Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion

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ABSTRACT: Oxygen uptake rates and microdistributions of O_2 in sediment of Aarhus Bay, Denmark, were studied over a year. Oxygen uptake was determined in the laboratory by 3 methods: (a) total O_2 uptake in closed cores, (b) O_2 flux through the diffusive boundary layer and (c) O_2 consumption within the oxic surface zone. The O_2 consumption rates in the oxic surface layer, calculated from (b) and (c) using molecular diffusion coefficients of O_2 , closely agreed and accounted for 70 % of the total O_2 uptake. The O_2 uptake rates strongly depended on *in situ* O_2 concentrations in the overlying seawater, which in the bay varied from 100 % air saturation during winter to 23 % during summer. The potentially higher O_2 respiration during the summer months was counteracted by a lower O_2 concentration in the bottom water, which led to a small seasonal variation in O_2 uptake. Depth of the oxic sediment zone reached 5.1 mm during winter, narrowed down rapidly to a few mm upon settling of a spring phytoplankton bloom, and was only 1.2 mm during summer. Modeling of O_2 consumption from O_2 microprofiles showed zero-order kinetics, i.e. constant O_2 consumption rates throughout the oxic zone during winter. Enhanced O_2 consumption was found at the oxic-anoxic interface during summer, presumably due to reducing solutes which diffused up from anoxic layers. Sediment O_2 uptake was impeded by 3 to 5 % during winter and by 12 to 16 % during summer due to transport resistance through the 300 μ m thick diffusive boundary layer. Results demonstrate the importance of the boundary layer for sediment O_2 uptake and its regulation.

INTRODUCTION

Oxygen consumption by marine sediments has been the most widely studied parameter to determine benthic metabolism and organic mineralization. Common techniques for such studies include O_2 uptake measurements in laboratory-incubated sediment cores or *in situ* measurements using benthic flux chambers (e.g. Pamatmat 1971, Smith 1978). In recent years, several studies have also used O_2 microelectrode data to determine the diffusive O_2 flux (Revsbech et al. 1980b, Reimers & Smith 1986, Booi 1989, Sweerts et al. 1989, Hofman et al. 1991). The role of O_2 respiration by the benthic fauna or of their transport of oxic water deep into the sediment has also been studied, either by

directly determining the respiration rate of the faunal community, by calculating their ventilation activity, or by subtracting the diffusive from the total O_2 uptake (e.g. Aller 1978, Kristensen 1985, Kannevorff & Christensen 1986).

The oxic surface zone of coastal sediments is generally a millimeter-thin layer within which intensive respiration takes place. By the use of O_2 microelectrodes it is possible to analyze the distribution of O_2 within this oxic layer at < 100 μ m resolution and thus experimentally to analyze the mechanisms of O_2 consumption in order to understand its regulation. Based on measured microgradients of O_2 , depth distribution of aerobic respiration within the oxic zone can be calculated by simple models (e.g. Revsbech et al. 1986, Nielsen et al. 1990). A diffusive boundary layer (DBL) of 0.2 to 1 mm thickness has furthermore been found in the water immediately over the sediment surface from such microgradient measurements

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(Jørgensen & Revsbech 1985, Jørgensen & Des Marais 1990, Gundersen & Jørgensen 1990, 1991). Oxygen and other dissolved compounds, which exchange across the sediment-water interface, move rapidly through this DBL by molecular diffusion along a near-linear concentration gradient. This diffusion flux can therefore be calculated directly from O_2 microgradients measured in the DBL.

In the present study, we combined measurements of the total O_2 consumption in incubated sediment cores with 2 methods for studying the diffusive O_2 uptake: flux calculations through the DBL and modeling of O_2 consumption rates within the oxic surface zone. Among the goals of the study was to determine how much of the total O_2 uptake was due to diffusion through the DBL and consumption in the oxic surface layer. Regulation of O_2 uptake by varying O_2 concentrations in the overlying water and by diffusion impedance due to the DBL were also studied.

MATERIALS AND METHODS

Study site. Seasonal oxygen uptake was studied in fine-grained sediment from 1 station (56°09.1' N, 10°19.2' E) in central Aarhus Bay, Denmark, at 15 m water depth. Samples were taken from onboard ship 24 times during the period March 1988 to May 1989 and were carefully transported to the laboratory in Aarhus for incubation within 3 to 5 h. Four other stations at 13 to 33 m water depth in southern Kattegat, situated in the Baltic Sea – North Sea transition area, were studied onboard ship during 2 cruises with RV 'Gunnar Thorson' (Danish National Agency for Environmental Protection).

Sediment sampling and incubation. Sediment was collected by a Haps corer (Kannevorf & Nicolaisen 1973). Only cores with a visibly undisturbed sediment surface and clear overlying water were accepted. Subcores of 5 cm diameter were taken in 20 cm long Plexiglas tubes for oxygen studies and other determinations. Twenty liters of seawater was taken with a Niskin bottle 0.5 to 1 m over the bottom for core incubations. Seawater samples were also taken from the surface and bottom for determination of temperature, salinity, and oxygen.

For each sampling occasion, 6 sediment cores were incubated uncapped, submerged in a dark aquarium containing bottom water from the sampling station. Water in the aquarium was maintained at *in situ* temperature and continuously flushed with an air/ N_2 gas mixture to maintain *in situ* O_2 concentrations over all sediment cores. A rotating, teflon-coated magnet, 3×15 mm, was attached to the inner wall of each tube over the sediment. Magnets rotated at 90 rpm, driven by a large, external magnet, and produced a turbulent

flow in the cores which was evaluated to be realistic relative to *in situ* flow velocities in Aarhus Bay observed by underwater video. Cores were pre-incubated for 2 h prior to measurements to assure steady-state oxygen distributions in the sediment. At the start of measurements, all cores were open at the top with homogeneously stirred sea water of *in situ* O_2 concentration. Microgradients of O_2 were measured, and only then were the cores stoppered for total O_2 uptake measurements.

Oxygen microgradients. The O_2 distribution was measured by O_2 microelectrodes provided with a built-in reference and a guard cathode (Revsbech 1989b). Electrodes had a sensing tip of 5 to 10 μ m and a linear O_2 response within 0 to 100 % air saturation. Velocity sensitivity of the electrodes (i.e. signal increase in flowing vs stagnant water) was $< 2-3$ %, and the 90 % response time was ca 1.5 s. Electrode currents for 0 % and 100 % air saturation of O_2 at 20 °C were 2 to 8 pA and 200 to 300 pA, respectively. Linear calibration was done for each O_2 profile between the overlying water of known O_2 concentration and the anoxic layer within the sediment.

The electrode was attached to a micromanipulator driven by a stepping motor and data were collected directly on a computer. Four O_2 profiles were measured in each of 6 cores at random positions. Oxygen measurements were taken at 50 to 200 μ m depth intervals. In order to position exactly the measured O_2 microprofiles relative to the sediment-water interface, and thereby to determine the thickness of the DBL, the sediment and the electrode tip were observed simultaneously under a dissecting microscope.

Diffusive oxygen flux. The diffusive flux, J , of O_2 downwards across the sediment-water interface was calculated from the measured O_2 microgradients, dC/dz , through the DBL (Crank 1983, Jørgensen & Revsbech 1985):

$$J = -D \, dC/dz \quad (1)$$

where D = molecular diffusion coefficient of oxygen, C = O_2 concentration, and z = depth ($z = 0$ at sediment-water interface). The flux can also be expressed as the finite shift in C across the DBL:

$$J = D(C_w - C_o)/z_\delta \quad (2)$$

where C_w = O_2 concentration in the mixed, overlying water, C_o = O_2 concentration at the sediment-water interface, and z_δ = the thickness of the effective DBL (cf. Jørgensen & Revsbech 1985). Values of D were taken from Broecker and Peng (1974) and were recalculated to *in situ* temperature using the Stokes-Einstein relation (Li & Gregory 1974).

Modeling of oxygen consumption: zero order. Oxygen consumption rates per unit sediment volume in the oxic surface zone were calculated from the measured O_2 microprofiles assuming zero-order or first-order consumption kinetics. By zero-order kinetics, the O_2 consumption rate was assumed to be independent of depth in the sediment. By first-order kinetics, it was assumed to be proportional to O_2 concentration. Reproducibility of O_2 microgradients over time showed that these were at steady state.

For zero-order kinetics, the depth-independent removal rate, R , of O_2 per unit volume of pore water at any given depth in the sediment is at steady state balanced by the supply due to diffusion:

$$R = D_S d^2C/dz^2 \quad (3)$$

where D_S = the sediment diffusion coefficient (Berner 1980) of O_2 and $C = O_2$ concentration in the pore water. Sediment porosity, and thus D_S , are assumed to be constant with depth (see below). Eq. (3), which determines the depth distribution of O_2 in the sediment, can be solved for C given relevant boundary conditions (Bouldin 1968):

$$C = (R/2D_S)z^2 - (2C_0R/D_S)^{1/2}z + C_0 \quad (4)$$

The flux of O_2 into the sediment is:

$$J = (2C_0RD_S)^{1/2} \quad (5)$$

The total depth of O_2 penetration, z_{max} , into the sediment can be found from Eq. (4) by setting $C = 0$:

$$z_{max} = (2C_0D_S/R)^{1/2} \quad (6)$$

By introducing the expression for J (Eq. 5), this equation for O_2 penetration is comparable to that used by Revsbech et al. (1980a):

$$z_{max} = 2C_0D_S\phi/J \quad (7)$$

where ϕ = sediment porosity.

For modeling of zero-order kinetics of O_2 consumption, we used the manual curve-fitting approach described by Nielsen et al. (1990), who found this simple method to yield rates which compared well to those obtained by computer simulation of O_2 microelectrode data. By this approach, O_2 profiles are visually fitted by one or several parabolas selected from graphs of families of parabolas on transparencies. Each parabola describes a second-order polynomial:

$$C = az^2 + bz + c \quad (8)$$

where a , b , and c are constants. The 2nd derivative of this polynomial is:

$$d^2C/dz^2 = 2a \quad (9)$$

The value of d^2C/dz^2 is thus determined from the a value of the parabola yielding the best fit to the O_2

data. Given a value for D_S (see below), the O_2 consumption rate, R , can then be calculated from Eq. (3).

From the O_2 consumption rates per unit volume of sediment, $R_s (= R\phi)$, the total oxygen consumption within the O_2 zone was determined per unit area by multiplying by the thickness of the oxic zone.

Modeling of oxygen consumption: first-order. The steady state depth distribution with O_2 at first-order reaction kinetics is exponential (Bouldin 1968):

$$C = C_0 \exp(-z/(K/D_S)^{1/2}) \quad (10)$$

where K is a constant describing the rate of O_2 consumption per unit volume as a function of O_2 concentration. The best fit of K can be found from the measured O_2 microgradients. Flux of O_2 across the sediment-water interface with first-order kinetics is simply proportional to the O_2 concentration:

$$J = C_0 (D_S K)^{1/2} \quad (11)$$

Modeling of oxygen consumption with DBL. The presence of a diffusive boundary layer is generally evident from measured O_2 microgradients, and the sediment-water interface is in many cases evident as a break in slope of the O_2 gradient, dC/dz , with a steeper gradient in the sediment than in the DBL (e.g. Gundersen & Jørgensen 1990). This is in accordance with simple 1-dimensional, Fickian diffusion theory. The steeper gradient is due to (a) the sediment diffusion coefficient, D_S , being lower than the molecular diffusion coefficient, D , in the water and (b) the porosity, ϕ , of the sediment being < 1 . To maintain mass conservation, the diffusive O_2 flux, J , must be the same just above and below the sediment-water interface. Consequently, the gradients must compensate for the shift in diffusion coefficients and in porosity:

$$\text{Diffusion in DBL: } J = -D (dC/dz)_{DBL} \quad (12)$$

$$\text{Diffusion in sediment: } J = -\phi D_S (dC/dz)_{sediment} \quad (13)$$

Thus

$$D (dC/dz)_{DBL} = \phi D_S (dC/dz)_{sediment} \quad (14)$$

or

$$(dC/dz)_{DBL} / (dC/dz)_{sediment} = \phi D_S / D \quad (15)$$

The DBL must be included in a realistic model of O_2 uptake (cf. Hall et al. 1989). This is done by equating the O_2 flux through the DBL (Eq. 2) with the O_2 flux from the sediment-water interface into the sediment [Eq. (5) for zero-order and Eq. (11) for first-order kinetics]. For zero-order kinetics:

$$(2C_0RD_S)^{1/2} = D (C_w - C_0)/z_\delta \quad (16)$$

This equation is then solved for C_o (Hall et al. 1989):

$$C_o = C_w + (z_\delta^2/D^2)RD_S(1 - (2D^2C_w/RD_Sz_\delta^2 + 1)^{1/2}) \quad (17)$$

When C_o is known from Eq. (17) for a given O_2 concentration, C_w , in the overlying, mixed seawater, the whole O_2 microgradient can be modeled by Eq. (2) in the DBL and by Eq. (4) within the sediment.

Similar calculations for first-order kinetics yield:

$$C_o(D_SK)^{1/2} = D(C_w - C_o)/z_\delta \quad (18)$$

This equation is similarly solved for C_o :

$$C_o = C_w / ((z_\delta/D)(D_SK)^{1/2} + 1) \quad (19)$$

and can then be used to compute the whole O_2 microgradient by Eqs. (2) and (10).

Total oxygen uptake. Rates of total O_2 consumption were measured in the same 6 sediment cores after microelectrode measurements. The following technique ensured identical conditions for the 2 sets of determinations.

A rubber stopper penetrated by a 5 mm interior diameter glass tube, just wide enough for the O_2 microelectrode to pass through, was carefully but tightly positioned on each coring tube. The stopper left a 6 cm high water column without air bubbles over the sediment. Water in the glass tube was replaced by paraffin oil which impeded O_2 exchange but allowed penetration of the O_2 microelectrode.

The O_2 concentration in the stirred water phase of each core was measured at 0.5 h intervals for 3 h, during which a linear O_2 decrease of 10 to 20 % was measured. The same O_2 microelectrode was consecutively inserted into each core. For each round of measurements, the electrode was calibrated at the same temperature in seawater bubbled with N_2 or air. At the end of incubation, the heights of the water columns were measured and the O_2 uptake rates were calculated in $\mu\text{mol } O_2 \text{ m}^{-2}$ of sediment surface h^{-1} . The sediment of some cores was subsequently sieved through 0.5 mm mesh size to collect the burrowing macrofauna. Faunal density was later related to the O_2 uptake of the sediment.

Control experiments with O_2 -depleted, sterile seawater in the coring tubes showed that penetration of O_2 into the tubes through the Plexiglas walls and stoppers during normal core incubation was $<2 \mu\text{M h}^{-1}$, which was insignificant ($<5\%$) for the O_2 uptake experiments. The thin film of paraffin oil coating the microelectrode tip by the present procedure does not affect electrode calibration (Revsbech & Ward 1983).

Effect of O_2 concentration on diffusive flux. The effect on the diffusive oxygen flux of the O_2 concen-

tration in the overlying water was determined experimentally on 2 occasions. Sediment cores were incubated under standard conditions at 100 % air saturation of O_2 for several hours. Incubations were done at *in situ* temperature and 4 O_2 microprofiles were measured at random positions. The O_2 concentration in the overlying water was then lowered to 75 % of air saturation and subsequently to 50 %, 25 %, and 10 %. The O_2 microprofiles were measured again at the same 4 positions at each constant O_2 level when steady state O_2 microgradients had been reached after about 2 h (cf. Booij 1989). The O_2 level was then increased stepwise again to the previous concentrations, and O_2 microprofiles were measured after 2 h equilibration.

Determination of sediment porosity, D_S , and organic carbon. The porosity, ϕ , was determined at 2 mm depth intervals from the weight loss upon drying at 105 °C of sediment core segments of known weight and volume. Values of the sediment diffusion coefficient, D_S , were then determined from the porosity according to:

$$D_S = D / (1 + 3(1 - \phi)) \quad (20)$$

This relation was found experimentally to account well for methane diffusing in similar fine-grained marine sediments from Danish waters (Iversen & Jørgensen in press). A relation proposed by Ullman & Aller (1982), $D_S = D \phi^2$, was found to generate D_S values 5 % higher.

The organic carbon content of dried sediment was determined by a C/N analyzer (Carlo Erba 1500) after acidification to remove carbonates. Total organic matter was determined as weight loss of dried sediment upon ignition at 540 °C for 3 h.

RESULTS

Diffusive oxygen flux

The diffusion of O_2 across the sediment-water interface was calculated according to Eq. (1) from each measured O_2 microgradient as shown in Fig. 1. In the 2 examples, there was a distinct DBL which could be recognized from 2 shifts in the slope of the O_2 gradient. The O_2 gradients increased by a factor of 1.9 (Curve A) and 1.7 (Curve B) at the transition from the DBL to the sediment. Given the measured porosity, $\phi = 0.87$ (Table 1), and calculated values of D and D_S of 1.57×10^{-5} and $1.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the expected factor of increase (Eq. 15) should be 1.6 [$D/D_S \phi = 1.57 \times 10^{-5} / (1.13 \times 10^{-5} \times 0.87)$]. Many of the O_2 gradients, however, did not show a detectable shift in slope across the sediment-water interface.

The O_2 gradient in the DBL was $460 \mu\text{M cm}^{-1}$ or $0.46 \mu\text{mol cm}^{-4}$ on 14 November (Fig. 1, Curve A). With a molecular O_2 diffusion coefficient, D , of $1.51 \times$

Fig. 1. Oxygen microgradients measured in Aarhus Bay sediment on (A) 14 November 1988 and (B) 5 July 1988. *In situ* and incubation O_2 concentrations in the overlying water were (A) 84 % and (B) 51 % of air saturation. The diffusive boundary layers (DBLs) were 400 μm thick. A linear slope was fitted to the O_2 gradient measured within the DBL and used to calculate the diffusive O_2 uptake rate of the sediment

$10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at the *in situ* temperature of 8.5 $^{\circ}\text{C}$, the calculated O_2 flux was $6.95 \times 10^{-6} \mu\text{mol } O_2 \text{ cm}^{-2} \text{ s}^{-1}$ or $251 \mu\text{mol } O_2 \text{ m}^{-2} \text{ h}^{-1}$. During summer, the DBL gradient was similar due to the lower O_2 concentration, whereas the O_2 diffusion coefficient was higher due to the higher temperature. The calculated O_2 uptake of the sediment was $282 \mu\text{mol } O_2 \text{ m}^{-2} \text{ h}^{-1}$ (Fig. 1, Curve B).

For each sampling date, 4 O_2 microgradients were measured in each of 6 cores, and the diffusive fluxes and the mean diffusive O_2 uptake were calculated. The relative standard deviation of this mean was $\pm 5\%$.

The DBL thickness in Fig. 1 was 400 μm . At the applied depth resolution of 100 μm , 3 to 5 data points generally fell within the DBL, which was just sufficient for the calculation of a slope. A resolution of 100 μm or less is thus required to identify the DBL. During the entire study, we found the mean DBL thickness for these sediments and flow conditions to be $299 \pm 99 \mu\text{m}$ ($\pm \text{SE}$, $n = 79$).

Modeling of oxygen consumption: zero-order

O_2 consumption rates within the oxic surface layer of the sediment were calculated from O_2 microgradients assuming zero-order kinetics. Fig. 2A and B show 2 examples of O_2 gradients measured in spring, just before and after settling of the spring phytoplankton bloom. Before settling, O_2 penetrated 5 mm into the sediment, while after the high input of fresh phytoplankton detritus, the O_2 zone was narrowed down to 1.3 mm.

Before the spring bloom, the whole O_2 gradient was modeled well by a single parabola (Fig. 2A) from which the curvature, d^2C/dz^2 , was calculated. Sediment porosity decreased with depth from 0.87 in the uppermost 0 to 2 mm to 0.80 at 30 to 40 mm depth (Table 1). Only the surface porosity of 0.87 was used here, and the calculated sediment diffusion coefficient was thus, $D_s = D/(1 + 3(1 - 0.87)) = 0.72 D$ (Eq. 20). At the *in situ* temperature of 4 $^{\circ}\text{C}$, the calculated O_2 consumption rate within the oxic zone was (Eq. 3):

$$R = (0.72) (1.28 \times 10^{-5}) (7.9 \times 10^3) \\ = 7.3 \times 10^{-2} \mu\text{mol } O_2 \text{ cm}^{-3} \text{ h}^{-1}$$

Following the spring bloom, the curvature and thus the O_2 consumption rate per sediment volume increased (Fig. 2B). Furthermore, the curvature was strongest at the bottom of the O_2 zone, which indicated a more intense O_2 consumption rate here. A maximal intensity of O_2 consumption near the oxic-anoxic

Table 1. Distribution of density, water content, porosity and organic content in Aarhus Bay sediment. Mean $\pm$ SE of 17 determinations during a year (E. Lomstein data)

Depth (mm)	Density (g cm^{-3})	Water content (wt/wt)	Porosity (vol/vol)	Organic matter (% dry wt)
0-2	1.18 ± 0.04	0.74 ± 0.03	0.87 ± 0.05	10.1 ± 0.9
2-4	1.22 ± 0.03	0.70 ± 0.03	0.86 ± 0.04	9.6 ± 0.9
4-7	1.24 ± 0.02	0.69 ± 0.02	0.85 ± 0.03	9.3 ± 0.6
7-10	1.25 ± 0.02	0.68 ± 0.02	0.85 ± 0.03	9.3 ± 0.6
10-15	1.26 ± 0.02	0.66 ± 0.02	0.83 ± 0.03	9.0 ± 0.6
15-20	1.28 ± 0.02	0.64 ± 0.01	0.82 ± 0.02	8.9 ± 0.7
20-30	1.30 ± 0.04	0.63 ± 0.01	0.82 ± 0.03	8.4 ± 0.6
30-40	1.32 ± 0.03	0.61 ± 0.02	0.80 ± 0.03	7.7 ± 1.0

Fig. 2. Oxygen microgradients measured on (A) 18 March and (B) 18 April. Parabolas [1 in (A), 2 in (B)] were fitted to the data sets and used to calculate the rates of O_2 consumption within the oxic sediment layer. After a phytoplankton bloom in late March, the oxic zone was reduced in thickness, and the intensity of O_2 consumption increased strongly with maximal rate near the oxic-anoxic interface

interface in the sediment was commonly observed and modeled during late spring and summer, but was not seen during the winter.

The total O_2 consumption per unit sediment area was calculated from the modeled O_2 consumption rates. It was found that this areal O_2 consumption calculation was not very sensitive to whether the O_2 microgradient was modeled by a single parabola or the oxic zone was divided into several depth intervals of different O_2 consumption rates.

Modeling of oxygen consumption with a DBL

It was generally possible to model the whole O_2 microgradient in both DBL and sediment by a single zero-order model given in Eqs. (17), (2) & (4). In the example shown in Fig. 3, the DBL was $400 \mu\text{m}$ thick, the diffusion coefficient in the water was $1.57 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and O_2 in the overlying water, $308 \mu\text{M}$, was close to air saturation at the *in situ* temperature. A constant O_2 consumption, R , of $0.108 \mu\text{mol } O_2 \text{ cm}^{-3} \text{ h}^{-1}$ yielded a perfect fit throughout the oxic zone and also generated the observed gradient in the DBL. The depth of O_2 penetration, z_{max} , was 4.6 mm and the total O_2 consumption rate per unit area was thus, $R z_{\text{max}} = (0.108)(0.46 \times 10^4) = 490 \mu\text{mol } O_2 \text{ m}^{-2} \text{ h}^{-1}$. The O_2 gradient, dC/dz , across the $400 \mu\text{m}$ thick DBL was $(308-273)/0.04 = 875 \mu\text{M cm}^{-1}$, and the diffusion flux was thus, $D dC/dz = (1.57 \times 10^{-5})(875) = 0.0138 \text{ nmol } O_2 \text{ cm}^{-2} \text{ s}^{-1}$ or $490 \mu\text{mol } O_2 \text{ m}^{-2} \text{ h}^{-1}$, i.e. identical to the O_2 consumption within the sediment.

The effects of increasing or decreasing the modeled rate of O_2 consumption in the sediment by a factor of 2 are shown in Fig. 3. The model is seen to be quite sensitive to the O_2 consumption rate. The dashed line in Fig. 3 shows the results of a calculation based on a

first-order kinetic model. It is evident that the calculated exponential O_2 distribution does not describe the data well. Based on the shape of O_2 microprofiles it was therefore concluded that O_2 consumption rates did not vary with depth in proportion to the O_2 concentration.

Seasonal variation in Aarhus Bay

Aarhus Bay is hydrographically a part of the Baltic Sea – North Sea transition system where brackish water and oceanic water meet with resulting seasonal

Fig. 3. Modeling of O_2 in both diffuse boundary layer and sediment from an O_2 microgradient (●) measured on 7 December. Dashed line: O_2 distribution calculated by first-order model; solid lines: O_2 distributions calculated by zero-order model with 3 different rates of O_2 consumption within the sediment. Numbers indicate rates in $\mu\text{mol } O_2 \text{ cm}^{-3} \text{ h}^{-1}$

stratification (Andersson & Rydberg 1988). Seasonal variations in temperature, salinity, and O_2 concentration in the water column overlying the sampling station are shown in Fig. 4. The whole water column was well mixed and oxygenated during winter. During spring and summer, stratification developed between the more brackish surface water from the Baltic Sea and more saline bottom water from the North Sea. This stratification was stabilized by a temperature gradient with a Δt of up to 12 °C in early summer when heating of the surface water was fastest. The seawater just over the sediment thus had temperatures varying from 4 to 15 °C over the year and salinities varying from 23 to 32 ‰ (Fig. 4). The pycnocline was mostly situated at

10 to 12 m water depth but varied considerably due to wind-induced seiching. Light penetration was limited by high phytoplankton biomass in the surface water and the euphotic zone did not extend down below the pycnocline during most of spring and summer.

Due to the stable stratification and to O_2 respiration in the bottom water and sediment, O_2 was strongly depleted below air saturation during spring, summer and fall (Fig. 4). The first decrease in O_2 concentration occurred just after the spring phytoplankton bloom at the end of March. Oxygen increased again during windy periods in July-August as the water masses in the bay were exchanged. A new, stable stratification in September led to extensive O_2 depletion in the 13 to 15 °C bottom water with an O_2 minimum of 23 % of air saturation.

Fig. 4. Seasonal variation in temperature, salinity, and oxygen concentration of Aarhus Bay water measured 1 m below the water surface and 1 m above the bottom. Temperature and salinity stratification, which developed during spring and summer and lasted into the fall, caused partial oxygen depletion in the bottom water

The oxic sediment zone

The depth of O_2 penetration into the sediment varied 4-fold over the seasons with a maximum penetration of 5.1 mm during winter and a minimum of 1.2 mm during spring and early fall (Fig. 5). As the spring phytoplankton bloom settled on the sediment surface at the end of March 1988, the thickness of the oxic zone decreased 2- to 3-fold within 1 to 2 wk. At this time there was a 1 to 2 mm thick, brown and flocculent layer of *Skeletonema costatum* and other diatoms on the sediment surface. Photosynthesis measurements by the light-dark shift technique (Revsbech & Jørgensen 1983) showed a slight photosynthetic response in O_2 concentration at the sediment surface in early April, but photosynthesis was not detectable at any other time of the year. The thickness of the oxic zone remained at 1.3 to 2.5 mm throughout the summer but reached a new minimum in September. During late fall and winter, oxygen slowly penetrated deeper into the sediment until the cycle was repeated next spring. There was, however, no distinct phytoplankton bloom during the spring of 1989.

The O_2 penetration into the sediment varied seasonally in close accordance with the O_2 concentration in the overlying seawater (Fig. 5). A decrease in the O_2 concentration of the water was thus immediately reflected in a narrower O_2 zone in the sediment. This shows the importance of measuring O_2 microgradients under *in situ* O_2 concentration and temperature conditions.

Oxygen uptake by 3 methods

Fig. 6 shows the O_2 uptake rates of Aarhus Bay sediment throughout a year as measured by 3 differ-

Fig. 5. Upper frame: Seasonal O_2 concentrations in the seawater 1 m above the sediment calculated as % of air saturation. Lower frame: O_2 penetration into the sediment shown as isopleths of O_2 concentration in % of air saturation (numbers on curves)

ent methods: (a) total O_2 uptake, (b) diffusive O_2 flux through the DBL and (c) modeling of O_2 microgradients. The total O_2 uptake was highest during summer and lowest during late winter while the calculated O_2 flux and the modeled O_2 uptake were rather constant over the year.

The O_2 uptake rates measured by the 3 methods were compared throughout the year. The annual mean O_2 diffusion through the DBL was $99 \pm 3\%$ of the modeled O_2 uptake. There was thus a close correspondence between the 2 approaches, which are based on different parts of the O_2 microgradients. The total O_2 uptake of the sediment was significantly higher, an average of 145 % of the flux and model rates over the whole year. The difference varied highly between sediment cores depending on the occurrence of macrofauna in each core. In the absence of macrofauna, total O_2 uptake was similar to diffusive O_2 uptake. When the numbers of macrofauna per core (20 cm^2) increased to 1–3, 4–6, and >7 individuals, total O_2

Fig. 6. Seasonal variations in O_2 uptake rates of Aarhus Bay sediment measured under *in situ* conditions of salinity, temperature, and pO_2 by 3 methods. Top: Total O_2 uptake. Middle: Diffusive O_2 uptake calculated from O_2 microgradients in the diffuse bottom layer. Bottom: O_2 uptake calculated by modeling O_2 microgradients within the sediment. Vertical bars indicate standard deviations

uptake exceeded diffusive O_2 uptake by 100–150 %, 150–200 %, and $>200\%$, respectively. Thus, the total O_2 uptake in excess of the diffusive uptake was strongly related to the ventilation and respiration by macrofauna.

Oxygen uptake regulation by oxygen concentration

Experimental variation of O_2 concentration in the seawater overlying the sediment cores showed how diffusive O_2 uptake and depth of the oxic zone depended on the O_2 saturation level. The diffusive O_2 uptake of the sediment decreased 7-fold when O_2

concentration in the seawater was stepwise reduced 10-fold, from 100 to 10 % of air saturation (Fig. 7A, solid circles). When O_2 concentration was subsequently increased again to 100 %, the original O_2 uptake was again nearly reached (open circles). The depth of O_2 penetration decreased only 2.5-fold when O_2 concentration was reduced 10-fold (Fig. 7B). Also the O_2 penetration was reversible, as seen when the original 100 % O_2 level was again reached. Regulation of the oxic zone under decreasing and increasing O_2 levels was thus reproducible under these experimental conditions. This experiment was repeated 3 mo later with similar results and conclusions.

In order to evaluate by which mechanisms O_2 concentration regulated O_2 uptake and depth of the oxic zone, data were modeled assuming zero-order kinetics. All parameters used in the model were independently determined or calculated according to Eqs. (17), (2) & (4). The mean measured DBL thickness was 300 μm .

Fig. 7A shows calculated O_2 fluxes (solid lines) at 3 different O_2 consumption rates and at varying O_2 concentrations in the seawater. A constant O_2 con-

sumption rate of $0.082 \mu mol O_2 cm^{-3} h^{-1}$ throughout the oxic zone gave the closest fit to the measured fluxes. Results from 2-fold higher or 2-fold lower activities (Fig. 7A) shows that the model calculations are very sensitive to rates of O_2 consumption. The zero-order model, however, did not produce as strong a variation in O_2 flux with changing O_2 concentration as was observed. Calculations using a first-order model (Fig. 7A, dashed line), in which the flux is proportional to C_o , exaggerated the variation relative to the observations.

Fig. 7B shows similarly the observed and the modeled depths of O_2 penetration into the sediment. Modeled data were calculated from the same parameter values as in Fig. 7A. Both zero-order and first-order models exaggerated the variation in thickness of the oxic zone with varying C_o , yet zero-order kinetics yielded the better fit.

Similar calculations were made with the best-fitting O_2 consumption rate of $0.082 \mu mol O_2 cm^{-3} h^{-1}$ but with DBL thicknesses of 0, 300, and 600 μm (Fig. 7C & D). For the present conditions of water flow, O_2 consumption rates, etc., there was only little effect of DBL thickness on O_2 flux or O_2 penetration.

Fig. 7. Oxygen uptake and penetration depth during experimental variation of O_2 concentration in seawater overlying sediment from Aarhus Bay, 19 November 1988. The O_2 concentration was changed stepwise from 100 to 10 % of air saturation (•) and stepwise back again (○) over a period of 16 h. (A) & (C) Rates of O_2 uptake calculated from diffusive flux through the DBL. (B) & (D) Depths of O_2 penetration. Solid lines: Modeling with zero-order kinetics; dashed lines: modeling with first-order kinetics. Model calculations were made for (A) and (B) using different O_2 consumption rates (numbers on curves indicate O_2 consumption rates in $\mu mol cm^{-3} h^{-1}$) and for (C) and (D) using different DBL thicknesses (numbers on curves indicate DBL thicknesses in mm)

Comparison with other sediment types

Sediment O_2 uptake and O_2 microgradients were studied in deeper and more open waters at several positions in Kattegat. The characteristics of these sediments are given in Table 2. At the times of sampling, the overlying seawater was partly depleted in O_2 (68 to 95 % saturation) with a low of 27 %. The O_2 uptake was generally lower than in Aarhus Bay while the oxic zone was thicker, up to 9.1 mm. The total O_2 uptake rates were 1.5- to 2.3-fold higher than the diffusive rates. This difference was not correlated to the O_2 concentration or the rate of O_2 uptake but was expectedly dependent on the activity of the benthic fauna and other factors such as sediment topography.

DISCUSSION

Three experimental oxygen uptake methods

Three different approaches were concurrently used in laboratory-incubated cores to measure the O_2 uptake of Aarhus Bay sediment. Two of the methods used the steady state microdistribution of O_2 to calculate (a) the diffusion flux through the diffusive boundary layer (DBL) from Fick's first law or (b) the depth-integrated O_2 consumption in the oxic sediment layer from Fick's second law assuming zero-order kinetics. It should be noted that, although these 2 methods apply the same oxygen microgradients for the calculations, the former uses data only from above the sediment-water interface while the latter uses data only from within the sediment. The third method, (c), measures the total O_2 uptake from the seawater into the sediment.

Diffusive oxygen flux

A DBL with a mean thickness of about 300 μm was consistently found over the sediment surface in the

incubated cores. The DBL thickness measured *in situ* throughout the year by a microprofiling lander instrument at the sampling station in Aarhus Bay was 250 to 500 μm (Gundersen & Jørgensen 1991). The experimental flow conditions were therefore considered an acceptable approximation of the natural flow conditions although the flow pattern was different. Thus, the occurrence of bursts, as predicted by turbulent flow theory (Boudreau 1988), was not observed during prolonged O_2 measurements in the DBL. The simulation of a natural DBL thickness is important for the O_2 flux into the sediment, especially at high O_2 uptake rates (Jørgensen & Des Marais 1990).

It was recently observed in our laboratory that the use of microelectrodes for DBL studies has a measurable effect on the hydrodynamics of the DBL and thus on the chemical microgradients (R. N. Glud unpubl.). Apparently, even the thin electrode tip of 5 to 10 μm diameter causes an acceleration of water flow. This results in a thinner DBL and a steeper O_2 gradient, which would result in an overestimation of the diffusive flux. The effect depends on flow velocity and other factors and has presently not been quantified. Judging from the close agreement between DBL flux and modeled O_2 consumption within the sediment, however, this experimental artifact did not appear to strongly affect calculated fluxes in the present study.

Calculation of the diffusive O_2 flux through the DBL requires a high resolution of the O_2 microgradient data. With a DBL thickness of 300 to 400 μm , measurements should be taken at 100 μm depth intervals or less. Furthermore, as the DBL has an inherent short-term instability, especially at low flow rates (Gundersen & Jørgensen 1991), the accuracy of the gradient determination can be improved by averaging for each depth in the DBL over time. Flux calculations in the DBL have, however, the advantage of being independent of porosity and tortuosity within the sediment. Flux calculations from pore water microgradients just

Table 2. Characteristics of sediment stations studied in southern Kattegat

Characteristics	October 1988			April 1989	
	Stn 1402	Stn 409	Stn 1243	Stn 1402	Stn 1505
Water depth (m)	29	13	33	29	25
Sediment type	Muddy sand	Fine sand	Sandy mud	Muddy sand	Muddy sand
Organic matter (% dry wt)	2–6	<1	3–5	2–6	3–5
Temperature ($^{\circ}\text{C}$)	12.7	11.2	5.5	5.3	5.5
Salinity (‰)	31.4	24.8	32	27	30
Water O_2 concentration (μM)	75	280	256	231	219
Water O_2 saturation (%)	27	95	80	70	68
Total O_2 uptake ($\mu\text{mol m}^{-2} \text{h}^{-1}$)	436 ± 56	539 ± 53	366 ± 75	320 ± 20	475 ± 76
Diff. O_2 flux ($\mu\text{mol m}^{-2} \text{h}^{-1}$)	188 ± 10	350 ± 23	160 ± 10	219 ± 13	247 ± 15
Total vs diff. O_2 uptake	$2.3 \times$	$1.5 \times$	$2.3 \times$	$1.5 \times$	$1.9 \times$
Depth of O_2 zone (mm)	1.9 ± 0.07	3.4 ± 0.16	9.1 ± 0.35	5.4 ± 0.13	6.0 ± 0.28

below the sediment-water interface indicated that these properties must be known with high resolution (Reimers & Smith 1986). Although an experimental approach to determine both porosity and sediment molecular diffusion coefficient for O_2 with micro-electrodes has been developed by Revsbech (1989a), flux determinations in the DBL depend on fewer variables and are thus simpler. In the present study we found a shift of the O_2 gradients across the sediment-water interface of around 1.6-fold (Fig. 1), corresponding to the relation: $\phi D_s = 0.63 D$. This is close to the relation, $\phi D_s = 0.64 D$, found experimentally by O_2 microelectrode methods under stagnant conditions in a fine-grained riverine sediment (Revsbech 1989a).

Modeling of oxygen consumption

Microgradients of O_2 in Aarhus Bay sediment were mostly found to follow parabolic depth distributions which could be closely modeled assuming zero-order kinetics of O_2 consumption. Parabolic depth distributions of O_2 , and thus apparent zero-order kinetics, have been most common in coastal sediments that we and several others have studied (cf. Booij 1989, Hofman et al. 1991). A similarly close fit to the data could not be obtained by exponential depth distributions corresponding to first-order kinetics (Fig. 3). First-order kinetics would imply that microorganisms living in the oxic zone are O_2 -limited even at near atmospheric O_2 concentrations. This is not in accord with the O_2 uptake kinetics observed in aerobic microorganisms, which may become O_2 -limited only at μM levels (e.g. Hao et al. 1983).

A constant O_2 consumption rate throughout the oxic zone is, however, an over-simplification due to expected microzonations of respiring organisms within this zone and of the availability of substrates. During the warm season, enhanced O_2 consumption was consistently found at the oxic-anoxic interface (Fig. 2B). This was presumably due to a high flux of reduced products, such as NH_4^+ , Fe^{2+} , or H_2S , diffusing up to the oxic zone. The enhanced O_2 consumption was first observed in mid April 1988, just after a rapid settling of the spring phytoplankton bloom (Fig. 5). During the following 2 wk, a thin sediment layer at 2 to 4 mm depth exhibited very high sulfate reduction activity, and a transient formation of a black band of iron sulfide at that depth indicated that rapid formation of H_2S took place (L. Moeslund, B. Thamdrup, & B. B. Jørgensen unpubl.). The enhanced O_2 consumption at the oxic-anoxic interface was thus expectedly due to reoxidation of H_2S . A similar enhancement, corresponding to 60 % of the O_2 consumption, due mostly to diffusing methane was found in a temperate lake sediment (Sweerts 1990).

More detailed analyses of O_2 microgradients have demonstrated that the uppermost part of the oxic zone, where freshly settling detritus or photosynthesis occurs, may also show elevated O_2 consumption rates (Revsbech et al. 1986, Gundersen & Jørgensen 1991). The precision of such calculations is, however, dependent on the determination of other model parameters such as the sediment diffusion coefficient, D_s , and porosity, ϕ . These were assumed constant in the model calculations although they do change with depth (Table 1). In particular at the sediment-water interface there is a gradual transition from water to sediment when observed at 100 μm resolution, and the assumption of constant D_s and ϕ leads to an underestimation of the O_2 consumption rate just below the sediment-water interface.

This problem may be enhanced by a flow-induced dispersion effect in the top few mm of the sediment. Based on a hydrodynamic model for the water-sediment transition, Svensson & Rahm (1991) concluded that pore water in the uppermost sediment layer is influenced by shear from the viscous sublayer and that this results in a higher effective exchange several mm into the sediment. Such an effect is observed mostly in sand (Revsbech et al. 1980a, Booij 1989), where flow of the overlying water tends also to create pressure gradients and thus permeation of the pore water (Hüttel 1988). The apparent diffusion coefficient of O_2 has also, however, been found to exceed the calculated molecular diffusion coefficient by 2-fold in the thin, oxic zone of fine-grained sediments (Lindeboom et al. 1985, Booij 1989, Hofman et al. 1991). Such an enhanced diffusion coefficient in the top few mm would explain why the O_2 gradient frequently did not show a break in slope across the sediment-water interface. Since the modeled O_2 consumption accounted for $100/1.45 = 69$ % of the total O_2 uptake, and since the benthic fauna and other factors must account for much of the remaining 31 %, the modeled O_2 consumption (and DBL flux) cannot be significantly underestimated. It is therefore concluded that the diffusion of O_2 within the oxic zone of this sediment is well described as molecular diffusion.

Although a zero-order model yielded the best fit to measured O_2 microgradients, it reproduced only moderately well the diffusive O_2 uptake and O_2 penetration depth during experimental shifts in O_2 saturation levels (Fig. 7). The experiment in Fig. 7 is thus a useful test of the validity of the model assumptions and demonstrates that a correct understanding of the regulation of O_2 uptake may require independent knowledge of its microdistribution. Apart from the diffusion coefficient of O_2 and the assumption of zero-order kinetics, however, all parameters entering the model were experimentally determined in this study.

Comparison of the 3 methods

Oxygen uptake per unit sediment area calculated from diffusion through the DBL and from modeling of O_2 microgradients agreed closely. Due to surface microtopography of the sediment, however, the actual, 3-dimensional diffusive flux may be underestimated when calculations are made only from vertical O_2 microgradients (Jørgensen & Des Marais 1990, Jørgensen & Gundersen 1991). As the sediment surface of the Aarhus Bay station was relatively smooth, microtopography did not appear to be of major importance for the present flux calculations. A practical method for quantification of the relevant sediment topography is, however, required to determine this effect routinely.

The total O_2 uptake exceeded the diffusive rates by an average of 45 % (Fig. 6). The difference was clearly related to the density of large burrowing animals such as bivalves (mostly *Abra alba*, *Macoma calcarea*, or *Nucula tenuis* of 13 to 30 mm length) and polychaetes (mostly *Nephtys* sp. or *Nereis* sp.) in each sediment core. The difference was largest, up to 2.6-fold, during summer when the animals were most active, but dropped during periods of O_2 depletion in the bottom water, possibly due to inactivation of the animals (Figs. 5 & 6). The relation between total and diffusive O_2 uptake in the surficial oxic zone was also studied in sediments in Kattegat where the difference was 1.5- to 2.3-fold.

Similar published comparisons from other sedimentary environments have reached widely differing conclusions. Reimers & Smith (1986) found the diffusive O_2 uptake to be close to the total uptake in pelagic sediments of the North Pacific. Andersen & Helder (1987) found the total uptake to exceed the diffusive uptake by 1.4- to 3.2-fold in intertidal sediments. Mackin & Swider (1989) found the same ratio to be 2- to 5-fold in Flax Pond, New York, USA, sediment but to be 1:1 in Long Island Sound, New York, sediment. They attributed the former difference to epifaunal respiration and concluded that infaunal irrigation was not important for the total O_2 uptake. In order to understand the regulation between the different mechanisms and components of the O_2 budget, future studies are needed in which total and diffusive O_2 uptake measurements are accompanied by analyses of the ventilation and respiration of the benthic fauna.

Total O_2 uptake was calculated in most of the cited studies from the apparently linear decrease of O_2 concentration in incubated cores over time. It was found by Hall et al. (1989) in benthic flux chamber studies that the apparently linear, initial decrease was in fact exponential and that a linear fit to the initial part of this decrease, down to about 100 μM , could lead to an underestimation of the actual O_2 uptake rate by 28 to 34 %. It is not known how large a problem this is in other studies.

Regulation of oxygen uptake

The experimental variation of O_2 (Fig. 7) showed that the diffusive O_2 uptake of the sediment was strongly dependent on O_2 concentration in the overlying water, at least under short-term exposure to reduced O_2 . This observation may explain the small seasonal variation in O_2 uptake, especially of the surficial oxic zone. The expected increase in O_2 uptake due to settling of the spring phytoplankton bloom or due to the higher temperatures during summer was counteracted by reduced O_2 concentration in the bottom water. This partial O_2 depletion had 2 effects on the O_2 flux: (1) it reduced the O_2 gradient across the DBL thus reducing the diffusive flux (Fig. 7A) and (2) it reduced the thickness of the oxic zone by 3-fold, thereby reducing the population of aerobic microorganisms which could respire with O_2 . Furthermore, the O_2 -depletion inactivated the bottom fauna and thus reduced their respiratory ventilation in the burrows.

It is not clear from the present results whether a long-term exposure to reduced O_2 would gradually be compensated for by increased growth of the aerobic microbial populations closer to the sediment surface, or whether anaerobic mineralization would take over. The latter would result in the accumulation of reduced products, e.g. sulfide bound as FeS , FeS_2 , or S^0 , which would subsequently require an equivalent amount of O_2 for reoxidation to sulfate. The accumulation of such an 'oxygen debt' seems indeed to take place in Aarhus Bay sediments, especially during calm and warm periods. The reoxidation with O_2 may occur during windy periods, often of short duration, when surface sediment is resuspended into the bottom water. Since this mechanism of rapid O_2 consumption is not included in laboratory core incubations, the measured O_2 uptake rates underestimate the total *in situ* rates by an unknown amount, at least when longer time-scales are considered.

The 300 to 400 μm thick DBL had only little effect on the regulation of O_2 uptake in Aarhus Bay sediments during winter (Fig. 7C). Modeling of the O_2 consumption at 100 % air saturation in November (Fig. 7) yielded an uptake rate of 438 $\mu mol m^{-2} h^{-1}$. In the absence of a DBL, the calculated uptake rate would be 455 $\mu mol m^{-2} h^{-1}$, given the same O_2 consumption rate per unit volume. Thus, an impedance of the diffusion flux posed by the DBL limited the flux by 3.7 %. The general impedance by the DBL was 3 to 5 % during winter, when the oxic zone was 4 to 5 mm thick, and 12 to 16 % during summer, when it was 1.5 to 2 mm thick. Oxygen uptake of the sediment is thus mostly regulated by the internal diffusion regime (cf. Boudreau & Guinasso 1982). In an *in situ* study of O_2 microgradients in sediments of the Pacific shelf off

the State of Washington, USA, Archer et al. (1989) found a DBL thickness averaging 1 mm and an oxic zone 5 mm deep. The authors calculated a limitation of the diffusive flux due to the DBL of about 10 % relative to the case of no DBL.

Seasonal dynamics of oxygen

The seasonal variation in O_2 uptake was small considering the 4 to 15 °C temperature variation and the strong seasonal variation in primary productivity of Aarhus Bay. Other studies of sediment O_2 uptake rates at similar latitudes have shown temperature variations with a Q_{10} of 2 to 3 (Jørgensen 1977, Kanneworff & Christensen 1986, Hall et al. 1989, Herndl et al. 1989). There was a significant increase in the diffusive O_2 uptake, 345 to 504 $\mu\text{mol m}^{-2} \text{h}^{-1}$, in March-April 1988 in response to the settling of the spring phytoplankton bloom. Within the Baltic Sea and Kattegat area, a similar increase, from 330 to 540 $\mu\text{mol m}^{-2} \text{h}^{-1}$, of O_2 uptake in response to the spring bloom was observed in Laholms Bight on the east coast of Kattegat (Enoksson 1987). A strong stimulation of the benthic bacterial activity was also shown following sedimentation of the spring phytoplankton bloom in the Kiel Bight, Germany, (Graf et al. 1982), while no immediate effect was observed on respiration rates in Øresund sediment (Kanneworff & Christensen 1986).

In spite of the limited seasonal variation in O_2 uptake of the Aarhus Bay sediment, there was a strong seasonality in the intensity of O_2 consumption within the oxic zone. Table 3 compares the situations during summer and before the spring bloom. The rate of O_2 consumption in the thin oxic zone, calculated by modeling the O_2 microgradients, was only 1.7-fold higher during summer than during early spring. The oxic zone was much thinner during summer, however, 1.3 mm versus 5.1 mm as measured with the microelectrodes and 1.1 mm versus 5.5 mm as calculated from the O_2 flux model (Eq. 7). The rate of O_2 consumption per volume of sediment was thus

7-fold higher during summer than during winter. The populations of aerobic microorganisms in the sediment therefore had a significant seasonality in their activity in spite of the rather constant areal O_2 consumption.

The dynamics of O_2 was also much more intensive during summer. Due to the low O_2 concentration, the total O_2 pool in the oxic zone of the sediment turned over within 6 min (0.10 h) during summer, while the turn-over time during early spring was 2.3 h (Table 3).

The thin oxic 'skin' of the sediment is a zone of extremely intensive respiration (per unit volume) as compared to the anaerobic respiration in anoxic layers below. Thus, following the sedimentation of the spring bloom, a zone of intensive sulfate reduction developed just below the oxic zone. Maximum reduction rates here reached 0.0026 $\mu\text{mol SO}_4^{2-} \text{cm}^{-3} \text{h}^{-1}$, which was equivalent to only 1.5 % of the oxic respiration (calculated as carbon equivalents oxidized per $\text{cm}^3 \text{h}^{-1}$). When compared on an areal basis, however, the anaerobic processes increase strongly in significance as they occur in much thicker zones. The same comparison on an areal basis thus showed that sulfate reduction in the upper 0 to 10 cm of the sediment was equivalent to 35 % of the O_2 consumption (Moeslund, Thamdrup & Jørgensen unpubl.).

Organic carbon is also mineralized rapidly in the oxic zone. The upper 0 to 2 mm of sediment had 770 $\mu\text{mol org C cm}^{-3}$. Given the rates of O_2 consumption in Table 3, this organic C could theoretically be mineralized by O_2 within 3 months during summer, whereas the winter rates of O_2 consumption would correspond to a mineralization over 2 yr.

When integrated over the whole year, the total O_2 consumption of the sediment was 10.1 $\text{mol O}_2 \text{m}^{-2}$. Primary production by plankton algae in the Aarhus Bay was about 200 $\text{g C m}^{-2} \text{yr}^{-1}$. This corresponds to 20 $\text{mol O}_2 \text{m}^{-2} \text{yr}^{-1}$ assuming a photosynthetic quotient of 1.2. The total sediment O_2 uptake thus corresponded to the mineralization of half of the primary production of the area. To this should presumably be added the intermittent reoxidation by O_2 of accumulated, reduced minerals during resuspension events.

Table 3. Oxygen dynamics in oxic zone of Aarhus Bay sediment for 2 seasons

Oxygen dynamics	Aug/Sept 1988	Mar 1989
Modeled O_2 uptake ($\mu\text{mol m}^{-2} \text{h}^{-1}$)	460	260
Measured depth of O_2 zone (mm)	1.3	5.1
Calculated depth of O_2 zone (mm)	1.1	5.5
O_2 uptake per vol. ($\mu\text{mol cm}^{-3} \text{h}^{-1}$)	0.35	0.051
O_2 pool in oxic zone ($\mu\text{mol m}^{-2}$)	45	600
O_2 turn-over time (h)	0.10	2.3

Acknowledgments. We are grateful to Niels Peter Revsbech for his help and advice throughout this study and to Per Hall for critically reading the manuscript. We thank Birger Kruse for invitations to join 2 cruises on-board RV 'Gunnar Thorson' and Erik Lomstein for permission to use unpublished data. The study was supported by the Danish National Agency for Environmental Protection and the Danish Natural Science Research Council.

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This article was submitted to the editor

Manuscript first received: December 27, 1991

Revised version accepted: March 16, 1992