Marine Biology (2003) 142: 1073–1082
DOI 10.1007/s00227-003-1022-y

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# Diffusive boundary layers and photosynthesis of the epilithic algal community of coral reefs

Received: 21 May 2002 / Accepted: 8 January 2003 / Published online: 25 March 2003


**Abstract** The effects of mass transfer resistance due to the presence of a diffusive boundary layer on the photosynthesis of the epilithic algal community (EAC) of a coral reef were studied. Photosynthesis and respiration of the EAC of dead coral surfaces were investigated for samples from two locations: the Gulf of Aqaba, Eilat (Israel), and One Tree Reef on the Great Barrier Reef (Australia). Microsensors were used to measure $O_2$ and pH at the EAC surface and above. Oxygen profiles in the light and dark indicated a diffusive boundary layer (DBL) thickness of 180–590 $\mu$m under moderate flow ($\sim$0.08 m $s^{-1}$) and $>$2,000 $\mu$m under quasi-stagnant conditions. Under light saturation the oxygen concentration at the EAC surface rose within a few minutes to 200–550% air saturation levels under moderate flow and to 600–700% under quasi-stagnant conditions. High maximal rates of net photosynthesis of 8–25 mmol $O_2$ $m^{-2}$ $h^{-1}$ were calculated from measured $O_2$ concentration gradients, and dark respiration was 1.3–3.3 mmol $O_2$ $m^{-2}$ $h^{-1}$. From light–dark shifts, the maximal rates of gross photosynthesis at the EAC surface were calculated to be 16.5 nmol $O_2$ $cm^{-3}$ $s^{-1}$. Irradiance at the onset of saturation of photosynthesis, $E_k$, was $<$100 μmol photons $m^{-2}$ $s^{-1}$, indicating that the EAC is a shade-adapted community. The pH increased from 8.2 in the bulk seawater to 8.9 at the EAC surface, suggesting that very little carbon in the form of $CO_2$ occurs at the EAC surface. Thus the major source of dissolved inorganic carbon (DIC) must be in the form of $HCO_3^-$. Estimates of DIC fluxes across the DBL indicate that, throughout most of the daytime under in situ conditions, DIC is likely to be a major limiting factor for photosynthesis and therefore also for primary production and growth of the EAC.

Communicated by L. Hagerman, Helsingør

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## Introduction

The use of oxygen microelectrodes has allowed detailed characterisation of the diffusive boundary layer (DBL) above the surface of aquatic organisms, biofilms and sediments (Jørgensen and Revsbech 1985; Gundersen and Jørgensen 1990; Jørgensen and Des Marais 1990; Kühl et al. 1995; Glud et al. 1994; De Beer and Kühl 2001. Jørgensen 2001). The effective DBL thickness can be defined as the height above the active surface where the linear slope of the curve of $O_2$ concentration within the boundary layer intercepts with the $O_2$ concentration of the bulk medium (Jørgensen and Revsbech 1985). Within the DBL, the transport of biologically important molecules, like oxygen and carbon species, is dominated by molecular diffusion and, therefore, has the potential to be limiting to photosynthesis. Consequently the effect of the DBL on benthic plants is an important consideration (e.g. Wheeler 1980; Koch 1993, 1994).

Oxygen microsensors have been used to study photosynthesis and respiration in various sediment and biofilm communities (e.g. Revsbech and Jørgensen 1986; Sand-Jensen and Revsbech 1987; Kühl et al. 1996; Wieland and Kühl 2000). However, with few exceptions (e.g. Kaspar 1992; Kühl et al. 2001; Roberts et al. 2002) this approach has not been exploited to characterise the diverse epi- and endolithic algal communities that occur

on and within hard substrata in many aquatic environments. This is surprising, since most algae, even those destined to emerge as macroscopic canopy formers far above the surface, begin life as members of this epilithic community in the form of sporelings or young plants.

The epilithic algal community (EAC, cf. Hatcher and Larkum 1983) of coral reefs is a 1–2 mm thick algal-dominated biofilm on dead limestone surfaces, and is recognised as one of the most important sites for primary production on coral reefs (Wanders 1976; Larkum et al. 1988; Carpenter et al. 1991). While the specific characteristics of the EAC at any location are dependent on region, latitude, season, habitat, depth, grazing and other factors, many generalities exist for the EAC. Hermatypic corals (corals with an endosymbiotic association with dinoflagellates of the genus *Symbiodinium*) are highly productive, but on an areal basis are often a smaller component of productivity compared to the dead limestone surfaces covered with EAC (e.g. Klumpp and McKinnon 1992); furthermore, the primary production of the coral symbiosis is retained largely within the corals themselves and supports few food chains (Lewis 1977). As a result, the EAC supports many of the food chains of coral reefs and, in particular, many of the grazing fish. Over 100 common eukaryotic algae, as well as many cyanobacteria, bacteria and protozoa, have been shown to form the EAC (Hatcher and Larkum 1983).

The EAC is a dynamic community generally prevented from growing $>1$–2 mm thick by the constant grazing of fish and many invertebrates (see e.g. Hatcher and Larkum 1983; Carpenter and Williams 1993). Caging experiments showed that the EAC can grow several centimetres thick, in a matter of weeks, in the absence of grazing (Hatcher 1982; Hatcher and Larkum 1983), but as it grows thicker the rate of primary production per unit biomass decreases sharply (Hackney and Sze 1988; Larkum, unpublished results). Major factors contributing to this decline are self-shading and increased heterotrophic activity within the thicker EAC.

There has been much speculation as to what controls the primary production of the EAC, apart from the animal grazing mentioned above. Since coral reefs characteristically grow in nutrient-poor waters (but see Atkinson et al. 1995 for exceptions), it has often been assumed that algae of coral reefs will be limited by nutrients, particularly nitrogen and phosphorus. Experiments have confirmed this for the macroalgae of coral reefs (e.g. Lapointe et al. 1987), and in some instances recycling of sediment nutrients appears to be an important factor (Larned and Atkinson 1997). Potentially, fast movement of water over the EAC may increase the flux of nutrients to the plants (Williams and Carpenter 1997, 1998). Furthermore inadvertent, man-induced eutrophication appears to have stimulated the growth of macroalgae at the expense of living corals in such places as Kaneohe Bay, Hawaii, and in Indonesia (Grigg 1995).

In the ENCORE experiment, conducted at One Tree Island (Great Barrier Reef), the effect of elevated levels of N and/or P on EAC were tested, under natural levels of grazing pressure (Larkum and Steven 1994; Koop et al. 2001). The results, for the EAC (Larkum and Koop 1997), showed no effect of elevated nutrient levels on the growth or primary productivity, despite documented effects during the experiment on other biota (Hoegh-Guldberg et al. 1997; Steven and Broadbent 1997; Koop et al. 2001). Furthermore, short-term experiments on EAC kept under elevated nutrient concentrations for up to 1 week had no effect either (Larkum and Koop 1997). Thus, the EAC may be nutrient sufficient, and factors other than nutrient supply may limit productivity. A study on an offshore reef in Key Largo, Florida, recently came to a similar conclusion (Miller et al. 1999).

In regard to the major limitation on photosynthesis (and primary production) of the EAC, possible effects of mass transfer resistance due to the presence of a diffusive boundary layer need to be assessed. Under saturating irradiance, the gross photosynthesis of the EAC occurs at a rate that may be as high as any plant community (Larkum 1983). Since this occurs over a vertical distance of only a few millimetres (the height of EAC plus DBL), it is possible that inorganic carbon flux is limiting under saturating light conditions. It therefore becomes necessary to measure the dissolved inorganic carbon (DIC) flux. Since the diffusion coefficients of $CO_2$, $HCO_3^-$ and $O_2$ are of similar magnitude (Larkum et al. 1989), diffusive fluxes of $O_2$ can be used to estimate the diffusive supply of DIC across the DBL. Oxygen microsensors are excellent tools to map DBLs (Jørgensen and Revsbech 1985; Jørgensen and Des Marais 1990), although their presence can lead to a local compression of the DBL (Glud et al. 1994), which must be taken into account at least over smooth surfaces (Lorentzen et al. 1995). Such data can then be further augmented in the context of DIC limitation by supplementary microsensor measurements of pH and $CO_2$ (see Kühl and Revsbech 2001 for a review of available microsensors).

In the present study samples of EAC from One Tree Island (Great Barrier Reef) and Eilat (Israel) were exposed to varying water flow rates and the DBL was quantified using microsensors. Our results indicate that the productivity of the EAC can be DIC limited, especially at slow to moderate water flow.

## Materials and methods

Samples of dead branches of *Stylophora* sp., ca. 0.8 cm in diameter and 10 cm in length, were obtained from Eilat, Gulf of Aqaba (34°95′E; 29°50′N), from a water depth of ~1 m. The specimens were known to be dead for 6 months or more and had been colonised by epilithic algae, of which the major species were the crustose coralline algae *Calothrix* spp. (Cyanobacteria), *Lyngbya* sp. (Cyanobacteria), *Giffordia* sp. (Phaeophyceae), *Ceramium* sp. (Rhodophyceae), *Polysiphonia* spp. (Rhodophyceae) and various unicellular cyanobacteria. The dead branches were shipped within 2 days of collection in watertight plastic bags with a small amount of seawater to keep samples moist.

Two-year-old *Porites lobata* coral blocks (8×8×2 cm) (Larkum and Koop 1997) were shipped in seawater (at room temperature) from One Tree Reef (152°06′E; 20°30′S), where they had been kept at ~0.5 m in the main lagoon, and arrived within 3 days of collection in our laboratory. Their algal composition was similar to that described by Hatcher and Larkum (1983) and Larkum et al. (1988). Of the two dead coral substrata, the *Stylophora* branches had much greater surface roughness, since they were whole skeletons with normal surface rugosity (corallite raised ~1 mm above the surface every 5–10 mm), whereas the processed *Porites* blocks were cut mechanically from larger compact skeletons, which produced a very flat surface, with, initially, the normal roughness of the coral matrix. Supplementary "on site" experiments were done in January 1998 on *P. lobata* coral blocks collected at One Tree Reef, which were stored in flowing seawater and analysed at the nearby Heron Island Research Station within 24 h of collection.

The shipped samples were kept in filtered North Sea water in aquaria at 25°C, under 14 h light:10 h dark cycles with fluorescent lights (350 $\mu$mol photons $m^{-2}$ $s^{-1}$) for up to 5 days after delivery. Since the EAC was released from grazing pressure under these conditions, longer incubation period yielded a thick heterogeneous biofilm community with significantly higher biomass and altered primary productivity as compared with the in situ EAC; experiments were therefore restricted to the first 3 days.

The microsensor measurements were made in a flow chamber (Lorentzen et al. 1995) with a height of water over the plates of 2 cm and flow rates of 0–0.10 m $s^{-1}$, controlled by the insertion of various short, narrow-bore glass tubes after the recirculation pump (E-Heim, Germany). Calibration of flows was done by measuring the volume of water delivered through the flow chamber during 1 min ($n=4$) and dividing this volume by the cross-sectional area of the chamber. Light was provided from a fibre-optic halogen lamp (Schott, KL-1500) equipped with a collimating lens to focus light onto the sample. Incident downwelling irradiance was measured, in water, at the level of the EAC with an underwater quantum irradiance meter (LiCor, USA). Photosynthetic transient experiments (light–dark transitions) were done with an electronic shutter (Vincent, USA) and a shutter controller with a response time of $<10$ ms. Irradiance levels were varied by inserting neutral density filters in the light path.

Oxygen profiles were measured with amperometric Clark-type $O_2$ microsensors equipped with a guard cathode (Revsbech 1989) and connected to a pA-meter. Transient experiments to measure gross photosynthetic rates employed fast oxygen microsensors with a 90% response time ($t_{90}$) of $<0.3$ s and a sensitivity to stirring of $<2$–3% (Revsbech 1989). The electrodes were calibrated linearly using readings in air-saturated and $N_2$-flushed seawater of known experimental salinity and temperature.

Measurements of pH were carried out with pH glass microelectrodes (Revsbech and Jørgensen 1986) and a standard calomel reference electrode (Radiometer) connected to a high-impedance mV-meter. The pH microsensors were calibrated with standard NBS buffers at pH 7.0 and pH 9.2.

The sensors, deployed at a zenith angle of 135°, were positioned in steps of 25 $\mu$m vertical intervals by motor-driven micromanipulators (Märtzhäuser, Germany) with computerised depth control (LOT-Oriel, USA; LabView, USA). The measuring signals were recorded on a strip chart recorder (Goertz, Germany) and on a PC equipped with an A/D converter (National Instruments, USA). Custom-made software controlled data acquisition, positioning of the micromanipulator, and the electronic shutter. A photoelectric cell registered the onset of darkness for the light–dark shift measurements of gross photosynthetic rate (Revsbech and Jørgensen 1983; Glud et al. 1992; Kühl et al. 1996), and readings of the oxygen depletion after darkening were taken at high frequency (~600 Hz) over the first 2 s after darkness.

Areal rates of net photosynthesis and $O_2$ consumption were calculated from steady-state oxygen profiles as the diffusive flux across the DBL such that:

$$J = D(C_\infty - C_0)/\delta_e \quad (1)$$

where $J$ is the flux of gas ($O_2$, $CO_2$) or $HCO_3^-$ (mol $m^{-2}$ $s^{-1}$), $D$ is the diffusion coefficient of molecular or ionic species in seawater ($m^2$ $s^{-1}$), $C_0$ is the concentration of species at the surface of the substratum (mol $m^{-3}$), $C_\infty$ is the concentration of species in the bulk medium and $\delta_e$ is the effective thickness of the DBL (see Jørgensen and Revsbech 1985).

Diffusive oxygen fluxes were also calculated from the linear part of the oxygen gradient ($dC/dz$) in the DBL from Fick's first law: $J = D dC/dz$.

Diffusion coefficients of $O_2$ ($D_{O2} = 1.98\times10^{-9}$ $m^2$ $s^{-1}$), $CO_2$ ($D_{CO2} = 1.55\times10^{-9}$ $m^2$ $s^{-1}$) and $HCO_3^-$ ($D_{HCO3^-} = 1.0\times10^{-9}$ $m^2$ $s^{-1}$) and their concentrations in air-saturated seawater at 25°C were taken from Larkum et al. (1989).

Gross photosynthetic rates, as nanomoles of $O_2$ per cubic centimetre per second, were calculated from the initial rate of oxygen depletion after a light–dark transition (Revsbech and Jørgensen 1983). Gross photosynthesis versus irradiance ($P$ vs. $E_d$) curves were fitted with the exponential function (Webb et al. 1974): $P = P_m[1-\exp(-\alpha E_d/P_m)]$, with $E_k = P_m/\alpha$. When fitting net photosynthesis versus irradiance curves the equation was extended with a third parameter for the oxygen respiration.

## Results

Oxygen profiles over EAC on dead branches of *Stylophora* sp. were measured at a flow rate of 0.08 m $s^{-1}$ and different light levels (Fig. 1A). The small patches of biofilm consisted mainly of filamentous and unicellular cyanobacteria together with unicellular green algae, filamentous Rhodophyceae such as *Ceramium* spp. and *Polysiphonia* spp. and many heterotrophic microorganisms. In addition, the plates had a rich subsurface layer of endolithic algae, including *Ostreobium* sp. and filamentous cyanobacteria (cf. Le Campion-Alsumard et al. 1995). Profiles measured over comparable sites on four additional pieces of *Stylophora* ($n=5$) at saturating irradiance (300 $\mu$mol photons $m^{-2}$ $s^{-1}$) yielded a mean DBL thickness of $201\pm51$ $\mu$m (SEM, $n=5$) and a mean surface $O_2$ level of $271\pm27$% air saturation (SEM, $n=5$). There was considerable variation in both $O_2$ concentration and DBL thickness, probably due to the position of the measurements along the rough surface and the effects that this had on the DBL thickness, which varied from 175 $\mu$m up to 455 $\mu$m. The thickness of the DBL without stirring was $2.1\pm0.3$ mm (SEM, $n=5$). In the dark, the $O_2$ level at the EAC surface was $77.6\pm4.1$% (SEM, $n=5$) of the surrounding air-saturated water. We calculated a mean net photosynthesis rate of $12.6\pm0.2$ mmol $O_2$ $m^{-2}$ $h^{-1}$ and a mean dark respiratory rate of $1.6\pm0.1$ mmol $O_2$ $m^{-2}$ $h^{-1}$ (SEM, $n=5$; see Table 1).

We also studied the $O_2$ levels after darkening, at a flow rate of 0.08 m $s^{-1}$. In a typical experiment, the oxygen level at the EAC surface reached ~400% air saturation after 10 min at an irradiance of 715 $\mu$mol photons $m^{-2}$ $s^{-1}$. When the sample was darkened, the $O_2$ level at the surface decreased slowly, reaching 110% air saturation after 7 min, 64% after 17 min and finally a steady-state level of 47% air saturation after ~25 min. This result, which was repeated several times, indicated that there is a considerable residual mass of $O_2$ in the

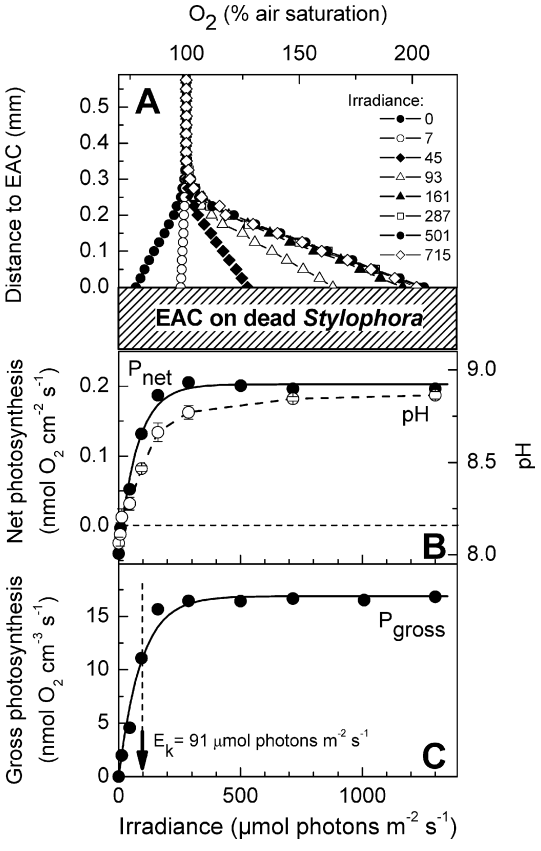


**Fig. 1A–C** Oxygen, pH and photosynthesis of epilithic algal community (*EAC*) on dead *Stylophora* sp. coral under a water flow of ~0.08 m $s^{-1}$. **A** Steady-state $O_2$ concentration profiles measured at increasing irradiance, as noted by the symbol type. **B** Areal net photosynthesis (calculated from the profiles in panel A) and the pH at the EAC surface as a function of irradiance. *Solid line* represents a curve fit ($r^2 > 0.98$) of the equation $P(E) = P_m \times [1 - \exp(-\alpha \times E/P_m)] + R$. **C** Gross photosynthesis measured at the EAC surface as a function of irradiance. *Solid line* represents a curve fit ($r^2 > 0.98$) of the equation $P(E) = P_m \times [1 - \exp(-\alpha \times E/P_m)]$, where $P(E)$ is the gross photosynthesis at irradiance, $E$; $P_m$ is the maximal gross photosynthesis; $\alpha$ is the initial slope of the $P$ versus $E$ curve; and $R$ is the oxygen respiration. The irradiance at onset of saturation of gross photosynthesis was calculated as $E_k = P_m/\alpha = 91$ µmol photons $m^{-2}$ $s^{-1}$. The compensation irradiance, i.e. the irradiance where areal net photosynthesis equalled zero, was $E_c = 15$ µmol photons $m^{-2}$ $s^{-1}$

EAC and the underlying coral matrix, which builds up when the EAC has been illuminated for a significant period. The $O_2$ concentration at the surface of the EAC, under a flow of 0.08 m $s^{-1}$, rose to an asymptotic level, with increasing irradiance as net photosynthesis approached light saturation (Fig. 1B). The compensation irradiance, $E_c$, where oxygen production balanced oxygen consumption of the EAC, was 15 $\mu$mol photons $m^{-2}$ $s^{-1}$. Similar experiments performed on the opposite side of the branches showed similar [$O_2$] versus $E_d$ curves (where $E_d$ is downwelling irradiance in µmol photons $m^{-2}$ $s^{-1}$), so these curves were apparently unrelated to different sun/shade-acclimated communities on opposite sides of the coral branches. Each of the five measurements referred to above was taken randomly on a different branch. The mean gross photosynthetic rate, at the same flow rate, measured by light–dark transients at the EAC surface, was 16.5 nmol $O_2$ $cm^{-3}$ $s^{-1}$ at light saturation (Table 1); note that this method gives a local volumetric rate representative for approximately the upper 100 µm of the EAC, which cannot be converted easily to an areal rate. The $P$ versus $E_d$ curve for gross photosynthesis showed an onset of saturation at $E_k = 91$ µmol photons $m^{-2}$ $s^{-1}$ (Fig. 1C).

Measurements of pH, under the same flow regime, within a few micrometres of the surface of two EAC patches showed a pH rising to a maximum of pH 8.7–8.9 at an irradiance of ~500 $\mu$mol photons $m^{-2}$ $s^{-1}$ (Fig. 1B). Evidently, a higher irradiance was needed to saturate the pH rise than for either the $O_2$ level (220 $\mu$mol photons $m^{-2}$ $s^{-1}$; Fig. 1B) or the photosynthetic rate (Fig. 1C). At the compensation irradiance of 15 $\mu$mol photons $m^{-2}$ $s^{-1}$ (see above) the pH was ~8.3. The pH at the surface of the EAC in the dark was 8.06. When the flow was stopped, the pH rose over a period of 10 min to 9.1 under light saturation and fell to 7.9 in the dark. The pH of bulk seawater was 8.2.

Oxygen profiles measured at flow velocities of 0.08 m $s^{-1}$ above the EAC on smooth *Porites* coral blocks from One Tree Island are shown in Fig. 2A. Similar profiles were carried out on other EAC patches, which covered up to 80% of the plate surface area. The microscopic topography of the investigated area (~4 $mm^2$) was dominated by the encrusting green alga, *Pseudopringsheimia* sp., as well as *Giffordia michelliae*, *Polysiphonia* spp, various cyanobacteria (the most common of which was *Calothrix corallina*) and crustose coralline algae. The mean DBL thickness was 301 ± 22 $\mu$m (SEM, $n = 5$; Table 1), the more consistent values in this material probably resulting from the somewhat more uniform and smoother surface of the coral block versus the *Stylophora* skeleton. At a flow rate of 0.08 m $s^{-1}$, the $O_2$ concentration at light saturation at the surface was 405 ± 13% (SEM, $n = 5$) of air saturation. The higher $O_2$ concentrations compared with the *Stylophora* specimens (Table 1) are consistent with the higher photosynthetic rates. The mean surface $O_2$ level in the dark was 46.5 ± 3.7% (SEM, $n = 5$) of air saturation. Net areal photosynthesis was 14.8 ± 0.3 mmol $O_2$ $m^{-2}$ $h^{-1}$ and dark respiration was 2.9 ± 0.1 mmol $O_2$ $m^{-2}$ $h^{-1}$, as calculated from steady-state $O_2$ profiles in light and darkness, respectively (SEM, $n = 5$, flow rate = 0.08 m $s^{-1}$). The $P$ versus $E_d$ curve for net photosynthesis showed a compensation irradiance of $E_c = 16$ µϖ mol photons $m^{-2}$ $s^{-1}$, and an onset of saturation at $E_k = 78$ µmol photons $m^{-2}$ $s^{-1}$ (Fig. 2B). The gross photosynthetic rate, at the same flow rate, measured by light–dark transients at the EAC surface was found to be 20 ± 0.4 nmol $cm^{-3}$ $s^{-1}$ at light saturation, which compares with 16.5 ± 0.3 nmol $cm^{-3}$ $s^{-1}$ for the *Stylophora* EAC (SEM, $n = 5$; see Table 1).

The effect of water flow on the $O_2$ concentration profile, DBL thickness and oxygen fluxes was investigated at a constant irradiance of 440 $\mu$mol photons $m^{-2}$ $s^{-1}$

**Table 1** Properties of the two epilithic algal communities studied. Errors are shown as mean ± standard error of the mean ($n = 5$). 100% $O_2$ saturation is equal to 206 mmol $O_2$ $m^{-3}$ (at 25°C and 33‰ salinity) (*in parentheses* results of experiments carried out "on site" on the *Porites* coral blocks in January 1998)

| | *Stylophora* branches | *Porites* coral block |
|---|---|---|
| Geographic location | Eilat, Gulf of Eilat 34°55′E; 29°36′N | One Tree Reef, Great Barrier Reef 152°06′E; 23°28′S |
| Sampling season | Late autumn | Late spring |
| Age | 6–8 months | > 2 years |
| Rugosity | Relatively high | Relatively low |
| Diffusive boundary layer, at 0.08 m $s^{-1}$ and saturating light | 201 ± 51 μm | 301 ± 22 μm (335 ± 13 μm) |
| Oxygen concentration, at surface at 0.08 m $s^{-1}$ and saturating light | 271 ± 27% air saturation | 405 ± 13% air saturation (580 ± 23% air saturation) |
| Light-saturated pH, at surface | 8.9 ± 0.05 | Not measured |
| Max. areal net photosynthesis (from diffusive fluxes) | 12.6 ± 0.2 mmol $O_2$ $m^{-2}$ $h^{-1}$ | 15.0 ± 0.3 mmol $O_2$ $m^{-2}$ $h^{-1}$ (21.4 ± 0.4 mmol $O_2$ $m^{-2}$ $h^{-1}$) |
| Max. volumetric gross photosynthesis (from light–dark shift) | 16.5 ± 0.3 nmol $O_2$ $cm^{-3}$ $s^{-1}$ | 20.0 ± 0.4 nmol $O_2$ $cm^{-3}$ $s^{-1}$ |
| Respiratory rate (in darkness) | 1.6 ± 0.1 mmol $O_2$ $m^{-2}$ $h^{-1}$ | 2.9 ± 0.1 mmol $O_2$ $m^{-2}$ $h^{-1}$ (3.1 ± 0.1 mmol $O_2$ $m^{-2}$ $h^{-1}$) |
| Irradiance at light saturation of $O_2$ gradient | 220 μmol photons $m^{-2}$ $s^{-1}$ | 300 μmol photons $m^{-2}$ $s^{-1}$ (482 μmol photons $m^{-2}$ $s^{-1}$) |
| Irradiance at light saturation of gross photosynthetic rate (light–dark shift) | 160 μmol photons $m^{-2}$ $s^{-1}$ | 160 μmol photons $m^{-2}$ $s^{-1}$ |

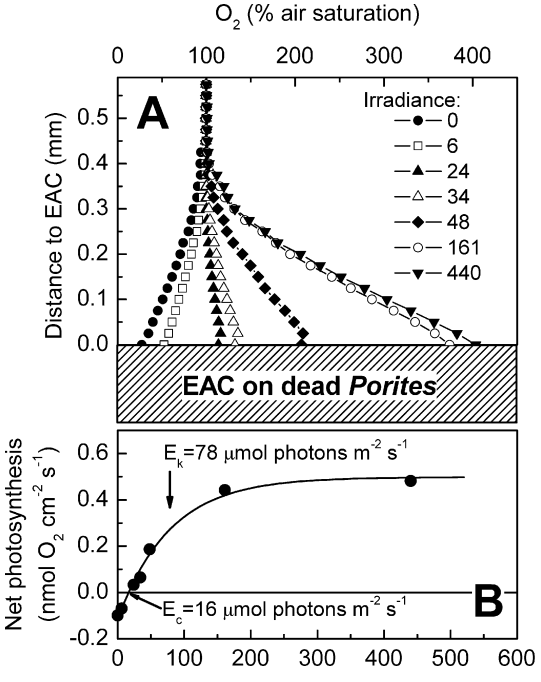


**Fig. 2A, B** Oxygen and photosynthesis of epilithic algal community (*EAC*) on dead *Porites* sp. coral under a water flow of ~0.08 m $s^{-1}$. **A** Steady-state $O_2$ concentration profiles measured at increasing irradiance, as noted by the symbol type. **B** Areal net photosynthesis (calculated from the profiles in panel A) as a function of irradiance. *Solid line* represents a curve fit ($r^2 > 0.99$) of the equation $P(E) = P_m \times [1 - \exp(-\alpha \times E/P_m)] + R$, where $P(E)$ is the gross photosynthesis at irradiance, $E$; $P_m$ is the maximal gross photosynthesis; $\alpha$ is the initial slope of the $P$ versus $E$ curve; and $R$ is the oxygen respiration. The irradiance at onset of saturation of gross photosynthesis was calculated as $E_k = P_m/\alpha$

(Fig. 3). As the flow rate was reduced from 0.08 m $s^{-1}$, the DBL thickness and the oxygen level at the EAC surface increased (Fig. 3A). At very slow flow rates of ~0.02 m $s^{-1}$, the flow became erratic, which accounts for the lack of smooth curves, and it was consequently difficult to determine an accurate boundary layer thickness. We estimated a DBL thickness of ~1.0 mm under these slow rates, and the $O_2$ concentration at the EAC surface rose to ~600% of air saturation. Under quasi-stagnant conditions the DBL was 1.55 ± 0.27 mm (SEM, $n = 5$), with $O_2$ concentration at the surface of 650–700% air saturation (not shown). Based on the oxygen levels at the EAC surface and the estimated diffusive boundary thickness at the investigated flow rates, we could calculate the oxygen efflux (the net photosynthesis), by Eq. 1, as a function of flow (Fig. 3B). Especially in the presence of a thick DBL, there was a pronounced effect of flow velocity on the net photosynthesis. Net photosynthesis increased by a factor of two from the lowest rates at quasi-stagnant conditions to the highest measured at a flow velocity of 0.08 m $s^{-1}$.

The above experiments were carried out after air transportation to the laboratory (see "Materials and methods"), and it was possible that some deterioration of samples had occurred during transport or that the use of North Sea seawater would affect the results. Therefore, some of the equipment was taken to Heron Island (Great Barrier Reef), and similar experiments were undertaken for rates of net photosynthesis and respiration on EAC blocks from One Tree Island. We did not have access to similar samples from Eilat in situ. Thus, the bulk of the results presented here were carried out in the laboratory in Bremen. However, the general shape of the profiles and the DBL thickness (335 ± 13 μm; SEM, $n = 5$) obtained on site on Heron Island were very similar to those obtained in the previous experiments in Bremen; the mean net areal photosynthesis rate was 21.4 ± 0.4 mmol $O_2$ $m^{-2}$ $h^{-1}$ and the respiratory rate in

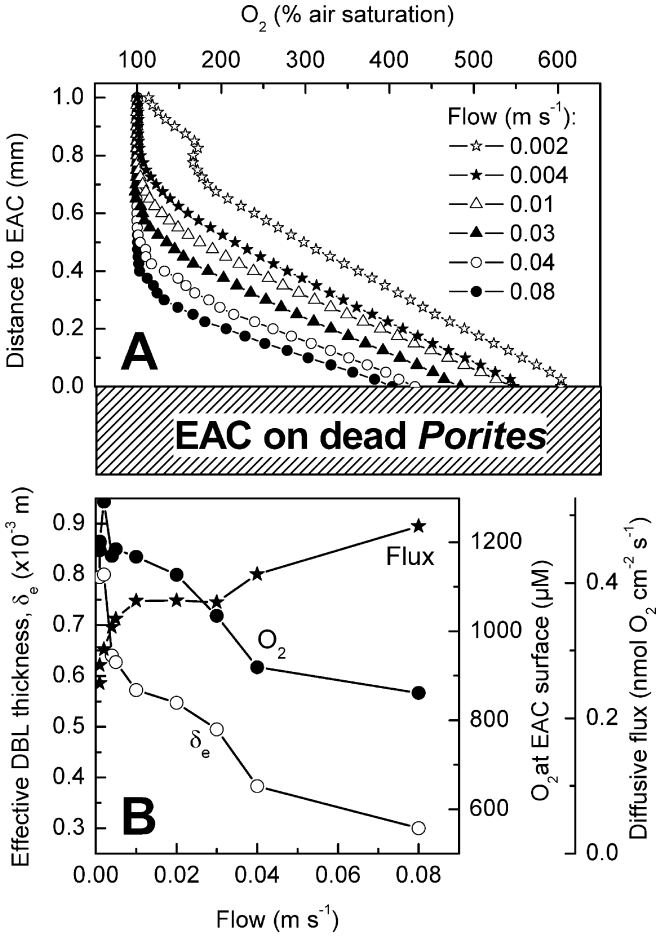


**Fig. 3A, B** Oxygen and net photosynthesis of epilithic algal community (*EAC*) on dead *Porites* sp. coral under an irradiance of 440 μmol photons $m^{-2}$ $s^{-1}$. **A** Steady-state $O_2$ concentration profiles measured at increasing flow velocity, as noted by the symbol type. **B** Oxygen concentration at the EAC surface ($O_2$), the effective diffusive boundry layer (*DBL*) thickness ($\delta_e$) and the areal net photosynthesis (*flux*, calculated from the profiles in panel A) as functions of flow velocity

the dark was $3.1 \pm 0.1$ mmol $O_2$ $m^{-2}$ $h^{-1}$ (SEM, $n = 5$; see Table 1).

## Discussion

### Rates of photosynthesis and respiration

The present results confirm a high rate of photosynthesis of the epilithic algal community growing on dead coral and limestone surfaces of coral reefs. The 6-month-old rough skeleton of *Stylophora* sp. from Eilat had a mean net photosynthetic rate of 12.6 mmol $O_2$ $m^{-2}$ $h^{-1}$ and a mean respiratory rate of 1.6 mmol $O_2$ $m^{-2}$ $h^{-1}$; the 2-year-old smooth *Porites* sp. coral blocks from One Tree Island (Great Barrier Reef) had a mean net photosynthetic rate of $15.0 \pm 0.3$ mmol $O_2$ $m^{-2}$ $h^{-1}$ and a mean respiration rate of $2.7 \pm 0.1$ mmol $O_2$ $m^{-2}$ $h^{-1}$ (Table 1). Two years later we measured a net photosynthetic rate of $21.4 \pm 0.4$ mmol $O_2$ $m^{-2}$ $h^{-1}$ and a respiratory rate of $3.1 \pm 0.1$ mmol $O_2$ $m^{-2}$ $h^{-1}$ for the *Porites* sp. blocks from One Tree Island on site. The higher rate may be due to a healthier sample or slight seasonal and sample-to-sample variation. However, the differences, while statistically significant ($p = 0.001$), are not large and indicate that the measurements on transported material were reliable. The differences between the two types of specimens (dead *Stylophora* vs. *Porites* coral block) (Table 1) were not large either.

The rates measured in this study compare well with literature values (Table 2). Wanders (1976) measured gross photosynthesis rates as high as 23 mmol $O_2$ $m^{-2}$ $h^{-1}$ for dense foliose algal turfs (similar to, but thicker than, the typical EAC studied here) 10 mmol $O_2$ $m^{-2}$ $h^{-1}$ for sparse vegetation on limestone surfaces (similar to the EAC studied here), and 4.7–10.6 mmol $O_2$ $m^{-2}$ $h^{-1}$ for crustose coralline algae. Our rates for the EAC translate into primary productivity values of 2.0–3.0 g C $m^{-2}$ $day^{-1}$, assuming an $O_2$ to C conversion ratio of 0.125 (based on a 10 h photosynthetic day and a

**Table 2** A comparison of rates of primary production by various shallow epilithic algal communities on coral reefs

| Area | Primary production (g C $m^{-2}$ $day^{-1}$) | Method | Study |
|---|---|---|---|
| Curaçao, Caribbean | 2.87[a] | 2–4 h Unstirred oxygen bottles | Wanders (1976) |
| St Croix, Caribbean | $2.1 \pm 0.1$ (winter) $3.1 \pm 0.2$ (summer) | 6 h Stirred oxygen chamber | Carpenter (1985) |
| Northern Great Barrier Reefs | 0.6–2.5 | 24 h Stirred oxygen chamber | Klumpp and McKinnon (1992) |
| Southern Great Barrier Reef | 0.8–2.9 | Biomass increment over ~30 days | Hatcher (1982) |
| Reef-flat rocks dominated by periphytic turf | 1.4–3.5 | A range of methods | Sorokin (1995; Table 10.4) |
| Southern Great Barrier Reef | 3.0–4.2 | 24 h Stirred oxygen chamber | Larkum and Koop (1997) |
| Eilat, Red Sea, and Southern Great Barrier Reef | 2.0–3.0 | Oxygen microelectrode technique | Present study |

[a]Calculated from gross photosynthesis and respiration rates assuming a 12 h day

photosynthetic quotient of 1.0). In other surface-associated communities even higher rates have been found. A cyanobacterial mat had a production of 37 mmol $m^{-2}$ $h^{-1}$ (Revsbech and Jørgensen 1986) and an eukaryotic algal mat had a rate as high as 47 mmol $m^{-2}$ $h^{-1}$ (Revsbech and Ward 1983). The upper limit for aquatic plant communities lies in the region of 60 mmol $m^{-2}$ $h^{-1}$ or ~8 g C $m^{-2}$ $day^{-1}$ for short-term measurements on very dense plant communities under very high stirring and saturating light (Krause-Jensen and Sand-Jensen 1998). However, it is not the absolute photosynthetic rate of the EAC, but the consistently high rates over a very large surface area and under high insolation that makes the EAC so important for coral reef primary production (Larkum 1983).

## Diffusive boundary layer thickness

Our results demonstrate for the first time some of the characteristics of the DBL for $O_2$ on active EAC of coral reef substrata. The DBL varied from 180–550 $\mu$m, at a flow rate of 0.08 m $s^{-1}$, to >1–2 mm, under slow flow rates or stagnant conditions, and the surface $O_2$ concentrations under light saturation varied between 200% and >600% of air-saturated seawater. While these levels are high, they are consistent with measurements made on other biofilms and microbial mats. For a crustose coralline red alga, with a very smooth surface and relatively low metabolic rates, Kaspar (1992) found a DBL thickness at comparable flows of 100–200 $\mu$m, and the $O_2$ concentration at the surface was 119–211% air saturation. For algal epiphyte communities on submerged macrophytes, forming an irregular surface topography, Sand-Jensen et al. (1985) found DBLs in the range of 200–1,000 $\mu$m under moderate stirring ("vigorously stirred by air-bubbling"). For an epilithic cyanobacterial biofilm, with a relatively smooth surface, Kühl et al. (1996) recorded DBLs of 200–250 $\mu$m for flows of 0.05–0.1 m $s^{-1}$. By comparison, studies of the DBL of hermatypic corals indicate a DBL thickness in the light under moderate water flow (0.02–0.06 m $s^{-1}$) of 150–500 $\mu$m and of >1–4 mm under stagnant conditions (Shashar et al. 1993; Kühl et al. 1995). The $O_2$ level at the coral polyp surface varied amongst coral species, from 191–373% air saturation at light saturation (980 $\mu$mol photons $m^{-2}$ $s^{-1}$) (Shashar et al. 1993). However, the complicated and dynamic topography of coral polyps lead to much more complex boundary layer conditions, which cannot be approximated by one-dimensional diffusion geometry as we apply it here for the EAC (Kühl et al. 1995).

## Limitation by inorganic carbon supply

Based on the known concentrations and diffusion coefficients (in seawater) of $CO_2$ and $HCO_3^-$ (Larkum et al. 1989), the fluxes of these solutes across the DBL (at light saturation and a flow velocity of 0.08 m $s^{-1}$) can be estimated (Table 3) by applying Eq. 1, making the simplifying assumption that the concentration of photosynthetically active carbon species at the EAC surface is close to zero (Table 2) and knowing the concentration of $O_2$ at the EAC surface (Table 1). It can be seen that the calculated influx of $CO_2$ is much smaller (by some 43- to 98-fold) than the $O_2$ efflux. On the other hand, the estimated $HCO_3^-$ influx is 2.8-fold greater than the $O_2$ efflux in the case of the *Stylophora* branches and 1.2-fold greater in the case of the *Porites* coral blocks. It can be assumed that $O_2$ exchange in photosynthesis is approximately the same as the dissolved inorganic carbon (DIC) exchange, based on measured photosynthetic quotients of ~1.0 (see Clavier et al. 1994; Rosenberg et al. 1995). These calculations suggest that DIC supply at light saturation would be adequate for the *Porites* coral blocks at a flow rate of <0.08 m $s^{-1}$ and at <0.04 m $s^{-1}$ for the *Stylophora* branches. Figure 3B also shows a strong dependency of the oxygen flux at DBL thicknesses <0.4 mm. Since not all algae are bicarbonate users and since the pH is higher than that of seawater close to the EAC surface in the light (Fig. 1), it is clear that under flow velocities of <0.04 m $s^{-1}$, closer to the conditions normally encountered by these EACs in situ (see below), the net photosynthesis would be significantly limited by the supply of DIC, in both substrata.

## Light saturation

The light saturation curve of photosynthesis and the associated saturation of $O_2$ and pH levels (Figs. 1B, C, 2B) indicate that the onset of light saturation occurs at

**Table 3** Fluxes of $CO_2$, $HCO_3^-$ and $O_2$ and diffusive boundry layers (*DBL*) for $O_2$ and limiting $HCO_3^-$ calculated on the basis of the following parameters: light saturation, flow rate (0.08 m $s^{-1}$) and concentration of solutes in bulk seawater ($CO_2$ = 10.2 mmol $m^{-3}$, $HCO_3^-$ = 2,000 mmol $m^{-3}$, $O_2$ = 206 mmol $m^{-3}$, concentration at epilithic algal community surface, dissolved inorganic carbon approaching zero, $O_2$ concentrations as in Table 1). The limiting $DBL_{HCO3-}$ was calculated for the condition whereby the influx of $HCO_3^-$ equals the efflux of $O_2$ (from Table 1). Diffusion coefficients from Larkum et al. (1989)

| | $CO_2$ influx (mmol $m^{-2}$ $h^{-1}$) | $HCO_3^-$ influx (mmol $m^{-2}$ $h^{-1}$) | $O_2$ efflux (mmol $m^{-2}$ $h^{-1}$) | $DBLO_2$ (measured) ($\mu$m) | Limiting $DBLHCO_3^-$ (calculated) ($\mu$m) |
|---|---|---|---|---|---|
| *Stylophora* sp. branch | 0.28 | 35.8 | 12.6 | 201 | 571 |
| *Porites* sp. coral block | 0.19 | 21.5 | 21.4 | 335 | 334 |

low irradiance levels of 80–100 $\mu$mol photons $m^{-2}$ $s^{-1}$ (with the exception of the surface pH which saturated above 500 $\mu$mol photons $m^{-2}$ $s^{-1}$). This suggests that the EAC is a shade-acclimated community, despite the fact that the EAC exists in a very high light environment. The work of Wanders (1976) showed that the EAC is saturated at similar levels to those reported here (viz. ~10% of full sunlight). Franklin et al. (1996) found that the EAC was quickly photoinhibited in moderately high light (800 $\mu$mol photons $m^{-2}$ $s^{-1}$) and suggested that upper layers may shade lower layers and that this may account for some of the shade characteristics. As discussed by Reiskind et al. (1989) most algae show characteristics of shade plants.

## Boundary layer pH

The high pH of 8.9 measured at the EAC surface at irradiance levels of > 500 $\mu$mol photons $m^{-2}$ $s^{-1}$ has important implications for photosynthesis in the EAC. This value compares well with a pH of 8.9 measured by Sand-Jensen et al. (1985) for the upper surface of a *Potamogeton crispus* leaf covered with epiphytes. Kühl et al. (1995) found that pH varied between 7.4 in darkness and 8.5 in light for hermatypic corals.

In photosynthesis, pH is an important physical parameter, especially in marine systems (Raven 1997). At the pH of seawater, ~8.2, the DIC (at 25°C) is proportioned into approximately (depending on alkalinity and partial pressure of $CO_2$) 2.5% dissolved $CO_2$ gas (~10 mmol $m^{-3}$), 90% $HCO_3^-$ (~2 mol $m^{-3}$) and 7.5% $CO_3^{2-}$ (~166 mmol $m^{-3}$). In algae, dissolved gaseous $CO_2$ seems to be the more general mechanism of DIC uptake, but many marine algae also have mechanisms to take up $HCO_3^-$ (Raven et al. 1995; Raven 1997), presumably because it is the prevalent form of DIC in seawater. With increasing pH above 8.2, the availability of $CO_2$ decreases, to ~1 mmol $m^{-3}$ at pH 8.5 and ~0.1 mmol $m^{-3}$ at pH 9.0. Thus, the existence of a pH of 8.9 or greater at the surface of the EAC under normal levels of daily irradiance means that the algae of the EAC will use predominantly $HCO_3^-$ and that the movement of DIC to the EAC from the bulk seawater is likely to be restricted, for the following three reasons. First, it can be assumed that there will be a DBL for $HCO_3^-$, similar in magnitude to that for $O_2$ (see above and Table 3). Second, whereas at lower pH there are two pathways for transport of DIC across this boundary, $CO_2$ and $HCO_3^-$, at high pH there is only one, $HCO_3^-$. Third, at a pH of 8.9 the concentration of bicarbonate has dropped considerably, so that there is a 1:1 proportion of bicarbonate and carbonate (and carbonate is not available for photosynthesis).

The existence of a high pH at the surface of the EAC might imply that all the algae of the EAC must be $HCO_3^-$ users. This is not necessarily so. The EAC, like other algal biofilms (e.g. Kühl et al. 1996), is a complex assemblage of microorganisms in which there are a large number of heterotrophic organisms. Therefore, there will be a significant evolution of $CO_2$ within the EAC at all times and this source may be utilised by some algae that lack a $HCO_3^-$ uptake mechanism. In a recent survey Raven et al. (1995) found that there are a considerable number of marine algae from a wide variety of algal groups that use only or mainly $CO_2$. These seem mainly to be shade-adapted plants and, therefore, are less likely to be represented in the high light environment of the EAC, but their presence in the EAC should not be dismissed categorically, because, as shown above, the EAC shows $P$ versus $E_d$ characteristics of shade algae, despite existing in a high light environment.

## Photorespiration

The restricted levels of DIC and the high $O_2$ concentrations at the EAC surface might suggest that photorespiration could also play a part in depressing net photosynthesis. Photorespiration is known to be directly related to $O_2$ concentration and DIC concentration inside the cell, since $O_2$ competes with $CO_2$ at the site of primary carboxylation by ribulose-1,5-bisphosphate carboxylase/oxygenase ("Rubisco"; EC 4.1.1.39) and leads to lower quantum yields for DIC fixation. However, Hackney and Sze (1988) made a specific study of the effect of $O_2$ on photosynthesis and photorespiration of algal turfs from a coral reef mesocosm, and found no evidence of enhanced photorespiration at elevated $O_2$. Also, for a temperate, diatom-dominated community under low light, Glud et al. (1992) estimated that photorespiration accounted for only 17% of the gross photosynthetic rate based on $O_2$ evolution, and for cyanobacterial-dominated communities it was much less. It seems likely that many of the algae of the EAC have a mechanism for controlling photorespiration. It is known that microalgae (Beardall 1989; Badger and Price 1992) have a carbon-concentrating mechanism (CCM), whereby the $CO_2$ concentration at the site of Rubisco is raised to high levels, out-competing $O_2$ and restricting the activity of photorespiration. In at least one potential member of the EAC, *Lyngbya birgei*, a CCM has been found (Beer et al. 1992). Thus, a similar CCM may be present in the algae of the EAC as an adaptation to high $O_2$/low DIC flux conditions.

## Future studies and conclusions

The present results show clearly the importance of water flow on physicochemical conditions at the EAC surface. Here, we have studied only the effects of unidirectional laminar water flow, while in situ the EAC is likely to be influenced by other types of flows, including turbulent and oscillatory flow (Denny 1988). Previous work suggests that the latter types of flow may produce enhanced photosynthesis compared to linear flow (Carpenter et al. 1991). This could well be the result of a reduced DBL

under turbulent and/or oscillatory flows (cf. Wheeler 1980; Koch 1994). The present substrata (coral skeletons) were taken from shallow semi-enclosed parts of the lagoon, where water movement is likely to be very restricted especially during low tide, when waves no longer propagate over the lagoon. Carpenter and Williams (1993) measured flow rates of up to 0.20 m $s^{-1}$ in a forereef at St Croix in the Caribbean, and showed that the height of the EAC had a significant effect on the flow speed within the EAC (see also Williams and Carpenter 1998). They found that for well-grazed EAC the flow rates were generally $< 0.02$ m $s^{-1}$. Larned and Atkinson (1997) estimated flow rates of 0.01–0.19 m $s^{-1}$ for forereef and reef flat sites in Kaneohe Bay. The large range in these two sets of measurements emphasises the need to make in situ measurements at the site of the EAC in question. However, since the present samples came from sheltered reef flat situations, it could well be that the flow regime would be in the lower part of this range.

In conclusion, the present measurements on the DBL of the EAC of coral reef substrata indicate that some limitation of photosynthesis may well occur as a result of the resistance to DIC diffusion across the DBL, at flow rates $< 0.04$ m $s^{-1}$ (a rate which is in the upper range for flows inside the rim of a coral reef). While the EAC of coral reefs is an exceptionally active algal biofilm, it seems likely that similar questions concerning high oxygen levels, high pH and flux limitation will arise for other algal biofilms as well; and here considerations must include most macroalgae, since even the massive canopy dominants begin life in an epilithic algal community.

**Acknowledgements** This work was supported by a travel grant to A.W.D.L. from the University of Sydney and a grant from the Australian Research Council. We wish to thank M. Waugh and Dr. A. Post for arranging the shipment of specimens from One Tree Reef and Eilat, respectively. M.K. acknowledges support by the Max-Planck Society (Germany) and the Danish Natural Science Research Council. The excellent technical assistance of G. Eickert, V. Hilmer and A. Eggers, and the kind help with LIX microsensors by E. Epping is gratefully acknowledged. B. Bebout, V. Meyer and R. Thar are thanked for their development of the software and hardware used with the automated microsensor set-up.

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