The diffusive boundary layer of sediments: Oxygen microgradients over a microbial mat

Bo Barker Jørgensen and David J. Des Marais

Abstract

Oxygen microelectrodes were used to analyze the distribution of the diffusive boundary layer (DBL) at the sediment–water interface in relation to surface topography and flow velocity. The sediment, collected from saline ponds, was covered by a microbial mat that had high oxygen consumption rate and well-defined surface structure. Diffusion through the DBL constituted an important rate limitation to the oxygen uptake of the sediment. The mean effective DBL thickness decreased from 0.59 to 0.16 mm as the flow velocity of the overlying water was increased from 0.3 to 7.7 cm s⁻¹ (measured 1 cm above the mat). The oxygen uptake rate concurrently increased from 3.9 to 9.4 nmol cm⁻² min⁻¹. The effects of surface roughness and topography on the thickness and distribution of the DBL were studied by three-dimensional mapping of the sediment–water interface and the upper DBL boundary at 0.1-mm spatial resolution. The DBL boundary followed mat structures that had characteristic dimensions >½ DBL thickness but the DBL had a dampened relief relative to the mat. The effective surface area of the sediment–water interface and of the upper DBL boundary were 31 and 14% larger, respectively, than a flat plane. Surface topography thereby increased the oxygen flux across the sediment–water interface by 49% relative to a one-dimensional diffusion flux calculated from the vertical oxygen microgradients.

The transfer of momentum in the turbulent flow of water above sediments is controlled by inertial forces while mass transport takes place by eddy diffusion. Within a few millimeters to centimeters from the sediment–water interface, surface friction retards the flow to the extent that it becomes dominated by viscous forces. The vertical flow component is in particular suppressed within this viscous sublayer, and just at the sediment–water interface the velocity approaches zero. The diffusion time for dissolved molecules decreases with the square of the distance. Molecular diffusion therefore becomes a more important transport mechanism relative to eddy diffusion as the sediment surface is approached (e.g. Wimbush and Munk 1970).

The diffusive boundary layer (DBL), also called the diffusive sublayer, is the thin layer of water adjacent to the sediment surface through which molecular diffusion is the dominant transport mechanism for dissolved material. As the sediment surface is approached within the viscous sublayer, the transition to the upper boundary of the DBL is found where the eddy diffusion coefficient, $K$, becomes smaller than the molecular diffusion coefficient, $D$. The transition from the relatively uniform distribution of dissolved compounds in the free-flow region to the diffusion gradient within the DBL can be quite sharp; $K$ decreases rapidly toward the surface in contrast to $D$ which is constant. According to Shaw and Hanratty (1977), the eddy diffusivity varies in proportion to $Z^{3.38}$, where $Z$ is the vertical distance above the sediment surface. At a distance of $0.5 \times Z_s$, the eddy diffusivity may thus drop to only 15% of $D$ (Boudreau 1988; $Z_s$ is the thickness of the DBL, cf. Jørgensen and Revsbech 1985).

The DBL is often only 0.2–1 mm thick (e.g. Boudreau and Guinasso 1982; Santschi et al. 1983; Jørgensen and Revsbech 1985; Sweerts et al. 1989). Yet, it may play an important role for the exchange of nutrients.
and gases across the sediment–water interface. As examples, the accretion rate of ferromanganese nodules on the sea floor has been found to depend strongly on transfer resistance of the DBL (Boudreau and Scott 1978; Santschi et al. 1983; Boudreau 1988). Flux-chamber data on the oxygen uptake of marine sediments have been described well by a model that included a DBL of 0.7–1.9 mm (Hall et al. 1989).

The vertical diffusive flux, $J$, through the boundary layer is described by Fick’s first law of diffusion as the product of the molecular diffusion coefficient of the dissolved compound and the linear concentration gradient (e.g. Crank 1975):

$$J = D(C_\infty - C_0)/Z_\delta \tag{1}$$

where $C_\infty$ and $C_0$ are the concentrations in the bulk fluid and at the sediment–water interface. By defining the mass transfer coefficient, $\beta = D/Z_\delta$, the following relation is derived (Boudreau and Guinasso 1982):

$$J = \beta(C_\infty - C_0) \tag{2}$$

If there is no production or consumption of the chemical compounds within the DBL but only diffusive flux, the one-dimensional diffusion gradients should be linear according to classical boundary-layer theory. There is a gradual transition at the upper DBL boundary toward the eddy diffusion region. A well-defined thickness of the DBL can, however, be found by extrapolation of the linear DBL gradient out to the bulk concentration. This distance is the thickness of the effective diffusive boundary layer, $Z_\delta$ (Jørgensen and Revsbech 1985). Determination of the effective DBL requires measurements of the whole gradient. A simpler identification of the upper DBL boundary was adapted in parts of this study for faster area1 scanning of its distribution. We used the level where the concentration had dropped below its free-flow concentration to 90% of its total gradient within the DBL. The DBL thickness defined in this way was found to deviate <10% from its precise thickness determined from whole gradients.

If the thickness, $Z_\delta$, of the DBL over a sediment can be determined experimentally for one chemical compound, it can be calculated also for other compounds. The thickness of the DBL, however, varies with $D$ because it is the layer in which $D$ is smaller than the hydrodynamically determined $K$. Shaw and Hanratty (1977) thus found the mass-transfer coefficient to vary with $D^{0.7}$. It is therefore necessary to correct for the diffusion coefficient of each dissolved compound. Oxygen microelectrodes have proven to be particularly well suited to analyze diffusive boundary layers of sediments. The technique has been used in the laboratory with artificial water flow over sediment cores (Jørgensen and Revsbech 1985) and also in the field with unimpeded, natural water flow (Reimers et al. 1986; Archer et al. 1989; Sweerts et al. 1989; Gundersen and Jørgensen 1990).

The surface roughness of a sediment is important for both the thickness and topography of the DBL. The effect depends on the height of the roughness elements, e.g. sediment grains, fecal pellets, ripples, or burrow structures of benthic animals, relative to $Z_\delta$. Boudreau and Guinasso (1982, p. 127) stated that “if the heights of the roughness elements are smaller than the ‘laminar’ portion of the viscous sublayer, then the presence of the roughness will have only a negligible effect on the flow and transport characteristics” and also that “when roughness elements are submerged within the layer, they are not capable of generating sufficient turbulence to disrupt the diffusive sublayer.”

It was the aim of the present study to analyze the relation between surface roughness, flow velocity, and the thickness and topography of the DBL. Oxygen microelectrodes were used to identify the boundary layer as well as the sediment–water interface at a spatial resolution of 0.1 mm. We chose a sediment covered by a benthic microbial mat as the study object because of its high oxygen uptake rate due to intensive bacterial respiration, because of its well defined sediment–water interface, and because the height of the roughness elements was similar to the DBL thickness.

Materials and methods

The study was done on a microbial mat collected from the bottom of a hypersaline pond at Guerrero Negro, Baja California.
Dijhive boundary layers

system of 0.5–1-m-deep, artificial salt ponds used to produce sea salt harbor 5–10-cm-thick cyanobacterial mats that cover a total area of ~100 km². Whole mat pieces of a few square decimeters surface area and 5 cm thick were carefully collected from Pond 5 which had a salinity of 108‰ and a temperature of 24°C. The mats, which have an extremely high respiration rate, were kept under a humid atmosphere rather than under water to prevent the surface from becoming anoxic during transport to the laboratory (NASA–Ames Research Center). The mats were kept for 4–6 d in a greenhouse under ~50% natural daylight in aquaria with aerated brine from the sampling site.

A mat core of 4-cm diameter was transferred to a flow aquarium with air-saturated brine of 106‰ salinity and a temperature of 26°C. The core surface was positioned flush with the surface of a surrounding, 15-cm-long and 8-cm-wide acrylic plate over which a 1.5-cm-deep water layer flowed. Large eddies were eliminated by passing the inflowing water at 10 cm upstream from the core over a threshold and through a 10-mm-thick plate densely perforated by 2-mm-wide holes. Water was circulated by a centrifugal pump, and the flow velocity was regulated.

It was not crucial for the determination of the diffusive boundary layer whether the oxygen concentration increased or decreased at the mat surface. The measurements could in principle be done either in the light, resulting in a net outflux of oxygen due to photosynthetic oxygen production within the mat, or in the dark, resulting in a net influx due to oxygen respiration. Observation of the position of the mat surface, however, required illumination. Photosynthetic oxygen production in the light was so intensive as to raise the oxygen concentration just below the mat surface to >1 atm. It gave rise to oxygen bubbles that influenced the boundary layer. To avoid this effect, we added an inhibitor of oxygenic photosynthesis, DCMU [3-(3,4-dichloro)-1,1-dimethyl-urea], to the water to a final concentration of 10 μM. It was thus possible to observe the phototrophic mat in bright light with only oxygen respiration affecting the oxygen microgradient.

Flow velocities were measured by tracing small, suspended particles at middepth in the flowing water. A dissecting microscope was used together with a stopwatch to determine the transport time over a known distance of five particles for each flow. Particle speeds varied by ±10–15%.

The diffusive boundary layer was identified from oxygen microgradients in the water above the mat surface. As boundary layers were <1 mm thick, a spatial resolution of ≤0.1 mm was required. The oxygen distribution was determined with an O₂ microelectrode with built-in guard cathode and reference electrode (Revsbech 1989a).

Three specifications of the applied microelectrode are important for its applicability for boundary-layer studies. The electrode tip was small, ~10 μm in diameter. It therefore caused minimal disturbance of the water flow. The 90% response time was 1 s. This is about five times slower than can readily be obtained with the Clark-type O₂ microelectrode (Revsbech and Jørgensen 1986). The relatively slow response was a tradeoff for optimizing the third property: the electrode had insignificant (<1%) stirring sensitivity, i.e. there was very little effect of flow velocity on electrode response.

The microelectrode was moved along X-Y-Z coordinates with a micromanipulator while observing the mat under a dissecting microscope. The precision of positioning was ±50 μm. Depth profiles of oxygen were measured at different X-Y positions over the mat surface and at different flow velocities.

The position of the mat surface was determined at ±50 μm precision by slightly vibrating the microelectrode as it was slowly moved downward. The position where a cyanobacterial filament, a diatom, or some other small particle at the mat–water interface was first observed to vibrate together with the electrode was defined as the mat surface. As the mat had a rather dense surface texture, this approach gave an identification of the mat–water interface reproducible within 0.1 mm.

A mapping of the diffusive boundary-layer thickness relative to the surface topography of the mat was done from multiple
depth determinations of the initial decrease in oxygen concentration as the microelectrode descended. For each X-Y position, the microelectrode was slowly moved downward while the oxygen level was read on a strip-chart recorder. The top of the boundary layer was found at the depth where the oxygen concentration had dropped to 90% of the free-flow concentration. The electrode was then moved further downward to determine the surface position. The most detailed mapping involved 360 profiles covering a 13-mm² grid of 18 × 20 data points at 0.2-mm horizontal X and Y increments. Repeated measurements at selected positions showed no detectable changes of surface topography during a 7-h period of continuous mapping. The coordinates for both the mat surface and the DBL surface were used to develop three-dimensional plots of the topographic surfaces by use of the program Surfer (Golden Software, Inc.). For each plot, a regular grid of 50 × 50 grid points was generated by an interpolation method in which the nearest 10 data points were weighted according to inverse distance. The Z contours of the topographic surfaces were then calculated and plotted.

Results

Stability of gradients—Oxygen concentrations measured by a microelectrode in the free-flow region of the water varied only slowly within ±5% over several hours. Also within the mat, O₂ was stable over the periods of measurement. In the DBL, however, concentration gradients showed significant fluctuations over seconds and minutes. In order to partly eliminate the time dependence of individual boundary-layer gradients, we measured each rapidly—within 30–50 s. The temporal stability of the oxygen distribution was analyzed by continuous concentration recordings with the microelectrode positioned at different depths in the boundary layer.

One such set of recordings was made over a point of the mat surface where the DBL was relatively thick, about 0.9 mm (position 1, see Fig. 4). In Fig. 1 the recordings have been traced accurately by hand from a strip-chart recorder output. There were no indications from the recorder output of oxygen fluctuations (“noise”) too rapid to be detected at the 1-s 90% response time of the microelectrode. The oxygen concentration in the circulating pond water over the mat was maintained at 100% air saturation. Starting ~1 mm above the mat surface, the oxygen concentration dropped below saturation and showed temporal fluctuations. At 0.9 mm above the mat the fluctuations were small but relatively rapid. The amplitude of the concentration fluctuations increased toward the central part of the DBL while the frequency decreased. At 0.5–0.2 mm above the mat there was a wide temporal spectrum of stochastic fluctuations ranging from a few seconds to several minutes. Closer to the mat surface, at 0.1 mm, the fluctuations were damped. The oxygen concentration just at the mat-water interface, 0.0 mm, remained within 6–8% of air saturation. At only 0.1 mm below the mat surface, the oxygen concentration was constantly zero.

Effect of flow velocity—To demonstrate how the oxygen microgradients and the DBL
were affected by water flow, we increased the flow velocity over the mat stepwise by roughly twofold increments. For each flow velocity, three or four oxygen profiles were rapidly measured at position 1 and the mean profile was calculated (Fig. 2). At the lowest flow velocity, the oxygen concentration started to drop below air saturation at 0.9 mm above the mat surface. The concentration was down to 6% of air saturation at the mat-water interface, and oxygen penetrated only 0.05 mm into the mat. The bars on the oxygen curve show the extremes of four repeated measurements at this flow velocity. Although the continuous recordings in Fig. 1 may give the impression of an unstable boundary layer, Fig. 2 shows that the time-averaged oxygen microgradients and the thickness of the DBL were well defined.

The magnitude of concentration fluctuations in the boundary layer depends on the product of the hydrodynamic fluctuations and the concentration gradients. The smaller oxygen fluctuations in the outermost DBL relative to the central part (Fig. 1) were due to the less steep concentration gradient at the transition toward the mixed zone (Fig. 2), not to lower turbulence.

As the middepth flow velocity was incrementally increased from 0.3 to 7.7 cm s\(^{-1}\), several important effects were evident from the oxygen microgradients (Fig. 2).

The thickness of the effective DBL decreased from 0.59 mm to 0.16.

The oxygen microgradients steepened. As the molecular diffusion of oxygen into the mat is proportional to the gradient at the mat-water interface, the steepening of the gradients caused a corresponding increase of the diffusive fluxes.

The amplitude of oxygen fluctuations (horizontal bars in Fig. 2) decreased, i.e. the DBL became more stable at higher flow velocity.

The oxygen concentration at the mat-water interface increased from 6% of air saturation at the lowest flow velocity to 40% at the highest.

The depth of oxygen penetration into the mat increased from 0.05 mm to 0.15. Thus, the zone of aerobic respiration as well as the availability of oxygen within the mat was highly regulated by the flow rate of the overlying water. The mat community obviously had a high potential respiration rate that was largely limited by the diffusive flux of oxygen through the boundary layer.

The oxygen fluxes into the mat by molecular diffusion through the DBL were calculated for each flow velocity from the linear oxygen gradient just above the mat surface according to Eq. 1. The molecular diffusion coefficient of oxygen in water at 28°C was calculated, by temperature and water viscosity correction from data given by Broecker and Peng (1974), to be $2.55 \times 10^{-5}$ cm\(^2\) s\(^{-1}\).

The oxygen flux was most sensitive to flow at low velocities (Fig. 3) where the mass-transfer resistance of the DBL was highest. There was a threefold increase in oxygen diffusion from the extrapolated flux at zero water flow to the highest flow velocity applied. The oxygen concentration at the mat-water interface increased correspondingly from 5 to 40% of the bulk concentration (Fig. 3).

Effect of topography—The DBL, which covers the entire mat surface like a thin blanket, must follow the surface topography or relief of the mat. A transect along the...
direction of flow showed how the upper limit of the boundary layer varied relative to mat structures of different dimensions (Fig. 4). The transect was constructed from 50 determinations of the vertical position of the DBL and the mat surface, respectively.

The main topographic features of the mat were a 4-mm-high ridge running perpendicular to the flow direction and small, circular mounds of 0.5-1-mm diameter created mostly by tufts of diatoms, e.g. positions 2 and 4 (Fig. 4). The mean DBL thickness over the smoother mat areas was 0.5-0.6 mm. As water flowed over the ridge, the DBL was reduced to 0.3 mm thick on the upstream side. The smaller diatom tufts protruding as structures 0.2-0.5 mm high above the mat surface caused only a slight bulging of the upper DBL limit.

The DBL limit was thus smoothed out over structures that had a characteristic dimension of about half the boundary layer thickness. Over larger structures such as the
Diffusive boundary layers

Fig. 5. Vertical microgradients of oxygen measured at the four positions of the transect in Fig. 4. The upper limit of the DBL was defined for mapping purposes (Figs. 4 and 6) by the vertical level where the oxygen concentration had dropped to 90% (broken line).

ridge it generally followed the topography but was thinner on the upstream slope. The shape of the oxygen microgradients within the DBL must thus vary strongly with position on the surface relief. This correspondence is demonstrated for the four positions shown in Fig. 4. In the upstream plateau, where the mat surface was relatively even, the oxygen microgradient was slightly steeper over the mounds (Fig. 5, positions 1 and 2). The gradient was steep on the slope of the ridge (position 3). The oxygen levels at the mat surface showed only small increases between position 1 and 3. The relatively high and narrow mound of position 4 penetrated far up into the boundary layer. It created a steep diffusion gradient that raised the oxygen level at the mat-water interface twofold relative to the surrounding mat surface.

The transect in Fig. 4 was measured again at a fivefold higher flow rate of 1.5 cm s⁻¹ (data not shown). The average thickness of the diffusive boundary layer over the smoother mat areas was reduced from 0.5–0.6 mm to 0.4 mm and the DBL limit more closely followed the topography of the mat surface.

Mapping of the boundary layer—Detailed topographic maps of the mat surface and of the diffusive boundary layer were made over a small area of the mat. The spatial resolution was 0.1 mm for X, Y, and Z dimensions. The mat topography included three main mounds created by diatoms and cyanobacteria plus some smaller structures (Fig. 6). An arbitrary level just below the mat surface was chosen to define Z = 0.0 mm. The highest peaks were at 0.9–1.1 mm. This mat structure was clearly reflected in the topography of the overlying diffusive boundary layer which also showed three main peaks (Fig. 6). The lowest valleys were at 0.7–0.8 mm and the peaks reached a height of 1.4–1.5 mm.

In order to show the precise relation between surface relief and DBL distribution, we also show the three-dimensional plot of Fig. 6 as a simple topographic map in Fig. 7. (Fig. 7 shows a map of the DBL thickness and not of its topography.) The boundary layer was thin, about 0.3 mm, over the three mounds and thinnest on the upstream side of the mounds. Over the valleys, the DBL was mostly 0.5–0.7 mm thick. It grew to a thickness of 0.8–1.1 mm over two narrow dents just downstream from the highest mound (top center of DBL map in Fig. 7).

The frequency distribution of DBL thicknesses within the mat area mapped in Figs. 6 and 7 is somewhat skewed toward greater values (Fig. 8). The mean thickness of the DBL based on all 360 data points was 0.52 mm.

The base area covered by the plots in Figs. 6 and 7 was 12.92 mm². The actual surface areas of the mat and of the DBL were, however, larger due to their irregular topographies. The areas of their topographic surfaces were calculated from the gridding files established to create the contour plots in Figs. 6 and 7. With the 0.1-mm spatial resolution of the data and with the applied smoothing routine of the gridding program (cf. Fig. 6), the following areas were calculated: mat surface = 16.9 mm²; DBL surface = 14.7 mm². Thus, the actual surface area of the microbial mat was 131% of the base area and the DBL surface area was 114%.

Due to the irregular topography of both DBL and mat surface, simple one-dimen-
relative to the horizontal plane, its surface area will be larger than the projected, horizontal base triangle by $1/cos \alpha$. On average, the surface area was 1.31-fold larger than the base area. Since there is a linear relation between area and $cos \alpha$ of all topographic surface triangles, the arithmetic mean of their relative area, 1.31, will give the arithmetic mean of $cos \alpha$ of all the triangles: $1/cos \alpha = 1.31$; mean $\alpha = 40^\circ$. Similarly, for the mean $cos \alpha$ of the DBL surface: $1/cos \alpha = 1.14$; mean $\alpha = 29^\circ$. The oxygen diffusion took place from 100% air saturation at the DBL surface toward the mat, so the area available for diffusion should be corrected by $1/cos 29^\circ$, i.e. by a factor of 1.14.

As an approximation, we then assume a linear gradient of oxygen from the free-flow concentration (100%) at the DBL surface to the mat surface. Furthermore, diffusion is assumed to follow the shortest path from each point on the DBL surface toward the mat surface. The gradient should therefore be measured perpendicular to the mat surface. The actual thickness of the DBL is therefore not $Z^*$ but $Z = Z/cos \alpha$ (Fig. 9).

The mean diffusional gradient is accordingly steeper, and the calculated flux should be corrected by $1/cos 40^\circ$, i.e. by a factor of 1.31.

From this double cosine correction we derive a topographically corrected diffusive flux, $J'$, through the DBL larger than that calculated from a one-dimensional gradient by 49% ($1.14 \times 1.31 = 1.49$):

$$J' = J \times \left(\frac{A'}{A}\right) \times \left(\frac{6}{Z^*}\right) = J \times \left(\frac{1}{cos 40^\circ}\right) \times \left(\frac{1}{cos 29^\circ}\right). \quad (3)$$

This approximaton is a product of the topographies of both the DBL and the sediment surface. A rather similar approximation could be made by taking the mean $cos \alpha$ of DBL and mat surface for both cosine corrections: mean $cos \alpha = (1.14 + 1.31)/2 = 1.23$; mean $\alpha = 36^\circ$. This double cosine correction yields $1.23^2 = 1.51$, i.e. only 2% higher than the former approach.

Discussion

Velocity sensitivity of microelectrodes—In order to correctly interpret the oxygen microelectrode data in terms of boundary layer characteristics, it is important that the elec-
The electrode itself does not change the boundary layer and that the electrode response is not affected by the boundary layer.

The oxygen microelectrode constitutes a physical barrier for the flow and could thus modify the flow pattern and the boundary-layer thickness. We have no quantitative measure of such a potential effect. The electrode tip had an external diameter of \( \sim 10 \) \( \mu \)m and tapered gradually toward the shaft. Thus, the electrode width was small relative to the dimensions of the boundary layer. The mapping of the boundary layer further showed that much larger structures protruding from the mat surface half way up into the DBL had a small effect on its extent. Consequently, we do not expect that the electrode could significantly have altered the distribution of the DBL.

A functioning microelectrode consumes oxygen in proportion to the electrode current (\( \sim 70 \) pA for the applied microelectrode at air saturation). The signal may therefore depend not only on the oxygen concentra-
tion but also on the external mass-transfer resistance as oxygen moves from the medium to the electrode tip. As mass transfer can be both by diffusion and by convective flow, oxygen flux to the electrode tip may be a function of flow velocity. The flow velocity decreases in the viscous sublayer from the bulk medium toward the sediment surface. This may cause a decrease in the oxygen transfer to the electrode tip, which would incorrectly be interpreted as a decrease in oxygen concentration through the DBL, independent of the actual gradient.

Such a potential artifact was recently demonstrated by Gust et al. (1987) who pointed out that microelectrodes have their own DBL around the tip and are therefore inherently sensitive to flow velocity. For the cathode-type oxygen microelectrodes they used, oxygen gradients are established in the medium just around the tip. As the electrodes of Gust et al. had very high currents and oxygen consumption rates, they were unusually sensitive to flow. Although the results may therefore not be representative for most other studies with oxygen microelectrodes, Gust et al. raise the important point that it is essential always to check the velocity sensitivity of microelectrodes.

The oxygen microelectrode we used was of the Clark type with built-in reference electrode. It furthermore had a guard cathode to reduce background current (Revsbech 1989a). In this type of electrode the main diffusion barrier and oxygen gradient in front of the cathode lies within the silicone membrane and not in the medium surrounding the tip. The electrode, as it is routinely made in our laboratory at the University of Aarhus, generally has a maximal velocity effect of <1% and a 90% response time of <1 s.

There is a tradeoff, however, between flow velocity sensitivity and response time. When the distance (membrane thickness) between electrode entrance and cathode tip is increased, there is a relative shift in the mass transfer resistance from the external medium around the electrode tip to the internal diffusion path within the electrode. As a result, the electrode becomes less sensitive to stirring but the response time increases. The oxygen microelectrode used in the present study had very small velocity sensitivity (<1%) to the detriment of the response time (1 s). Revsbech (1989a) demonstrated that an electrode with these properties showed no artificial oxygen gradients in the DBL.

Oxygen microelectrodes with velocity effects in excess of a few percent are consequently not suited for DBL studies (and should preferably not be used at all to measure oxygen concentrations). It is an interesting possibility, however, to make use of the adverse effects of flow: the combined use of microelectrodes with and without a strong velocity sensitivity could theoretically be used to measure flow velocities in microscale at <0.1-mm resolution.

Stability of the DBL—Oxygen concentrations measured in the mat and in the bulk medium at >1 mm from the sediment surface were very stable over time. Variations over a few minutes were generally <2% but some long-term drift over tens of minutes occurred, possibly due to variations in oxygen saturation level or in mat respiration rate (data not shown). Within the boundary layer, however, oxygen concentrations fluctuated in response to turbulence and to patterns of water flow from upstream regions. Close to the mat–water interface, the fluctuations were strongly suppressed.

Patterns of flow and oxygen exchange over a rough sediment–water interface are very complex. In addition to stochastic fluctuations caused by turbulent flow components in the inertial flow region, sudden “bursts” of strong water movement also occur in the boundary layer (Boudreau 1988). Although such bursts are difficult to describe mathematically, the mass transfer calculated from a bursting model is similar to that calculated from classical boundary-layer theory when averaged over a period of several bursts. The oxygen microgradients at the point of measurement are also affected by the upstream oxygen consumption within the DBL and thus by fluctuations in horizontal flow. Although these phenomena may give the impression of an unstable boundary layer, the time-averaged mass transfer by molecular diffusion is still much faster than the eddy diffusion in the DBL.

An independent check of this assertion could be done by comparing the calculated
Diffusional flux with the total oxygen uptake over the mat–water interface. Such a comparison was not made in the present study, but has been done for a marine sediment (H. Rasmussen and B. B. Jørgensen in prep.). The calculated diffusional flux averaged 69% of the total flux. This estimate did not take into account the double cosine correction for surface topography or the ventilation by burrowing animals, which may well account for the “unexplained” 31% in that sediment. The oxygen flux calculation based on pure molecular diffusion thus provided a realistic estimate of the total oxygen uptake.

In spite of the fluctuating concentrations shown in Fig. 1, the mean oxygen gradients through the DBL were quite reproducible when consecutive profiles were measured (Fig. 2). The reproducibility increased with the flow velocity and, thus, inversely with the thickness of the DBL (Fig. 2 and data not shown).

The characteristic period of fluctuations was a few seconds to a few minutes (Fig. 1). We did not notice any fluctuations at >1 Hz frequency, only as occasional electrical noise independent of electrode position. Gust et al. (1987) reported fluctuations of 1–10 Hz from measurements with both microelectrodes and skin-friction sensors in the boundary layer of a laboratory microcosm. With a 90% response time of 1 s, we would not have seen the full amplitude of >1-Hz fluctuations but should still have been able to notice their presence. Recent microelectrode studies over a marine sediment have shown that the frequency of fluctuations increases strongly with increasing flow velocity (Gundersen and Jørgensen 1990).

Effect of flow—The fluctuating components of the flow velocity generally decrease as the sediment surface is approached. The distance above a sediment surface where the flow changes from predominantly turbulent to predominantly viscous depends on the flow velocity. Higher flow velocity increases the eddy diffusion coefficient, $K$, and thus decreases the distance from the sediment surface, $Z_v$, where $K$ becomes smaller than the molecular diffusion coefficient, $D$.

The DBL constitutes a barrier to mass transfer across the sediment–water interface. The microbial mat studied here had such intense oxygen respiration that the external transfer resistance in the DBL was large at all flow velocities relative to the internal resistance caused by diffusion within the mat and by the reaction kinetics of oxygen consumption. The oxygen uptake of the mat thus was largely governed by DBL impedance. It was therefore highly sensitive to variations in DBL thickness and thus to flow velocity. As flow velocity increased, the oxygen concentration at the mat surface increased, the depth of oxygen penetration into the mat increased, and the mass transfer resistance partly shifted from external toward internal. The diffusive flux had relatively little flow sensitivity at high velocities, >3 cm min$^{-1}$. Extrapolation of the flux-vs.-flow curve (Fig. 3) to zero flow indicated a flux of perhaps 3 nmol O₂ cm$^{-2}$ min$^{-1}$, i.e. a third of the maximal flux calculated. This relatively high flux may be explained by the residual flow and eddy diffusion due to, for example, thermal convection over the mat. Such convection remained in the absence of an externally forced circulation.

A predominant DBL mass-transfer resistance for oxygen as observed here is characteristic of organic-rich sediments with high rates of microbial respiration at the surface. Typical examples are coastal sediments covered by microalgae or by colorless and phototrophic sulfur bacteria where oxygen penetration below the sediment–water interface is only on the order of 0.1 mm (Jørgensen and Revsbech 1985). The oxygen penetration in most sediments is considerably deeper, >1 mm. Based on oxygen microelectrode data obtained by an in situ profiling instrument from the outer continental shelf, Archer et al. (1989) calculated that the natural DBL slowed the diffusive flux of oxygen by only 10%. The depth of oxygen penetration that they measured was ~5 mm and the DBL thickness was 0.5–1.5 mm. Calculations of the accretion rate of Mn nodules on the deep-sea floor indicate that this relatively slow process is also controlled by molecular diffusion of dissolved metals through the DBL surrounding the nodules (Boudreau and Scott 1978; Boudreau 1988). This calculation shows that the mass-transfer resistance of the DBL does not depend
only on total diffusive flux but rather on the concentration drop across the boundary layer relative to the free-flow concentration.

Effect of surface roughness—A number of earlier studies seem to disagree concerning the effects of surface roughness on mass transfer over a solid-water interface (see Boudreau and Guinasso 1982). In some experimental studies an increase in surface roughness resulted in an increase in mass transfer of heat or chemical species, but in others it resulted in a decrease. On the basis of the present data (Fig. 6), the explanation for such disagreement could be that surface roughness has two opposing effects that may balance differently between studies. At a fixed forcing level for the flow, increased surface roughness tends to retard the flow and thus to increase DBL thickness. This thickening decreases the diffusive flux through the DBL. Increased surface roughness at the same time increases the actual surface area of the DBL, which increases the diffusive flux. For the slow flow (0.4 cm s\(^{-1}\)) and < 1 mm surface relief studied here, the latter effect increased the diffusive flux by 49%. Higher flow velocity or stronger relief would increase the percentage further.

In conclusion, we find that oxygen microelectrodes are excellent tools to demonstrate the distribution and properties of diffusive boundary layers. It is a requirement, however, that the surface sediment has a sufficiently high respiration rate. The minimum respiration rate required can be calculated as follows. We assume a DBL thickness of 0.5 mm and a minimal decrease in oxygen concentration, \(C_\infty - C_0\), of \(\sim 5\%\), which is necessary to determine the gradient. If \(C_\infty\) at air saturation is 250 \(\mu\)M, the minimal gradient is 250 mmol cm\(^{-1}\). The molecular diffusion coefficient at, e.g. 10°C, is \(1.57 \times 10^{-5}\) cm\(^2\) s\(^{-1}\) (Broecker and Peng 1974). The minimal diffusional flux is thus

\[
250 \times 1.57 \times 10^{-5} \times 60 = 0.24 \text{ nmol cm}^{-2} \text{ min}^{-1} \text{ or } 3.5 \text{ mmol m}^{-2} \text{ d}^{-1}.
\]

This requirement limits the approach to sediments of the continental shelf and upper slope or to freshwaters where sediment respiration generally exceeds this limit. Once the DBL distribution has been determined from oxygen microgradients, the data can also be used to study the flux of other dissolved compounds across the sediment-water interface.

The oxygen uptake rate of aquatic sediments shows varying sensitivity to flow velocity (stirring) and to the oxygen concentration of the overlying water (e.g. Boynton et al. 1981; Campbell and Rigler 1986). The observed dependence of the diffusive oxygen flux on roughness and bulk oxygen concentration may explain many of these observations as an effect of the relative mass-transfer resistance of the DBL. Calculation of oxygen uptake rates from DBL gradients rather than from gradients in the sediment has the advantage that the diffusion is independent of sediment porosity. Both porosity and the diffusion coefficient are difficult to determine at sufficient spatial resolution in sediments to constrain diffusion calculations, although microelectrode techniques to do so have been developed (Revsbech 1989b).

References


Gust, G., K. Boou, W. Hendler, and B. Sundby. 1987. On the velocity sensitivity (stirring effect) of po-


