Oxygen demand in coastal marine sediments: comparing in situ microelectrodes and laboratory core incubations

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Abstract

A study coupling core incubation and a large number of in situ microelectrode measurements (n = 18) was performed at a single station in the Golfe de Fos, a semi-enclosed estuarine system in the South of France on the Mediterranean Sea. Total and diffusive oxygen fluxes were determined for two different seasons (October 2000 and May 2001). The average total and diffusive oxygen fluxes were 21.5 and 12.7 mmol m⁻² day⁻¹, respectively, in October and 18.5 and 16.5 mmol m⁻² day⁻¹, respectively, in May. The average total oxygen demand does not vary significantly between the two periods (21.5 ± 5 to 18.5 ± 4 mmol m⁻² day⁻¹). The spread of the values obtained by microelectrode measurements reveals the variability at the decimeter scale indicating a control by small-scale processes. Little difference was found in May between the total and diffusive oxygen fluxes when the number of microelectrode profiles (n = 18) and core incubation (n = 9) was sufficient to catch larger fluxes linked to “organic hot spots”. Although present at a population density of 5700 individuals for 0.1 m², macrofauna is mostly composed of surface deposit feeders. The little difference found between total and diffusive oxygen demand points towards not only the population density but also the faunal assemblage as a determining factor for sediment irrigation.

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1. Introduction

Oxygen demand in coastal sediments is a key issue in determining water quality. Indeed, hypoxic events which occur in stratified waters are known to severely impact the composition of coastal waters and affect the living infauna (Smetacek et al., 1991; Justic et al., 1994). In this regard, benthic oxygen dynamics play a determining role in controlling the amount and timing of peaks of sediment oxygen demand (SOD) with regards to pelagic production or water stratification. It is thus of importance to quantify precisely and identify the processes responsible for sediment oxygen demand in shallow coastal environments.

Oxygen distribution in coastal sediments is also crucial to the importance of processes such as organic matter preservation (Hartnett et al., 1998), denitrification (Seitzinger, 1988; Seitzinger and Giblin, 1996; Devol, 1991) or trace metal speciation and mobility linked to the iron cycle (Lovley, 1987; Shaw et al., 1990; Shimmield and Pedersen, 1990).

Different techniques for estimating the oxygen demand of sediments have been reported. Core or benthic chambers incubations provide the total oxygen demand and oxygen microprofiles coupled to estimation of the formation factor yield diffusive oxygen demand. Yet, the estimates of the two techniques show contrasted results. Archer and Devol (1992) found an excess of the total oxygen demand compared to the diffusive flux by a factor of 2–3 on the continental shelf whereas Reimers et al. (1992) found a fair agreement between the two values on the Pacific slope and rise below 1000 m. In the shallow coastal regions, similar contrasted results were found: Lindeboom et al. (1985) found a factor of 2 between the total and diffusive fluxes but Rasmussen and Jorgensen (1992) calculated a difference of only 30% between the annual averages of these two fluxes with larger discrepancies in summer. It is thought that the agreement between the two techniques depends on the macrofaunal activity promoting bioirrigation with a ratio of 1 in the deep-sea to 3–4 in the slope and shelf (Wenzhoefer and Glud, 2002).

In this paper, we propose an estimation of the oxygen mass balance in coastal sediment from a semi-enclosed estuarine system in the Mediterranean Sea obtained by two techniques: (i) laboratory core incubations and (ii) in situ microelectrodes profiles. We explore the similarities and differences between the two techniques, approach the spatial scale of lateral heterogeneity of the oxygen demand and discuss the processes related to this variability.

2. Material and methods

2.1. Sampling site

The Golfe de Fos is a Mediterranean semi-enclosed estuarine system located in the south of France close to Marseille (France), near the mouth of the Rhône river (Fig. 1). It covers a surface area of 42 km² and has an average depth of 8 m. Golfe de Fos is surrounded by an industrial area with a large harbour (petroleum, gas and ore tankers) and associated industries. We studied a station located in the closed part of the Golfe (station no. 24, 43°22'893N 4°54'225E, depth 9 m), where sediments are mostly muddy sands.
performed two series of measurements using the R.V. George Petit in October 2000 and R.V. Tethys II in May 2001. All microelectrode measurements were performed in a circle of 75-m radius and all coring in a circle of 100 m of diameter at the same station.

2.2. Methods

2.2.1. Microelectrode measurements

During these experiments, in situ microsensor measurements of four vertical O$_2$ distributions were acquired using a microprofiler (Unisense®) together with one resistivity depth distribution on a single deployment. The profiler, mounted on a tripodal frame, was settled on the sea floor by divers with minimum disturbance of the sediment. A minimum time of 30 min was allowed before the measurement programme started.

Dissolved O$_2$ concentrations were measured by polarographic oxygen microelectrodes provided with a built-in reference and an internal guard cathode (Revsbech, 1989). The O$_2$ microsensors had tip outer diameters of 100 μm, a stirring sensitivity of <1% (i.e. signal increase in flowing vs. stagnant water), a 90% response time of 10 s, and the current drift was less than 1%/h. The zero oxygen currents were typically on the order of 0–12 pA, in accordance with values measured in the laboratory with an ascorbic acid solution, and the bottom-water signals ranged from 150 to 270 pA, depending on the exact geometry of the electrode tip (Gundersen et al., 1998). The electrode signals were recorded in the overlying water both before and after the profile, to assess the stability of the measurements. Linear calibration of microelectrodes was achieved between bottom-water oxygen value estimated by Winkler titration (Grasshoff et al., 1983) and the anoxic zone of the sediment. The vertical resolution of the measurements was generally 200 μm (with two profiles performed at 100-μm resolution—1505-pA2 and 1505-pA3).
The position of the sediment–water interface (SWI) relative to the in situ oxygen profiles was determined from O$_2$ microprofiles using a modified version of the technique of Sweerts et al., (1989) which consists in assigning the interface position to a break in the oxygen concentration gradient. The observed slope increase in the sediment is due to the decreased diffusion coefficient compared to the diffusive boundary layer. For most profiles in our case, the slope break was not clearly visible; rather we observed a steady increase of the slope towards a maximum within the first millimeter below the initial concentration decrease. We adopted the position of this maximum gradient as the sediment–water interface. Oxygen penetration depth was determined by using the depth where O$_2$ microelectrode signal reached the zero current.

Resistivity measurements were made with an electrode similar to that described by Andrews and Bennet (1981). Four thin parallel wires were buried in a matrix of epoxy, with only their tips in electrical contact with seawater. The resistivity sensor has a rectangular section of 10 $\times$ 3 mm and is edged at the lower end. Recordings were made at 200 $\mu$m as for the oxygen but the pertinent resolution is certainly around 1 mm due to the shape of the sensor. Since the sensors interact with the sediment before penetration (Andrews and Bennet, 1981), the interface position was estimated using test in the laboratory where interface was estimated visually. The uncertainty on the interface position is $\pm$ 2 mm. Resistivity recordings were converted to formation factor values by the formulation of Berner (1980).

$$F = R_z/R_{bw}$$

where $F$ is the formation factor, $R_z$ is the mean of the resistivity at a given depth $z$ and $R_{bw}$ is the average resistivity in bottom-water. We calculated an average profile of formation factor from the four profiles displayed in Fig. 2, and translated it to porosity using a two-points calibration acquired for the Golfe de Fos (Lansard et al., submitted for publication) following the relationship:

$$\phi = \frac{F^{-1} + 0.1582}{1.1582}$$

The flux estimates from the oxygen microprofiles were achieved with two different methods.

(1) We calculated the oxygen flux at the sediment–water interface by the following formula:

$$F_{O_2} = F^{-1}D_{O_2}^0[dO_2/dx]_{x=0}$$

where $F^{-1}$ is the inverse of the formation factor at the sediment–water interface (SWI), assumed constant for all profiles (0.88), $D_{O_2}^0$ is the diffusion coefficient at in situ temperature and $[dO_2/dx]_{x=0}$ is the oxygen gradient at the SWI (estimated from the profiles).

(2) We used the PROFILE software (Berg et al., 1998) which calculates the consumption rates with depth by adjusting the calculated oxygen profile to the observed one. For these calculations, we used an average porosity profile (Fig. 2)
Fig. 2. (a) Inverse of the formation factor ($F^{-1}$) plotted versus depth for the period of May 2001. (b) Average $F^{-1}$ and calculated porosity profile.
Fig. 3. All oxygen profiles measured during Modelfos 2 (May 2001). Groups of profiles are also shown for four different deployments during Modelfos 2 (each curve represents a single electrode profile) showing the large heterogeneity at small space scale.
for the station from the different resistivity measurements performed during the cruise.

2.2.2. Sediment oxygen demand (SOD) determined by whole core incubation

Cores were sampled with a sediment multicorer (Mark VI, Bowers and Connelly) especially designed to obtain simultaneously four large diameter (15 cm) perspex cores (50 cm height with around 20 cm of overlying water and 30 cm of sediment). Cores were

![Graphs showing oxygen profiles and consumption rates](image-url)

Fig. 4. Individual oxygen profiles showing the measured values (filled dots), the PROFILE fit (plain curve) and the consumption rate calculated by PROFILE (dashed line). (a) For Modelfos 1 (October 2000) and (b, c, d, e) for Modelfos 2 (May 2001).
brought to the laboratory immediately after retrieval and incubations generally started within 4 h after sampling. We followed the incubation procedure and experimental settings previously detailed (Denis, 1999; Denis et al., 2001). Briefly, cores were incubated in dark thermoregulated cabinets at in situ temperature, after a careful sealing excluding air bubbles. Overlying water was continuously homogenised with a rotating floating magnet fixed to the upper cap (Cowan and Boynton, 1996). Each core was linked by tubing to an inflatable reserve tank filled with bottom-water. Plastic syringes were used to sample reserve tank and overlying water, and the volume removed in each core tube was replaced with bottom-water from the reserve tank. Generally six to eight samplings (120 ml) were performed during incubations lasting 15–20 h. We determined oxygen concentration in

Fig. 4 (continued).
the overlying water of each core and the reserve tank by mean of micro Winkler titration (Grasshoff et al., 1983). Fluxes were then calculated by regressing the change of oxygen concentrations in the overlying water against time. A correction for overlying water

Fig. 4 (continued).
dilution with bottom-water at each sampling point was applied. The change of concentration with time was statistically tested ($t$-test, $p < 0.05$). When significant changes were recorded in the reserve tank, the rate of change was subtracted to the one calculated in each core tube.

3. Results

Oxygen profiles acquired during Modelfos 1 and Modelfos 2 cruises all showed a decrease with depth indicating oxygen consumption in the sediments (Fig. 3).
Penetration depths of oxygen ranged from 0.3 to 1.5 cm with an average of 0.4 cm. A slight but not statistically valid differences were found between October (0.3 ± 0.1 cm; n = 3) and May (0.5 ± 0.3 cm; n = 18) for this parameter. Consumption patterns calculated from PROFILE (Berg et al., 1998) typically showed a large consumption close to the sediment–water interface (first millimeter) and a lower consumption at the oxic–anoxic boundary indicating that reduced chemical species diffusing from deeper layer contribute to the oxygen consumption in these sediments (Fig. 4). The number of equally spaced zones was not always similar during the fitting procedure by the software, which explains the changing resolution from one individual profile to the other. Some profiles show a small gap around 3–4 mm which creates a deficit in
oxygen consumption rate. This could be due to a thin layer of less permeable sediment, which would disrupt the oxygen concentration profile.

3.1. Oxygen fluxes during Modelfos 1—October 2000

Four oxygen profiles were performed during this cruise. The oxygen consumption was calculated by the two methods indicated above (Table 1). The interface gradient method provided an average diffusive flux of 12.3 mmol m$^{-2}$ day$^{-1}$ whereas fluxes

<table>
<thead>
<tr>
<th>Sediment oxygen demand (SOD) estimation with the different techniques</th>
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<td>Sediment oxygen demand (mmol m$^{-2}$ day$^{-1}$)</td>
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<table>
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<tr>
<th></th>
<th>Interface gradient method</th>
<th>PROFILE method</th>
<th>Total flux</th>
<th>Core incubations</th>
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</thead>
<tbody>
<tr>
<td><strong>Modelfos 1—October 2000</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pA1 4/10</td>
<td>13.7</td>
<td>11.6</td>
<td>4/10-St 24-1 #1</td>
<td>21.2</td>
</tr>
<tr>
<td>pA3 4/10</td>
<td>11.7</td>
<td>9.1</td>
<td>#2</td>
<td>23.8</td>
</tr>
<tr>
<td>pA1 5/10</td>
<td>16.6</td>
<td>18.3</td>
<td>#3</td>
<td>18.8</td>
</tr>
<tr>
<td>pA4 5/10</td>
<td>7.3</td>
<td>#4</td>
<td>5/10-St 24-2 #1</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
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<td>20.0</td>
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<td>#3</td>
<td>20.9</td>
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<td>#4</td>
<td>27.7</td>
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<td></td>
<td>8/10-St 24-3 #1</td>
<td>13.6</td>
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<td></td>
<td></td>
<td></td>
<td>#2</td>
<td>15.1</td>
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<td></td>
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<td></td>
<td>#3</td>
<td>18.9</td>
</tr>
<tr>
<td><strong>Average flux</strong></td>
<td>12.3</td>
<td>13.0</td>
<td></td>
<td>21.5</td>
</tr>
</tbody>
</table>

| **Modelfos 2—May 2001** |                       |                |            |                  |
| 1405-pA2              | 47.2                     | 27.6           | 10/5-St 24-1 #1 | 24.0            |
| 1405-pA3              | 13.6                     | 12.0           | #2         | 17.2             |
| 1405-pA4              | 14.0                     | 10.9           | 12/5-St 24-2 #1 | 20.0            |
| 1405-pA5              | 12.9                     | 9.8            | #2         | 16.1             |
| 1505-pA2              | 38.0                     | 19.6           | #3         | 12.8             |
| 1505-pA3              | 25.1                     | 19.3           | #4         | 13.4             |
| 1605-pA2              | 11.5                     | 14.9           | 13/5-St 24-3 #1 | 21.2            |
| 1605-pA3              | 5.1                      | 15.4           | #2         | 16.8             |
| 1605-pA5              | 15.9                     | 8.6            | #3         | 25.4             |
| 1605_2-pA5            | 9.7                      |                |            |                  |
| 1705-pA2              | 28.3                     | 17.0           |            |                  |
| 1705-pA3              | 12.7                     | 12.9           |            |                  |
| 1705-pA4              | 27.0                     | 26.5           |            |                  |
| 1705-pA5              | 14.1                     |                |            |                  |
| 1705_2-pA2            | 26.9                     | 12.4           |            |                  |
| 1705_2-pA3            | 6.6                      | 4.8            |            |                  |
| 1705_2-pA4            | 10.1                     | 8.8            |            |                  |
| 1705_2-pA5            | 20.6                     | 13.9           |            |                  |
| **Average flux**      | 18.8                     | 14.7           |            | 18.5             |

Interface gradient and PROFILE methods refer to the calculation of diffusive SOD from oxygen micro-profiles. Core incubations provide a measurement of total SOD (see text for details).
calculated using the PROFILE software provided an average of 13 mmol m\textsuperscript{-2} day\textsuperscript{-1} excluding one profile which typically showed a burrow structure. The total flux estimated by core incubations \((n = 11)\) amounted to 21.5 mmol m\textsuperscript{-2} day\textsuperscript{-1} and is a factor of 1.8 larger than the diffusive flux (Fig. 5).

3.2. Oxygen fluxes during Modelfos 2—May 2001

During this second cruise, 18 oxygen profiles were acquired at the same station together with nine core incubations. The diffusive oxygen fluxes estimated by the two calculation methods showed very similar patterns with PROFILE fluxes being most often lower especially for extreme values (Fig. 5d). The average flux estimated by the interface gradient method \((n = 18)\) was 18.3 mmol m\textsuperscript{-2} day\textsuperscript{-1} whereas the average for the PROFILE method was 14.7 mmol m\textsuperscript{-2} day\textsuperscript{-1} \((n = 16)\). The spread of the flux distribution is very high with a factor of 6–9 between the lowest and highest fluxes for the two methods.

The incubation fluxes \((n = 9)\) showed an average of 18.8 mmol m\textsuperscript{-2} day\textsuperscript{-1} with a limited deviation around the average since a factor of 2 only was found between the extremes (Fig. 5c).

The statistical distribution was performed by separating the diffusive fluxes in classes of 10 mmol m\textsuperscript{-2} day\textsuperscript{-1} and core incubation fluxes in classes of 5 mmol m\textsuperscript{-2} day\textsuperscript{-1}.

Fig. 5. Sediment oxygen demand measured during the Modelfos 1 (October 2000) and Modelfos 2 cruise (May 2001). (a and c) Total flux refers to core incubations and (b and d) diffusive flux refers to microelectrode estimation through the different methods (see text for details).
day$^{-1}$ (Fig. 6). Diffusive fluxes show a non-Gaussian distribution extending largely towards large flux values whereas incubation fluxes showed a regular Gaussian distribution.

4. Discussion

We investigate the reasons of the observed differences between the diffusive and total flux estimates with respect to seasonal variations of oxygen demand and spatial heterogeneity at all space scales. Three main features emerge from this study: (i) the relative constancy of the total oxygen demand between October 2000 and May 2001, (ii) the large spatial heterogeneity captured by the microelectrodes and (iii) the little difference observed between total and diffusive fluxes in May 2001.

Fig. 6. Statistics on the estimated oxygen fluxes. (a) For diffusive fluxes with the two methods used for calculation (b) comparing the distribution of core incubation and diffusive flux estimated by PROFILE.
4.1. Potential biases on the determination of microelectrode or incubation fluxes

Before going into the discussion, some methodological issues which could have biased the results need to be addressed. The observed spread of the diffusive fluxes is partly attributable to the method of selection of the sediment–water interface. Since the diffusive boundary layer and the associated constant gradient were not obvious in our study (due to a resolution of 200 \( \mu \text{m} \) in general), we assigned the sediment–water interface to the position of the maximum gradient when this maximum was within the first millimeter below the start of the oxygen variation. The diffusive flux for the interface gradient method was then estimated using this maximum gradient using two successive oxygen concentrations at the SWI. This can lead to over- or underestimation of the flux due to the noise on the oxygen record and could have caused some of the observed variability. Nevertheless, this variability was also observed on the oxygen profile shapes with oxygen penetration depths ranging from 3 to 15 mm clearly reflecting the heterogeneity of the sediment (Fig. 3), thus suggesting that the bias introduced by the calculation method is limited. Furthermore, flux values obtained by the PROFILE software which takes into account the overall oxygen profile also show a spread (Fig. 5d) excluding a major artefact of the interface gradient method. This spread is very likely linked to the natural variability of the sedimentary environment.

The choice of the interface location as the maximum oxygen gradient could also explain the larger SOD values generally found for the interface gradient method compared to the PROFILE method, which takes into account the complete oxygen profile. If the “true” interface was situated slightly above or below this maximum, then the flux calculation would decrease by 10–20% because of the rapid change of the gradient in the interface zone. For the PROFILE method, one clear potential bias is the choice of the adequate profile for porosity (Epping and Helder, 1997; Elberling and Damgaard, 2001). We chose to average \( F^{-1} \) profiles for the station rather than to use individual formation factor profiles in order to have a robust estimate of this parameter at the station space scale. The few formation factor profiles gathered from the station show some degree of heterogeneity in the first centimeter (Fig. 2), but except for one profile, the scatter is not very large. The calculation of the oxygen consumption rate by the PROFILE method is sensitive to the shape of porosity profile, which therefore limits the accuracy of oxygen flux estimation. The interface method is less sensitive to the porosity variation since most \( F^{-1} \) profile show a value close to 0.88 in the first sediment layer.

Core incubation in the laboratory is also a source of potential bias. Previous comparison with in situ incubation showed contrasted results. Based on results from the Washington continental shelf, Devol and Christensen (1993) proposed a general underestimation of fluxes from shipboard incubation due to poor representation of macrofauna irrigation in small cores compared to larger in situ benthic chambers. We used large diameter cores (15 cm I.D.), which minimises this artefact. It has been shown for the deep-sea (Glud et al., 1994a) that core incubated on deck displayed oxygen demands which were 1.5–2 times larger than in situ incubations. It was believed that pressure release was the main factor influencing this variation. In the coastal ocean at 9-m depth, decompression is not important and most of the fauna remained alive after the core transfer to the laboratory. Another issue is the core compression during core liner penetration in the sediment. With
the large diameter corers (I.D. 15 cm), compression of the core during sampling was
minimised. Incubation conditions were strictly controlled (temperature, darkness, limited
oxygen deficit) which insure that the total flux reflects the in situ value.

4.2. Temporal and spatial variations of the sediment oxygen demand

The SOD found in this study are in the same order of magnitude as previously reported
oxygen fluxes for shallow regions of the coastal ocean, e.g. the Northern Adriatic (Epping
and Helder, 1997), the North Sea (Lohse et al., 1996), the Washington shelf (Archer and
Devol, 1992), Swedish fjords (Hall et al., 1989) or Danish coastal waters (Rasmussen and
Jorgensen, 1992; Glud et al., 1994b).

Core incubations reveals that oxygen flux has not varied significantly between October
2000 and May 2001. Indeed, the total oxygen demand varies from 21.5 ± 5 to 18.5 ± 4
mmol m$^{-2}$ day$^{-1}$. The October cruise was performed at the end of the summer period and
we might expect that most of the spring and summer production was deposited at the
sediment surface, which would create a large SOD. The second cruise took place during
the spring bloom period when we expect fresh organic material to be deposited at the
sediment interface. This could explain the similarities of SOD between these two periods.
Other studies performed in different context showed some variation of the SOD with time.
Lohse et al. (1996) found a large variation of the diffusive flux between August and
February in the North Sea (average of 6 mmol m$^{-2}$ day$^{-1}$ with values as high as 25 mmol
m$^{-2}$ day$^{-1}$ in August), which was linked to turbulent diffusion, Epping and Helder
(1997) also found a large variation in the Adriatic Sea between March (6.4–17.1 mmol
m$^{-2}$ day$^{-1}$) and August (16.3–30 mmol m$^{-2}$ day$^{-1}$), which was due to benthic
photosynthesis during the summer months and Rasmussen and Jorgensen (1992) found
little variation of the diffusive oxygen demand over a year in Aarhus Bay (9.6 ± 2.4 mmol
m$^{-2}$ day$^{-1}$) while the total oxygen demand varied from 20 mmol m$^{-2}$ day$^{-1}$ in summer
to 7.2 mmol m$^{-2}$ day$^{-1}$ in winter. This was due to a countereffect of oxygen decrease in
the overlying water and larger deposition of organic matter during summer. In the Golfe de
Fos, oxygen decrease in the bottom-water during summer is limited, the turbulence in the
water column does not affect diffusion coefficients in the sediment and benthic photo-
synthesis is weak due to constant turbidity of the water in this part of the Golfe.
Consequently, large variations of the SOD are not expected.

The picture that dominates our data set for Modelfos 2 (May 2001) is the large
heterogeneity at small spatial scale. The spatial scales investigated cover the decimeter
to the decameter. Each individual set of profile is concentrated on less than 10 cm (the
distance between the different electrodes on our measuring cylinder), and each launch of
the profiler was achieved on the same station in a circle of 75 m of diameter. The scatter
observed at the station level (tenth of meters) is also observed at the decimeter scale, which
indicates that the spatial heterogeneity can be assigned to this space scale and therefore
linked to small scale processes (e.g. faunal burrows, local deposition of organic matter)
rather than larger scale change (bathymetric heights, macrofauna patchiness). Processes
causing lateral variations of oxygen profiles are microscale changes of the quantity/quality
of deposited organic matter (Archer and Devol, 1992), thickness of Diffusive Boundary
Layer (DBL) linked to microtopography (Rasmussen and Jorgensen, 1992), horizontal
diffusion of oxygen from biological structure (occupied or empty burrows; Jorgensen and Revsbech, 1985), or enhanced availability of reduced chemical species (Canfield et al., 1993) generated by the anoxic oxidation of organic matter in deeper sediments (Fig. 7). Two of these processes cause an increase of the oxygen demand of the sediment (increase in quality or quantity of organic matter deposited, or increased generation of reduced chemical species) whereas the presence of lateral diffusion of oxygen will create deeper penetration of oxygen by resupply at depth and simulate a lower oxygen demand of the sediment. This is certainly the case for profiles pA5-1405, pA3-1605, or pA5-1605 (Fig. 4) which all show lower than average values of oxygen consumption and larger oxygen penetration. An increase of the DBL thickness would not modify the oxygen demand of the sediment, but would create a shallower penetration depth of oxygen by increasing the concentration change in the DBL rather than in the sediment (Jorgensen and Revsbech, 1985).

The statistical plot of the oxygen diffusive fluxes calculated from the microprofiles (Fig. 6) shows a near Gaussian distribution around the average with a long tail extending towards larger values. These rare and larger values contribute to the average diffusive SOD significantly. They constitute around 10% of the measured values but the average diffusive oxygen demand increases by 15–20% when they are included in the data set. These larger values could represent hot spots of bacterial organic matter degradation which could contribute significantly to the overall diffusive oxygen flux for a station and are taken into account if a sufficiently large sampling ($n \geq 20$) is performed.

4.3. Comparison between the incubation and microelectrode fluxes

The two techniques used during this study to estimate the SOD (core incubation and microelectrode profiles) provide different insight on the diagenetic system. The surface

Fig. 7. Schematic plot of the effect of increasing the following parameters: organic carbon content or reactivity, DBL thickness, flux of reduced chemical species from anoxic sediments. The inclusion of burrows is also shown. On each graph, the dashed profile represents the “standard” situation and the plain curve represents the altered profile.
area and the processes covered by these techniques are very different. Core incubation typically integrates on the surface area of the core (177 cm², in our case). We propose that the surface area studied by microelectrodes is not directly related to their tip size (in our case, an external diameter of 0.1 mm) but rather to the diffusion distance on a profile time scale (typically a few hours). Indeed, any changes occurring within this distance during the profiling operation will influence the profile shape and therefore the calculated diffusive oxygen flux. The typical diffusive distance can be calculated as follows:

\[
x = \sqrt{2Dt}
\]

For a diffusion coefficient \((D)\) of \(10^{-5}\) cm²/s, and a time \((t)\) of 10,000 s (3 h), the value of \(x\) is 0.4 cm and the area investigated by the electrode is in the order 0.1 cm², a factor of 1000 less than the core incubation. This is only a rough estimate and other calculation based on the oxygen residence time (around 30 min in our case) would provide \(x\) of 0.2 cm.

The processes taken into account by the two techniques are also different. Total flux estimated by core incubation typically integrates all processes linked to oxygen transfer: diffusion and advective movement of pore water induced by faunal activity (active pumping in burrows, biodiffusion due to erratic movements of the fauna,....). Diffusive fluxes estimated from microelectrode profiles assume that the transport of chemical species is accomplished by molecular diffusion excluding the other transport processes.

In our study, we find that the diffusive flux for the most documented period (Modelfos 2—May 2001) is very close to the total flux. The flux calculated by the interface gradient method exactly agrees with the total flux, whereas the flux estimated by the PROFILE method is 20% lower than the total flux. The presence of very large diffusive fluxes (above 25 mmol m⁻² day⁻¹, Fig. 6a) which are rather rare was statistically not caught by the previous studies relying on a reduced number of oxygen profiles. The inclusion of these fluxes in our calculation could explain the little difference between total and diffusive oxygen demand. In fact, removing these larger fluxes would drive the difference between the two types of fluxes up to 50%. Former studies (Lindeboom et al., 1985; Archer and Devol, 1992) have found a factor of 1.5 to 3 between total and diffusive fluxes for coastal or shelf stations. Other authors found a relatively good agreement between diffusive and total oxygen fluxes (Reimers et al., 1992) on the continental slope and rise between 1000 and 4000 m deep. In a recent review of margin and deep-sea oxygen demand in the Atlantic, Wenzhoefer and Glud (in press) showed that the ratio between total and diffusive fluxes vary from three to four on the upper continental slope to almost one in oligotrophic regions related to the irrigation by macrofauna (Rasmussen and Jorgensen, 1992; Glud et al., 1994a).

Yet, the studied area of the Golfe de Fos is occupied by a macrofaunal assemblage (>250 μm) characteristic of muddy sand of sheltered areas (Pères, 1982) presenting a mean density integrated over 20-cm depth of 5770 ± 1860 individuals for 0.1 m². Polychaetes compose more than 60% of the community and crustaceans are the second most dominant group. Seventy percent of the organisms are surface deposit feeders. Macrofauna is present down to 20-cm depth in the sediment but more than 70% of the community colonize the first 5 cm of the sedimentary column. All species
present display small sizes and no collected individual is able to make large burrows capable of inducing a significant oxygen transfer towards deep sediment layers.

From our case study, it seems that the difference between diffusive and total fluxes is not solely related to the macrofaunal population density as stated earlier but also on the assemblage composition which defines the potential for bioirrigation.

5. Conclusions

In this paper, a detailed study of the benthic oxygen demand at a single station in the Golfe de Fos (Mediterranean Sea) is presented for two different periods (October 2000 and May 2001). The use of two different methods, core incubations and in situ microelectrodes, allowed us to compare total and diffusive oxygen demands. Diffusive fluxes were calculated by two different computation methods: interface-gradient and PROFILE Software (Berg et al., 1998) on a large number of oxygen microprofiles ($n = 18$ for May 2001).

The main conclusion of this study is that temporal variation as recorded by the total sediment oxygen demand ($21.5 \pm 5$ to $18.5 \pm 4 \text{ mmol m}^{-2} \text{ day}^{-1}$) was not significant. Spatial variation of diffusive oxygen fluxes evidenced by microelectrode measurements was very large: a factor of 6–9 was found between the minimum and maximum values depending on the calculation methods. Since this variation was found on single lander deployments, it reflects the natural heterogeneity of the sedimentary system at the decimeter scale rather than at the station scale (75 m). This indicates that the observed spread of oxygen microprofiles is linked to small scale processes such as variation in the organic input, lateral input of oxygen from biological structures or enhanced supply of reduced species from deeper sediment layers.

Another conclusion concerns the difference between total and diffusive fluxes in these shallow coastal sediments (9-m deep), which is around 20% suggesting that the oxygen demand is mostly diffusive contrarily to previous observations in the coastal zone. This may be related to the large number of oxygen microprofiles performed, which thus took into account larger oxygen fluxes linked to rare “organic hot spots”. This little difference between total and diffusive fluxes in our study with a significant macrofaunal abundance largely composed of surface-deposit feeders points towards the assemblage composition as a controlling variable of bioirrigation rather than population density only.

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