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Oxygen in the Sea Bottom Measured with a Microelectrode

Abstract. *The depth of penetration of oxygen into coastal marine sediments (water depth, 4 to 44 meters; 6° to 10°C) varied from 1 to 5.5 millimeters, as measured with membrane-covered oxygen microelectrodes. Below these upper few millimeters, oxygen was present only in the immediate vicinity of animal burrows. The depth of oxygen penetration is related to the rate at which oxygen is consumed in the sediment.*

Although the oxygen supply of marine sediments is of great importance to the benthic community, such information has been virtually nonexistent. The main reason is that no satisfactory method has been available for the accurate detection of sedimentary pore water concentrations. Because better estimates are lacking, the thickness of the brown, oxidized surface sediment having a positive oxidation-reduction potential has often been used as an indication of the penetration depth of oxygen into sediments (*1*). With the aid of polarographic oxygen microelectrodes, we have made the first accurate measurements of oxygen in marine sediments and have demonstrated the absence of oxygen in the deeper parts of this layer (*2*). The anoxic part of the brown layer is often much thicker than the oxic part. Earlier estimates of the depth of oxygen penetration into sediments therefore tend to be too high. We found that it is possible to calculate the approximate depth of oxygen penetration from the rate of oxygen uptake by the sediment surface, and this parameter is normally measured in sediment studies.

All the sediment samples were collected during a 2-week period in late November 1978. The sampling localities, all in coastal Danish waters, were situated at water depths from 4 to 44 m. The sediment was sampled with a Haps corer (*3*), from which subsamples were taken out with Plexiglas cylinders (inside diameter, 46 mm). Only cores for which there was no resuspension of the sediment material during the sampling procedure were used in the analysis. Oxygen profiles and the oxygen consumption rate of the sediment were determined while the cores were protected from light, immediately after sampling. The oxygen profiles were measured with the oxygen microelectrode of Baumgärtl and Lübbers (*4*), which has a tip diameter of 2 to 8 μm and therefore creates almost no physical or chemical distortion when it is inserted into the sediment. [The use of oxygen microelectrodes in sediments is described in (*2*).] The electrodes were introduced stepwise into the sediment from above with the aid of a micromanipulator, and the oxygen concentrations read at 0.5- or 1.0-mm intervals. The water above the sediment was stirred and kept saturated with air by bubbling. The oxygen consumption per unit area was calculated from the rate of decrease in oxygen concentration of the water above the sediment, as measured in stoppered sediment cores. Mean values of five cores with gently stirred water and five cores with no stirring were used (*5*). The porosity of the sediment (ϕ) was determined as the weight loss of a known volume of surface sediment (0 to 1 cm) after drying at 105°C for 24 hours.

The oxygen concentration in the pore water, C_x, at depth x may be calculated from (*6*):

$$C_x = \frac{R}{2D}\left[x^2 - 2x\left(\frac{2DC_0}{R}\right)^{1/2} + \frac{2DC_0}{R}\right] \qquad (1)$$

where R is the oxygen uptake rate per unit volume of pore water, D is the diffusion coefficient of oxygen in the sediment, and C_0 is the oxygen concentration at the sediment surface. Equation 1 is valid only if the rate of oxygen consump-

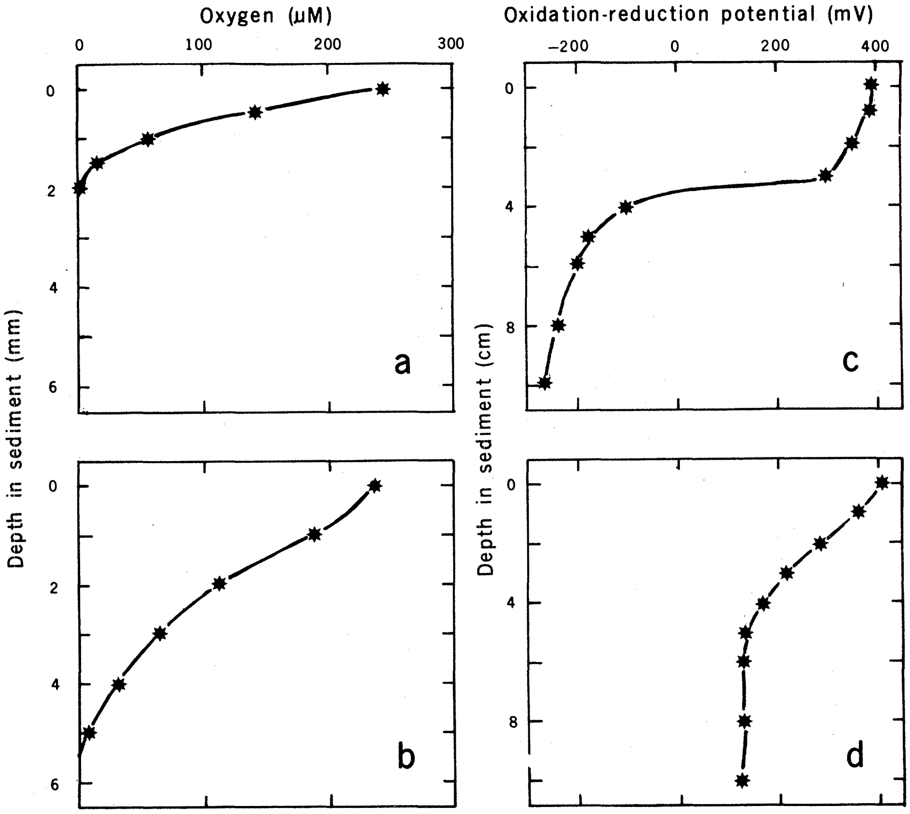

Fig. 1. Oxygen and oxidation-reduction profiles from two different sediments. (a) Oxygen profile showing the normal, nearly parabolic shape predicted by Eq. 1. (b) Sigmoidal oxygen profile, indicating turbulent oxygen transport in the upper 1 mm. (c) Oxidation-reduction profile from the same locality as (a). (d) Oxidation-reduction profile from the same locality as (b). A platinum electrode was used for the oxidation-reduction measurements (*15*). At both localities, the oxidized sediment layer having a positive oxidation-reduction potential was much thicker than the oxic layer.

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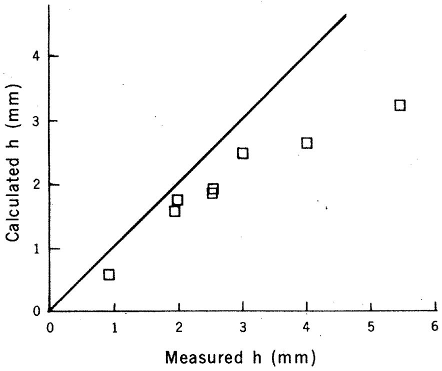

Fig. 2. Calculated and observed values of the depth of oxygen penetration (*h*) into eight different sediments. The line corresponds to the equation *h* (measured) = *h* (calculated). Because of burrowing animals and the turbulence in the surface layer, the calculated values are all lower than the measured ones and can thus be regarded as "minimum oxygen penetration depths."

tion per unit volume of pore water is uniform throughout the oxic zone. This also means that the rate of oxygen consumption should be independent of oxygen concentration, which is true to a certain degree for bacterial respiration (*7*) but not for purely chemical oxidation processes. We also assumed that ϕ and D are constant with depth. As these assumptions apply to a sediment layer only a few millimeters deep, the error probably will be small. For all the investigated sediments we assumed a value for D of 8×10^{-6} cm^2 sec^{-1} (*8*). The value of C_0 was assumed to be 80 percent air saturation (240 μM) to allow for some decrease in the absence of very vigorous stirring (*2*). No corrections were made for the small differences in temperature (6° to 10°C).

Figure 1a shows a typical oxygen profile measured with the microelectrodes; the shape of the curve is nearly parabolic, as predicted by Eq. 1. The penetration depth of oxygen, h, at which $C_x = 0$, is at the vertex of the parabola:

$$h = \left(\frac{2DC_0}{R}\right)^{1/2} \qquad (2)$$

According to the above assumptions,

$$R\phi = \frac{J}{h} \qquad (3)$$

where J is the rate of oxygen consumption per unit area (the flux). Thus the following expression is obtained:

$$h = \frac{2DC_0\phi}{J} \qquad (4)$$

Experiments were conducted in sediments ranging from clay to medium sand; the porosity varied from 47 to 78 percent. If an average porosity of 70 percent is assumed, Eq. 4 can be written in the form

$$h\ (\text{cm}) \times R\ (\mu\text{mole cm}^{-2}\ \text{sec}^{-1}) = 2.7 \times 10^{-6}\ \mu\text{mole cm}^{-1}\ \text{sec}^{-1} \qquad (5)$$

Measured and calculated values of h are shown in Fig. 2; the actual porosities were used in these calculations. The calculated values of h are always smaller than the measured ones. This is to be expected, as oxygen transport other than diffusion plays a significant role in natural sediments. Oxygen may locally be pumped by burrowing animals deep into the anoxic strata where irregularly high oxygen readings have been obtained (*5*). A fraction of the oxygen that is pumped down into the burrows is consumed by the animals themselves, but an additional large fraction is consumed in the sediment around the burrows.

Vigorous stirring (at the current velocity where the sediment started to go into suspension) as compared with gentle stirring only increased the penetration depth of oxygen into a sandy sediment from 2.5 to 3.5 mm thick (*2*). The effect of stirring depends upon the stability of the sediment surface. A sigmoidal oxygen profile would indicate turbulent oxygen transport in the upper layer of the sediment. The oxygen profile having a penetration depth of 5.5 mm (Fig. 1b) was actually a sigmoidal curve. The sediment surface at this locality was very unstable. As the experimental water current probably caused a much higher turbulence than there was in situ (at a depth of 44 m), the in situ oxygen penetration is probably less than 5.5 mm.

The oxidation-reduction profiles from the two localities are shown in Fig. 1, c and d. At both localities the upper several centimeters had positive oxidation-reduction potentials, and there seemed to be no correlation between the oxidation-reduction potential profile and h. The finding that even oxidized sediments were oxygen-free below the upper few millimeters implies that the benthic organisms in nonexposed shallow-water sediments live largely in an anoxic environment. Most of the bigger animals are able to ventilate their burrows with oxic surface water, but the meiofauna and bacteria that live below the upper few millimeters must obtain their energy from anaerobic metabolism. The electron acceptor used in the microbial metabolism in the oxidized but anoxic sediment is not known; we could measure only a low rate of sulfate reduction and denitrification in such sediment layers (*5*). It is possible that the unknown electron acceptor is ferric iron (*9*), but the mechanism of electron transport is unknown. The iron compounds also constitute the major part of the oxidation-reduction buffer capacity of the sediment (*10*). The burrowing activities of the infauna in the anoxic sediment cause local and temporal oxygenation (*5*). This activity produces patchiness in the degree of sediment oxidation (*11*). Wave action (*12*) and intertidal pumping (*13*), on the other hand, may be important for a periodic, uniform oxidation of the surface layers of coastal sediments.

The sediments that we investigated in this study were from relatively shallow-water localities. In very oligotrophic deep-sea sediments, h may be considerably larger. The lowest reported R value for a deep-sea sediment is 2.5×10^{-8} μmole cm^{-2} sec^{-1} (*14*); this corresponds to an oxygen penetration depth of about 1 m if Eq. 5 is valid for such a sediment.

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