

## Effect of the diffusive boundary layer on benthic mineralization and O<sub>2</sub> 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 O<sub>2</sub> exchange and O<sub>2</sub> consuming pathways. The analysis documents that the DBL has only minor importance for the annual O<sub>2</sub> uptake of coastal cohesive sediments. Imposing static DBL thicknesses of 300–900 μm decreased the annual O<sub>2</sub> uptake by only 2–10% in comparison to a situation without any DBL. Lower O<sub>2</sub> 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 O<sub>2</sub> uptake was caused mainly by higher benthic release rates of NH<sub>4</sub><sup>+</sup> and Mn<sup>2+</sup>. 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 O<sub>2</sub> distribution and in the benthic O<sub>2</sub> 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 O<sub>2</sub> microprofiles are transient by nature. Dynamic modeling showed that the benthic O<sub>2</sub> concentration and the O<sub>2</sub> 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 O<sub>2</sub> 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  $\sim 10^{-2}$  cm<sup>2</sup> s<sup>-1</sup>, 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<sub>0</sub>) of  $\sim 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> dynamics within the DBL followed (e.g., Gundersen and Jørgensen 1990; Jørgensen and Des Marais 1990; Røy et al. 2004). From high-resolution O<sub>2</sub> microprofiles based on averaged O<sub>2</sub> 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 ( $\delta_{O_2}$ ) 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  $\delta_{O_2}$  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-km<sup>2</sup> 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  $\sim 120$  g C m<sup>-2</sup>. 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  $\sim 6$ ,  $\sim 9$ , and  $\sim 3$ , respectively, with average values of  $\sim 230$   $\mu\text{mol L}^{-1}$ ,  $\sim 2.5$  mm, and  $\sim 25$  mmol m<sup>-2</sup> d<sup>-1</sup>, 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  $\sim 300$   $\mu\text{m}$ , 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<sub>2</sub> 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<sub>10</sub> 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 10<sup>-6</sup> s<sup>-1</sup> and 1.2 10<sup>-8</sup> s<sup>-1</sup> (at 9°C), respectively.

The validated model successfully simulated observed concentration profiles of (1) pore-water species: O<sub>2</sub>, dissolved inorganic carbon (CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>S, and PO<sub>4</sub><sup>3-</sup>); (2) solid species: organic matter (OM), FeOOH, MnO<sub>2</sub>, S<sup>0</sup>, FeS, and FeS<sub>2</sub>; (3) measured sulfate reduction rates; and (4) sediment–water exchange rates of O<sub>2</sub>, CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> (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<sub>2</sub> consumption rates*—In situ microelectrode measurements performed during 1990–1992 showed that the DBL thickness (δ<sub>O<sub>2</sub></sub>) at the investigated site varied between 299 and 706 μm with an average value of 451 μm (*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 microsensors 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 600–700 μm. To evaluate the impact of DBL thickness on seasonal O<sub>2</sub> uptake, we first ran the model with four different static δ<sub>O<sub>2</sub></sub> 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<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> in (R1) is stoichiometrically balanced to the N and P content of the organic matter (OM).

OM + O <sub>2</sub>	→	CO <sub>2</sub> + NH <sub>4</sub> <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup> + H <sub>2</sub> O	(R1)
NH <sub>4</sub> <sup>+</sup> + 2O <sub>2</sub>	→	NO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O + 2H <sup>+</sup>	(R2)
2Mn <sup>2+</sup> + O <sub>2</sub> + 2H <sub>2</sub> O	→	2MnO <sub>2</sub> + 4H <sup>+</sup>	(R3)
4Fe <sup>2+</sup> + O <sub>2</sub> + 6H <sub>2</sub> O	→	4FeOOH + 8H <sup>+</sup>	(R4)
H <sub>2</sub> S + 2O <sub>2</sub>	→	SO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup>	(R5)
FeS + 2O <sub>2</sub>	→	Fe <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup>	(R6)
2FeS <sub>2</sub> + 7O <sub>2</sub> + 2H <sub>2</sub> O	→	2Fe <sup>2+</sup> + 4SO <sub>4</sub> <sup>2-</sup> + 4H <sup>+</sup>	(R7)
CH <sub>4</sub> + 2O <sub>2</sub>	→	CO <sub>2</sub> + 2H <sub>2</sub> O	(R8)

The independent modeled O<sub>2</sub> uptake in large captured the seasonal variability of the O<sub>2</sub> uptake as measured in recovered sediment cores incubated at in situ conditions in the laboratory at an average δ<sub>O<sub>2</sub></sub> value of 457 μm (Fig. 1). Previous experimental work has shown that the annual variability in the benthic O<sub>2</sub> uptake at this site is controlled primarily by changes in the sedimentation rate of organic material, bottom water temperature, and O<sub>2</sub> concentration (Rasmussen and Jørgensen 1992; Glud et al. 2003). The model results showed that the presence of a static 900-μm-thick DBL reduced the benthic O<sub>2</sub> uptake during most of the year (from days 60 to 341), with a maximum reduction of ~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<sub>2</sub> uptake rates in the presence of the 900-μm-thick DBL (Fig. 1). The presence of a static DBL thus dampened the seasonal fluctuations in the benthic O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> debt” is subsequently “repaid” during the winter, leading to an elevated O<sub>2</sub> oxidation during this period. Without any DBL, the O<sub>2</sub> 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-μm-thick DBL reduced the modeled benthic O<sub>2</sub> uptake by 10% (from 8.8 to 7.9 mol m<sup>-2</sup> yr<sup>-1</sup>) as compared to a situation without a DBL (Fig. 2). An average DBL thickness of 900 μm is, however, extreme. When imposing a more realistic value of 600 μm, the annual O<sub>2</sub> uptake was reduced by 5%, while the reduction with a 300-μm-thick DBL was only 2%.

The presence of a DBL thus had only a modest effect on the annual O<sub>2</sub> uptake even in this diagenetically relatively active sediment (a factor of 1.02–1.10 for δ<sub>O<sub>2</sub></sub> values of 300–900 μm). Yet the DBL had a major impact on the relative contributions of the O<sub>2</sub>-consuming processes (Fig. 2). The model results showed that imposition of a 900-μm-thick DBL reduced the O<sub>2</sub> respiration by 54% (from 2.6 to

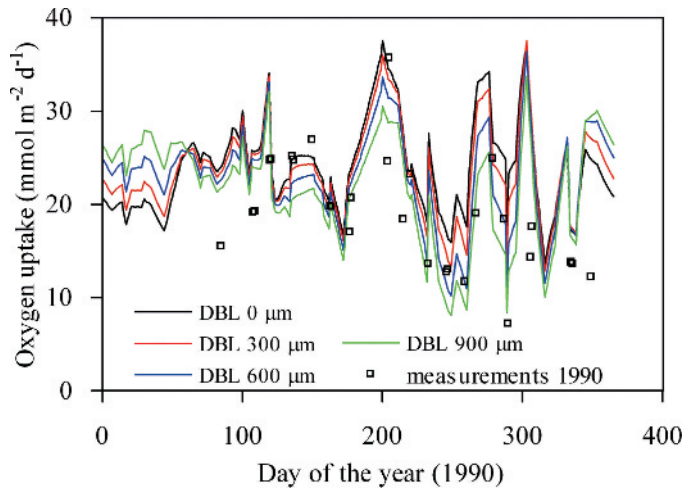


Fig. 1. Dynamics of the benthic  $O_2$  uptake rate throughout a year as modeled at four different static DBL thicknesses. Actual laboratory measurements are extracted from Glud et al. (2003) and are included for comparison (open squares).

$1.2 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) 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.

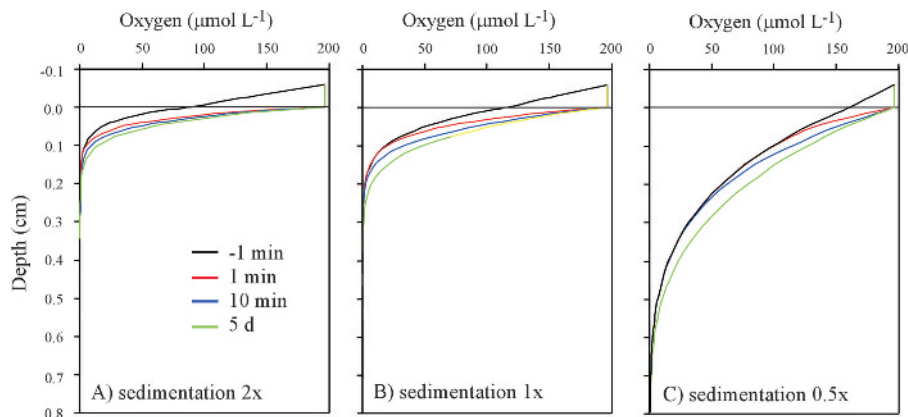


Fig. 3. Benthic  $O_2$  microprofiles as modeled before and 1 min, 10 min, and 5 d after eliminating a  $600\text{-}\mu\text{m}$ -thick DBL in sediment exposed to three different sedimentation regimes (2, 1, and 0.5 times the loading experienced in 1990). The horizontal lines indicate the position of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

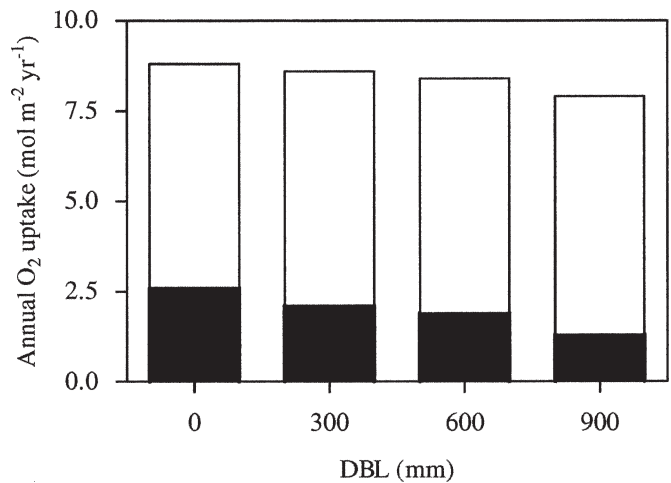


Fig. 2. The annual  $O_2$  uptake as derived from the described model at four different static DBL thicknesses. Closed bars reflect  $O_2$  being consumed by heterotrophic activity ( $O_2$  respiration), while open bars reflect  $O_2$  being used for oxidation of reduced constituents from the anaerobic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

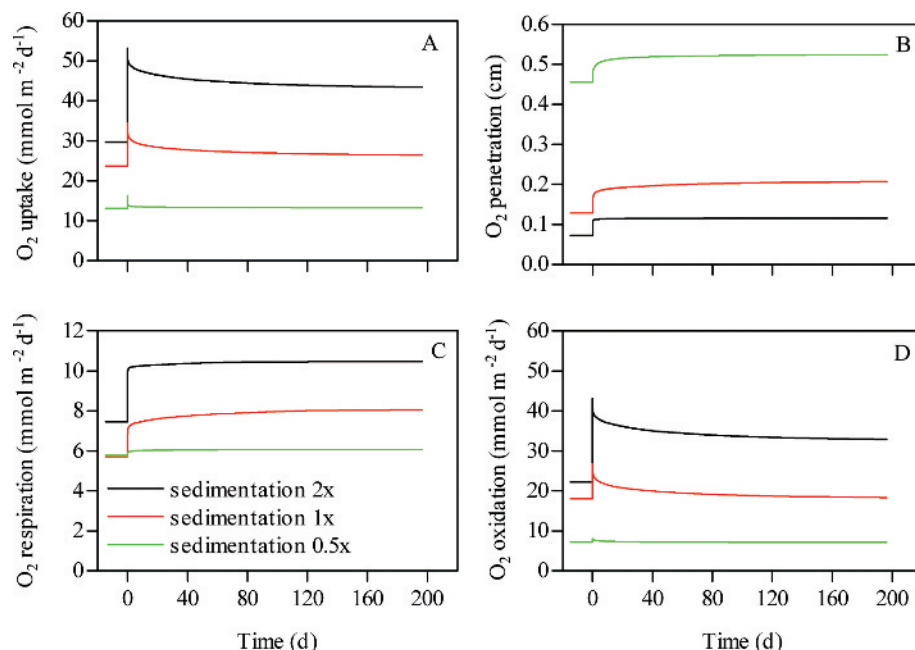


Fig. 4. (A) Total O<sub>2</sub> uptake, (B) O<sub>2</sub> penetration depth, (C) amount of O<sub>2</sub> consumed by aerobic respiration (O<sub>2</sub> respiration), and (D) reoxidation processes (O<sub>2</sub> oxidation) before and after the elimination of a 600- $\mu$ m DBL at time 0. The dynamic response 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<sup>-2</sup> d<sup>-1</sup>. However, the O<sub>2</sub> 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 O<sub>2</sub> uptake following DBL elimination was the net result of changes in three O<sub>2</sub>-consuming processes, each showing different kinetics: O<sub>2</sub> respiration, O<sub>2</sub> oxidation of reduced solutes, and O<sub>2</sub> oxidation of reduced solids. After DBL elimination, the O<sub>2</sub> respiration increased gradually along with the increasing O<sub>2</sub> penetration depth (Fig. 4B,C). However, the O<sub>2</sub> oxidation declined after the initial stimulation as the reduced pools of solutes (Fe<sup>2+</sup> and Mn<sup>2+</sup>) and solids (FeS and FeS<sub>2</sub>) 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> uptake is minor, as changes in the O<sub>2</sub> respiration following changes in O<sub>2</sub> availability are counterbalanced largely by corresponding changes in O<sub>2</sub> oxidation rate, adjusting both in time (seasonally) and in space (sediments depth) to the DBL variations.

*Effects of variable flow velocity on the O<sub>2</sub> 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<sup>-1</sup> reduced the  $\delta_{O_2}$  by ~50% from 620 to 300  $\mu$ m (Fig. 6). There exist only very few simultaneous recordings of the in situ flow velocity and the DBL thickness, but several combined data

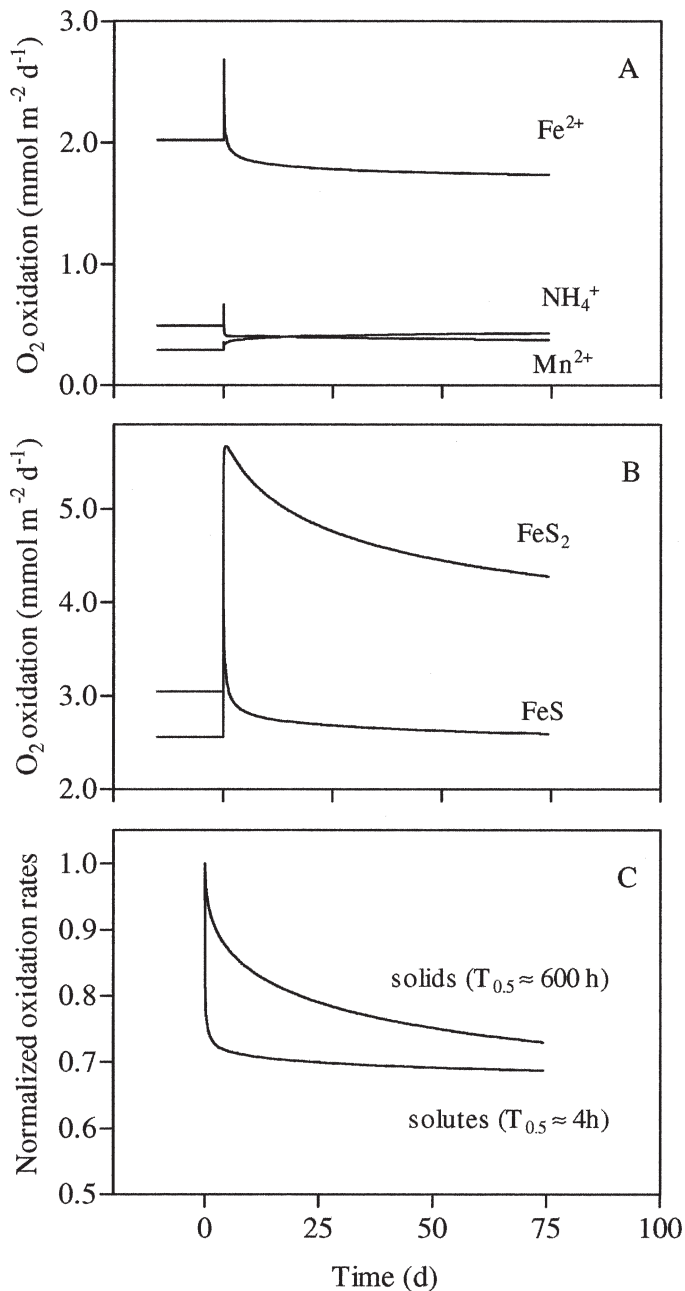


Fig. 5. (A,B) The O<sub>2</sub> oxidation rate related to oxidation of NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, FeS and FeS<sub>2</sub> according to the redox equations of Table 1 before and after elimination of a 600- $\mu$ m-thick DBL at time 0. (C) Normalized oxidation rates as a function of time for all reduced solutes and solids after removal of a 600- $\mu$ 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

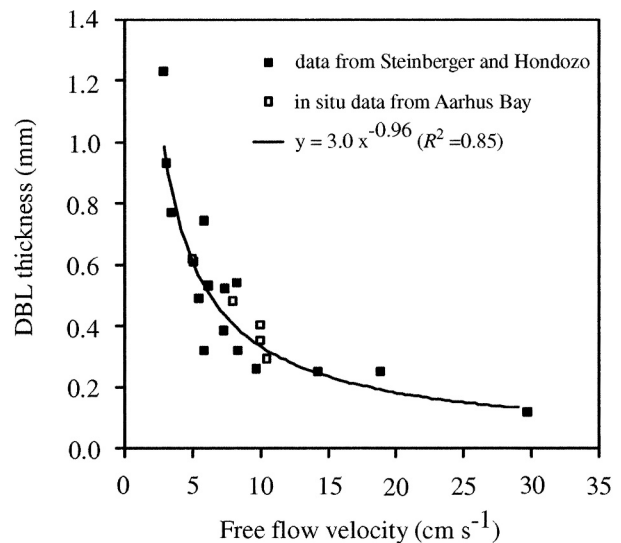


Fig. 6. Closed symbols show the DBL thickness versus free-flow velocity as measured by an oxygen microelectrode in a laboratory flume (Steinberger and Hondzo 1999). Open symbols show measurements made in situ by an autonomous profiling instrument deployed in central Aarhus Bay (Gundersen et al. 1995; 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  $\delta_{O_2}$  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  $\delta_{O_2}$  estimates, we did not allow  $\delta_{O_2}$  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  $\delta_{O_2}$  values of the previous analysis.

The result expressed extensive short-term variability in the instantaneous benthic O<sub>2</sub> uptake, in the O<sub>2</sub> concentration at the sediment surface, and, to lesser extent, in the O<sub>2</sub> penetration depth (Fig. 7). On time scales of a few hours, the benthic O<sub>2</sub> uptake could vary by 10–30% of the O<sub>2</sub> uptake modeled using a static annual mean DBL thickness of  $790 \mu\text{m}$ . However, the modeled annually O<sub>2</sub> uptake was identical during the two DBL scenarios. These findings strongly suggest that the in situ O<sub>2</sub> dynamics are much more extensive than previously anticipated. This is most clearly seen by focusing in on some specific periods with nearly constant O<sub>2</sub> concentration in the bottom water (Fig. 8). Despite the relatively stable O<sub>2</sub> concentration in the overlying water, the O<sub>2</sub> concentration at the sediment

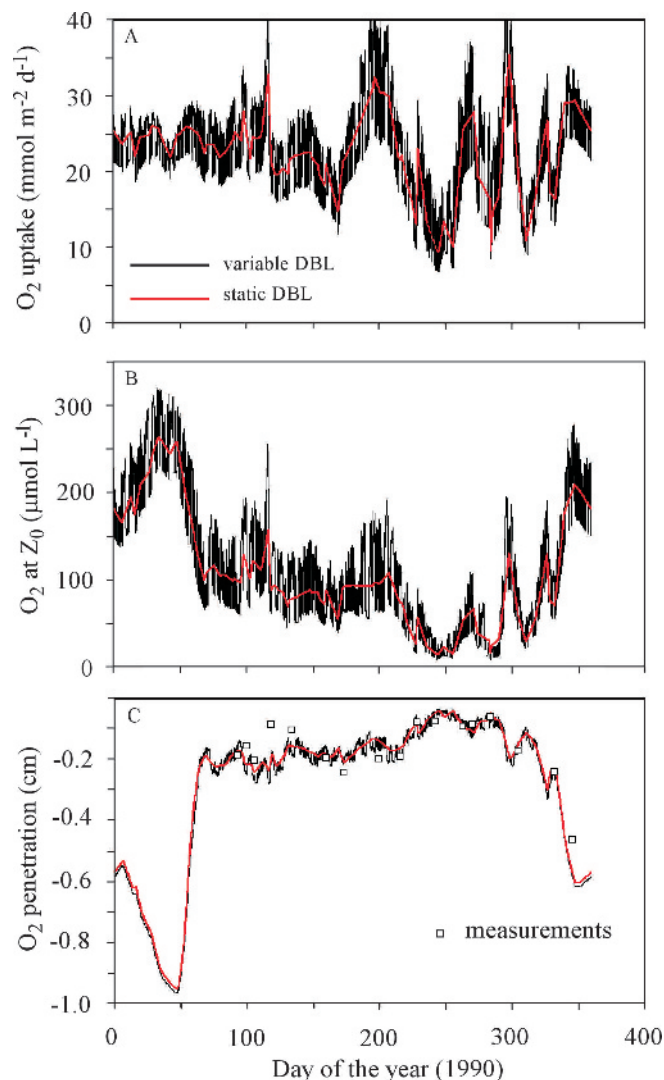


Fig. 7. (A)  $O_2$  uptake, (B)  $O_2$  concentration at the sediment surface, and (C)  $O_2$  penetration depth. All modeled with a variable (black line) and a static (red line) DBL thickness ( $790 \mu\text{m}$ ).

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  $\text{NH}_4^+$ ,  $\text{Mn}^{2+}$ ) 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  $1\text{-mm}$ -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

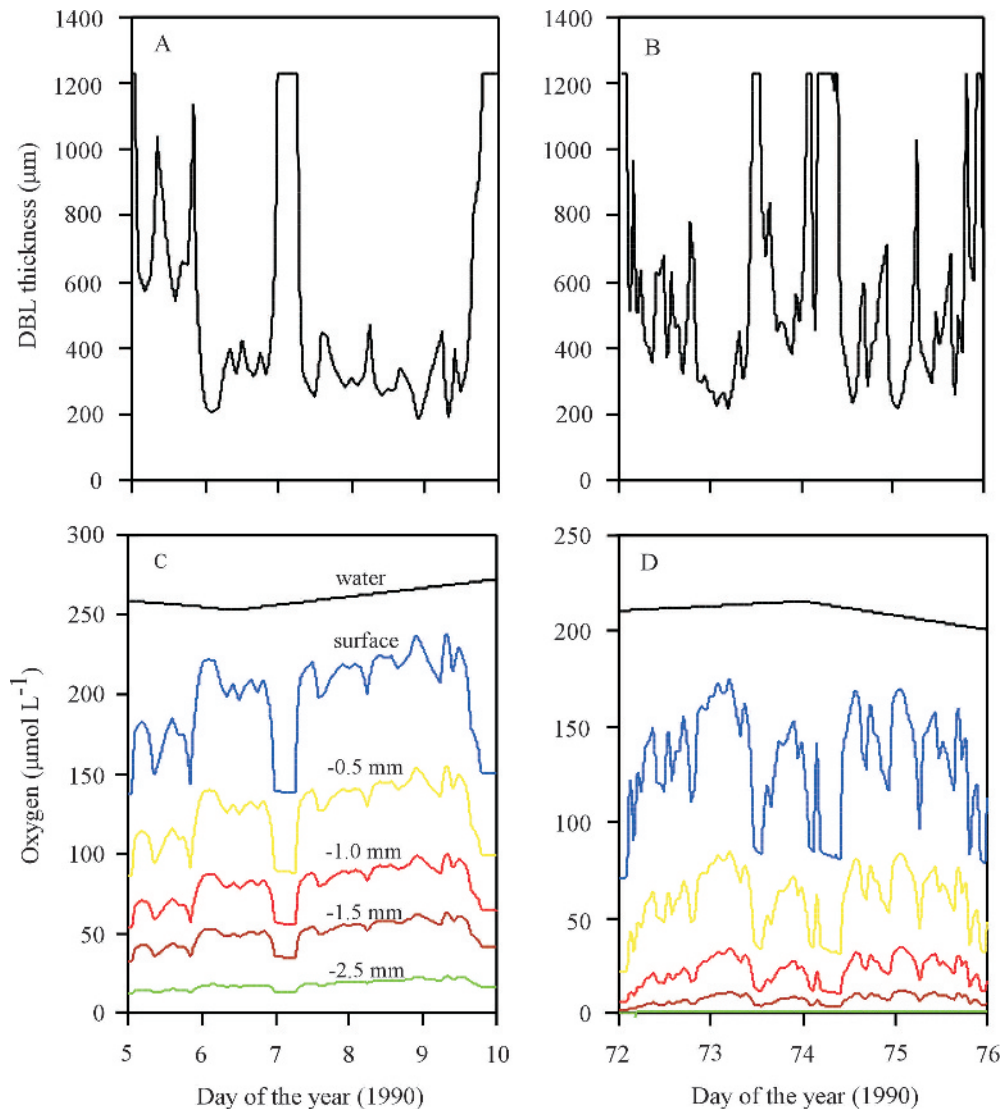


Fig. 8. (A,B) The DBL thickness calculated from the regression curve in Fig. 6 and in situ flow velocities measured in central Aarhus Bay (Valeur et al. 1992) for two 4–5-d periods in mid- and late winter of 1990. Panels (C) and (D) show the modeled  $O_2$  concentration in the water column and at five 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  $O_2$  uptake only by roughly 20–25%. For typical coastal sediments, variations in the DBL should be of minor importance for the long-term benthic  $O_2$  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  $O_2$  penetration depth is measured in centimeters, however, and the large interstitial  $O_2$  pool has a lifetime of several hours or days (Wenzhöfer and Glud 2002). Thus, the diffusion time for  $O_2$  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  $O_2$  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  $O_2$  is in the order of seconds, and the  $O_2$  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  $O_2$  uptake rate, as a correspondingly larger fraction of the  $H_2S$  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  $\text{SO}_4^{2-}$  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  $\text{O}_2$  uptake or carbon mineralization in most marine sediments. The dynamic modeling also documented that instantaneous  $\text{O}_2$  exchange rates were significantly affected by changes in the DBL thickness. The changes in  $\text{O}_2$  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  $\text{O}_2$  dynamics*—Microsensor studies of the sediment–water interface have documented that eddies from the overlying water induce stochastic  $\text{O}_2$  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  $\text{O}_2$  concentration remain stable (Røy et al. 2004). The theoretical analysis presented here predicts that the in situ  $\text{O}_2$  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  $\text{O}_2$  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  $\mu\text{m}$  also biased the analysis, as can be seen in Fig. 8. However, without this boundary condition, the fluctuations in the  $\text{O}_2$  concentration and the  $\text{O}_2$  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  $\text{O}_2$  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  $\text{O}_2$  concentration in the upper 1–2 mm of the sediment. Further, the microsensor measurements documented that the  $\delta_{\text{O}_2}$  varied by a factor of 5 (from 160 to 840  $\mu\text{m}$ ) on a diel scale, and hydrodynamic analysis indicated that internal seicheing was responsible for the variations in the DBL thickness and thereby the interstitial  $\text{O}_2$  distribution (Lorke et al. 2003). Even though in situ microsensing provides high-quality data on the benthic  $\text{O}_2$  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  $\text{O}_2$  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  $\text{O}_2$  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  $\text{cm s}^{-1}$ , which resulted in a range of  $\delta_{\text{O}_2}$  values between 800 and 343  $\mu\text{m}$  ( $\pm 24 \mu\text{m}$  [ $n = 7$ ]) as measured with the microelectrode. Increasing the flow velocity clearly induced a gradual increase in the  $\text{O}_2$  concentrations within the sediment. A shift in the DBL thickness from the maximum to the minimum caused the  $\text{O}_2$  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  $\text{O}_2$  concentration 0.5 mm below the surface increased by 25  $\mu\text{mol L}^{-1}$  on the same time scale. The  $\text{O}_2$  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  $\text{O}_2$  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  $\text{O}_2$  concentration and  $\text{O}_2$  microprofiles measured at the seabed are more transient by nature than generally believed. The  $\text{O}_2$  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  $\text{O}_2$  microprofiles (or  $\text{O}_2$  exchange rates derived by chamber incubations) is not trivial, as the  $\text{O}_2$  distribution and the  $\text{O}_2$  exchange rate change along with variations in the hydrodynamic forcing. The  $\text{O}_2$  variability following changes in the DBL thickness overlay other

factors that affect the interstitial O<sub>2</sub> 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<sub>2</sub> variations and that benthic nitrogen cycling (i.e., nitrification, denitrification, and anammox) are affected by DBL-induced changes in the O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> concentration. Another open question is to what extent in situ-chamber derived O<sub>2</sub> 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.

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