. MÜLLER, M. MAERKI, AND A. WÜST. 2003. Breathing sediments: The control of diffusive transport across the sediment-water interface by periodic boundary layer turbulence. *Limnol. Oceanogr.* **48**: 2077–2085.
- PARKER, W. R., K. DOYLE, E. R. PARKER, P. J. KERSHAW, S. J. MALCOM, AND P. LOMAS. 2002. Benthic interface studies with landers: Consideration of lander/interface interactions and their design implications. *J. Exp. Mar. Biol. Ecol.* **286**: 179–190.
- RASMUSSEN, H., AND B. B. JØRGENSEN. 1992. Microelectrode studies of seasonal oxygen uptake in a coastal sediment: Role of molecular diffusion. *Mar. Ecol. Prog. Ser.* **81**: 289–303.
- REIMERS, C. E., AND R. N. GLUD. 2000. In situ chemical sensor measurements at the sediment water interface, p.249–282. In M. Varney [ed.], *Chemical sensors in oceanography*. Gordon and Breach Science.
- , R. A. JAHNKE, AND L. THOMSEN. 2001. In situ sampling in the benthic boundary layer, p.245–263. In B. P. Boudreau and B. B. Jørgensen [eds.], *The benthic boundary layer*. Oxford Univ Press.
- ROBERTS, J., AND A. MCMINN. 2004. Marine diffusive boundary layers at high latitudes. *Limnol. Oceanogr.* **49**: 934–939.
- RØY, H., M. HUETTEL, AND B. B. JØRGENSEN. 2002. The role of small-scale sediment topography for oxygen flux across the diffusive boundary layer. *Limnol. Oceanogr.* **47**: 837–847.
- , ———, AND ———. 2004. Transmission of oxygen concentration fluctuations through the diffusive boundary layer overlying aquatic sediments. *Limnol. Oceanogr.* **49**: 686–692.
- STEINBERGER, N., AND M. HONDZO. 1999. Diffusional mass transfer at the sediment-water pnterface. *J. Environ. Eng.* **125**: 192–199.

- STEN-KNUDSEN, O. 2002. Biological membranes: Theory of transport, potentials and electrical impulses. Cambridge Univ Press.
- THAMDRUP, B. 2000. Microbial manganese and iron reduction in aquatic sediments. *Adv. Microb. Ecol.* **16**: 41–84.
- VALEUR, J. R., M. PEJRUP, AND A. JENSEN. 1992. Particulate nutrient fluxes in Vejle Fjord and Aarhus Bay. Havforskning fra Miljøstyrelsen—Hav-90 rapport 14, Miljøstyrelsen, Copenhagen.
- WENZHÖFER, F., AND R. N. GLUD. 2002. Benthic carbon mineralization in the Atlantic: A synthesis based on in situ data from the last decade. *Deep-Sea Res.* **49**: 1255–1279.
- WESTRICH, J. T., AND R. A. BERNER. 1984. The role of sedimentary organic matter in bacterial sulfate reduction: The G-model tested. *Limnol. Oceanogr.* **29**: 236–249.

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