minority-serving institutions (other than UPR) are at campuses developed enough to confer doctoral degrees in aquatic sciences. This means that one or more of the traditional majority institutions must offer such a program. When this happens, we may see a steady flow of minority students earning Ph.D. degrees in the aquatic sciences. These students will then serve as role models and mentors, priming the pump to get the pipeline flowing.

However, do the students themselves perceive a need for such a minority-targeted program? A survey was conducted of 50 student participants in the 2001 ASLO Minorities Program to assess student response to such a program. Half the students responded, and all gave strong support to the idea (Table 5). Recently Kellogg (2001) reported on a similar University of Maryland program to produce minority Ph.D.s in mathematics. They have graduated numerous African American Ph.D.'s in the last decade, noting that once a critical mass was reached, "The students became the draw." (Kellogg, 2001).

There is a clear need for a special focused program as proposed above, but this is not the sole avenue to success. Minority Ph.D's have and will continue to come through institutions without any special programs. Indeed, a number of the students surveyed preferred the "traditional" approach (Table 5). Professors and departments recruiting students should always cast their nets broadly and actively seek minority applicants. Simple steps include contacting the programs listed in Table 4, and interacting with students at the annual ASLO Minorities Program. Individuals inspired to greater levels of action can contact the federal agencies that fund aquatic research to take advantage of existing programs and to propose new ones. In addition to NSF, other agencies (e.g., NOAA, USEPA, and USGS) offer a variety of programs designed to promote diversity (Jearld, 1999). With some thought and effort, we can all become part of the solution.

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OXYGEN TRANSPORT ACROSS THE BENTHIC BOUNDARY LAYER: FROM A 1-D TO A 3-D VIEW

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The sediment-water interface is a fascinating environment. Bordering the dynamic processes between hydrosphere and geosphere, it is the gate-keeper for the benthic-pelagic coupling of carbon and nutrient cycles in aquatic ecosystems. In this region boundary layer hydrodynamics interact with transport processes across the interface, organic matter deposited on the sediment surface supports and focuses the biological activity to a thin veneer teeming with life, and steep chemical gradients provide diverse zones for biological and geochemical processes.

Just as the earth surface appears flat when viewed from orbit, the sediment surface appears flat when we read most biogeochemical literature which describes it with only a vertical axis. However, many aspects of sediment biology and geochemistry require a three-dimensional view to understand their essential properties. We need novel approaches with greater information capacity to study the spatial structures of biota, environments, and processes. To stimulate the development of such approaches, this short review will discuss

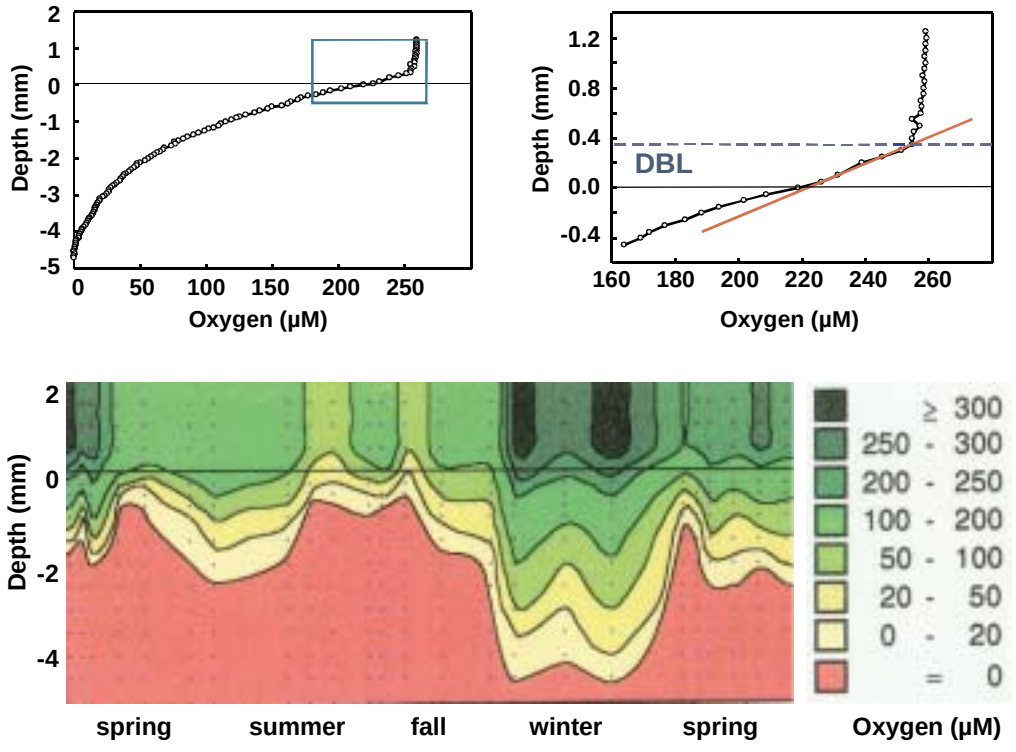
some of the small-scale characteristics of the benthic boundary layer, and illustrates the 3-D world of the sea floor based on recent progress in analytical and experimental techniques. The few examples used are taken mostly from the work of our own group since brevity forces us to neglect the excellent work of many colleagues.

As we cross the benthic boundary layer, the hydrodynamic properties of water flow change fundamentally as the sediment surface is approached (Boudreau and Jørgensen, 2001). Descending from the free flow region to less than a meter above the sea bed, we enter the logarithmic layer affected by sediment friction and roughness. Much nearer to the sediment surface, in the centimeter thick viscous sublayer, internal friction strongly dampens turbulence and the eddy diffusivity, E, falls below the kinematic viscosity, ν, of water ($\nu \approx 10^{-2}$ cm^2 s^{-1}). The eddy diffusivity continues to decrease steeply as the sediment is further approached. At ≤1 mm from the sediment surface, it drops below the molecular diffusivity ($D \approx 10^{-5}$ cm^2 s^{-1}), and molecular diffusion becomes the faster process of vertical solute transport. This transition establishes the diffusive boundary layer (DBL) which is a well-defined water film for non-porous sediments. In sandy sediments the transition is more gradual and complex. Shear stress from the overlying water flow may penetrate a few sandgrains depth into the porous sediment and thus define the Brinkman layer. Lateral pressure gradients caused by interactions between the boundary layer current and sediment topography drive deeper advective flows through t he pore space of the permeable sediments (Hüttel et al., 1998).

Diffusive boundary layers occur everywhere at solid-water interfaces. They blanket the surface of non-permeable sediments, they envelop plants, animals, and even sinking aggregates and phytoplankton. The existence of a benthic DBL has been known for decades from hydrodynamic theory and, for example, from the growth rate of ferro-manganese nodules or from *in situ* experiments on the dissolution rate of alabaster plates positioned on the sea floor (Santschi et al., 1991). As microelectrodes were first used to measure oxygen microgradients across the sediment-water interface in the early 1980's, the chemical diffusive boundary layer suddenly became very visible (Jørgensen and Revsbech, 1985). The diffusive oxygen uptake of sediments could now be calculated from microsensor data, either by modeling the oxygen profile within the sediment or from the oxygen gradient in the DBL: O_2 flux = $D \cdot (dC/dz)$, where D is the molecular diffusion coefficient. The latter approach appears simpler, but it requires a spatial resolution of 50-100 µm in order to obtain sufficient data points in the 0.3-1.0 mm thick DBL for a linear regression (Fig. 1). Such a resolution is possible by the use of micro-sensors, and data for oxygen and a range of other gases and ions are today obtained both in laboratory experiments and directly on the sea floor using benthic *in situ* instrumentation.

Figure 1 shows, as an example, how the seasonal variation of oxygen distribution in a coastal marine sediment responds to the governing processes. After the deposition of spring and fall phytoplankton blooms, oxygen penetrated <1 mm into the sediment and the diffusive uptake rate reached 35 mmol O_2 m^{-2} d^{-1}. The theoretical maximum, which would be reached if the oxygen concentration at the sediment surface dropped to zero, is about 85 mmol O_2 m^{-2} d^{-1} and depends on the flow velocity and thickness of the DBL, the oxygen concentration in the overlying water, and the temperature (and thus the diffusion coefficient). In winter, the oxic zone was 4-5 mm thick and the uptake rate was 13 mmol O_2 m^{-2} d^{-1}. The oxygen

Figure 1. Oxygen distribution in a coastal marine sediment over the year. An oxygen profile measured during winter by a benthic lander and microelectrode profiler reveals a ca. 400 µm thick diffusive boundary layer, clearly visible when the profile at the sediment-water interface is shown with expanded scales. The linear regression of oxygen in the DBL is used to calculate the diffusive flux of oxygen to the sediment. Isopleths of oxygen show how the seasonal variations in organic sedimentation and temperature regulate the depth of oxygen penetration. Data are from Aarhus Bay, Denmark, at 16 m water depth (Gundersen et al., 1995)

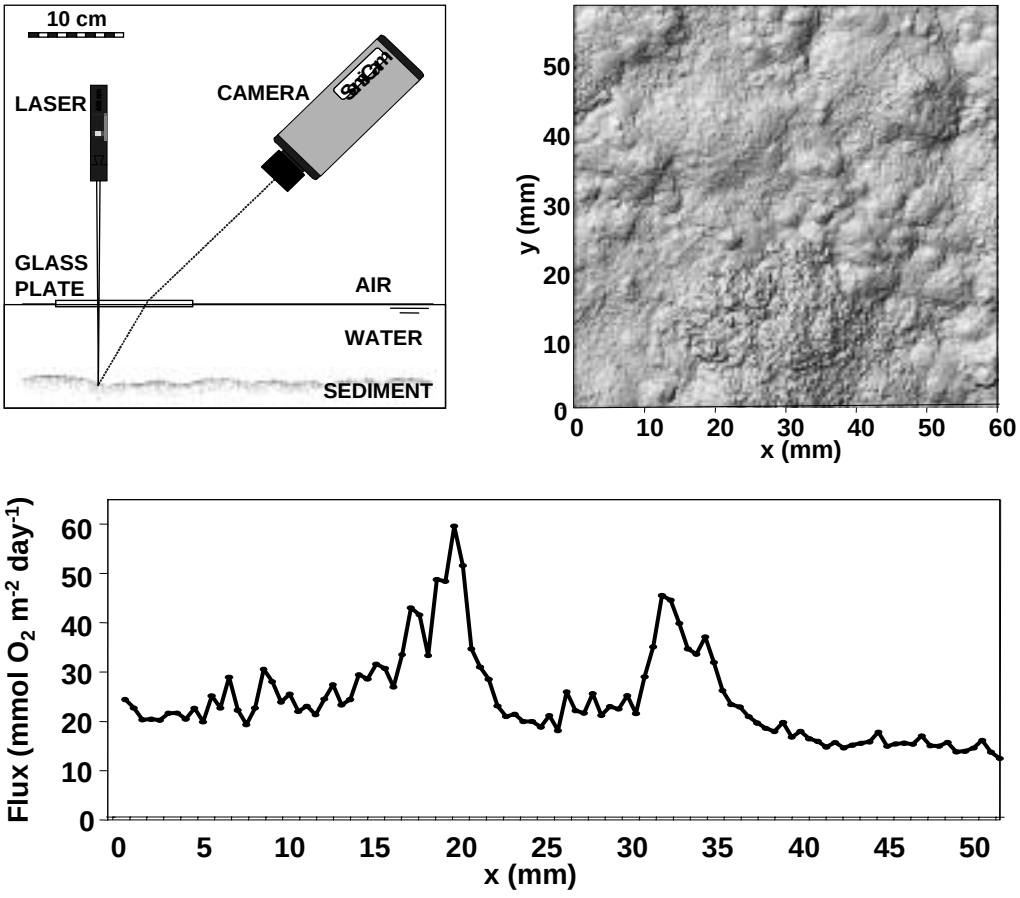


pool in the sediment is extremely dynamic, with a turnover time ranging from 40 seconds in summer to 37 minutes in winter. Although the DBL is only a fraction of a millimeter thick, it constitutes a diffusion barrier between water and sediment which may impede the oxygen uptake, particularly in summer. The diffusion time of oxygen across a 450 µm thick DBL is: $t = \pi \cdot \delta_e^2/4D = 3.14 \cdot 0.045^2/4 \cdot 1.6 \cdot 10^{-5} = 100$ seconds, where δ_e is the effective thickness of the DBL and D is the molecular diffusion coefficient of oxygen at 13°C. Thus, the DBL also causes a significant delay in the chemical exchange across the sediment-water interface.

The water flow near the sediment surface should ideally be measured at similarly high resolution as the chemical species. *In situ* measurements using an acoustic doppler anemometer currently reach a resolution of 0.5-1 cm, whereas the equivalent laser doppler technique has a 10-fold higher resolution, but is not yet developed into a practical field instrument. A flow microsensor was recently constructed which has a 20 µm wide tip and may cover ranges of flow velocities from 10 µm s^{-1} to 6 cm s^{-1} (J. K. Gundersen et al., unpublished). The first DBL results from this sensor have been obtained at a 50 µm resolution with the sensor pentrating from within the substrate and out into the flow to avoid disturbance. The results show zero flow at the solid-water interface and a linear increase of mean flow velocity with height above the interface within the DBL. Although these results are in accordance with a simple transition from inertial to viscous flow as the sediment surface is approached, the DBL is not a stable environment. Turbulence in the overflowing water induces fluctuations of the flow and the chemical gradients within the DBL, yet the net result is a diffusive transport which may be described by the mean gradients (Gundersen and Jørgensen, 1990)

In the preceding discussion, the 1-dimensional flux calculations from vertical gradients assume a perfectly flat sediment surface. However, at the sub-millimeter scale of the DBL the sediment is a spectacular landscape of mountains and valleys, and diffusion takes place across an interface of complex topography. Accordingly, the effective area available for diffusion exceeds that of a flat plane, and diffusion is not just vertical, but takes the shortest path across the sloping DBL. Topographic mapping of surfaces at sufficiently high spatial resolution is now possible with different laser techniques, both in the laboratory and in the field. A simple approach is illustrated in Fig. 2 together with a digitally generated image of a 6x6 cm sediment surface recorded at 50-100 µm resolution. The relation between the simple vertical flux, J_z, across a flat plane and the 3-D flux, J', across the topographic surface can be approximated by the simple square cosine law: $J' = J_z \cdot (1/\cos \alpha)^2$, where α is the mean slope for the entire topographic surface (Jørgensen and Des Marais, 1990). This angle, however, depends on the spatial resolution of surface topography which should first be mathematically smoothed using a smoothing kernel of similar size as the DBL thickness (H. Røy, M. Hüttel and B. B. Jørgensen, manuscript submitted).

Figure 2. Topography of a sediment surface sculptured by burrowing fauna and analyzed by laser optics. A fine line is illuminated across the sediment surface (perpendicular to the image plane) and photographed by a CCD camera. Some 600 consecutive images, each shifted to the left by 100 µm, create the basis for the shaded 3-D topographic map. From series of oxygen gradients measured in the DBL, the heterogeneous distribution of diffusive oxygen uptake can be mapped. A 50 mm long transect shows two distinct peaks of oxygen flux caused by worms which transport reduced sediment up on the sediment surface. Data from a marine coastal sediment maintained in a laboratory flume for a month (H. Røy, M. Hüttel and B. B. Jørgensen, submitted manuscript).

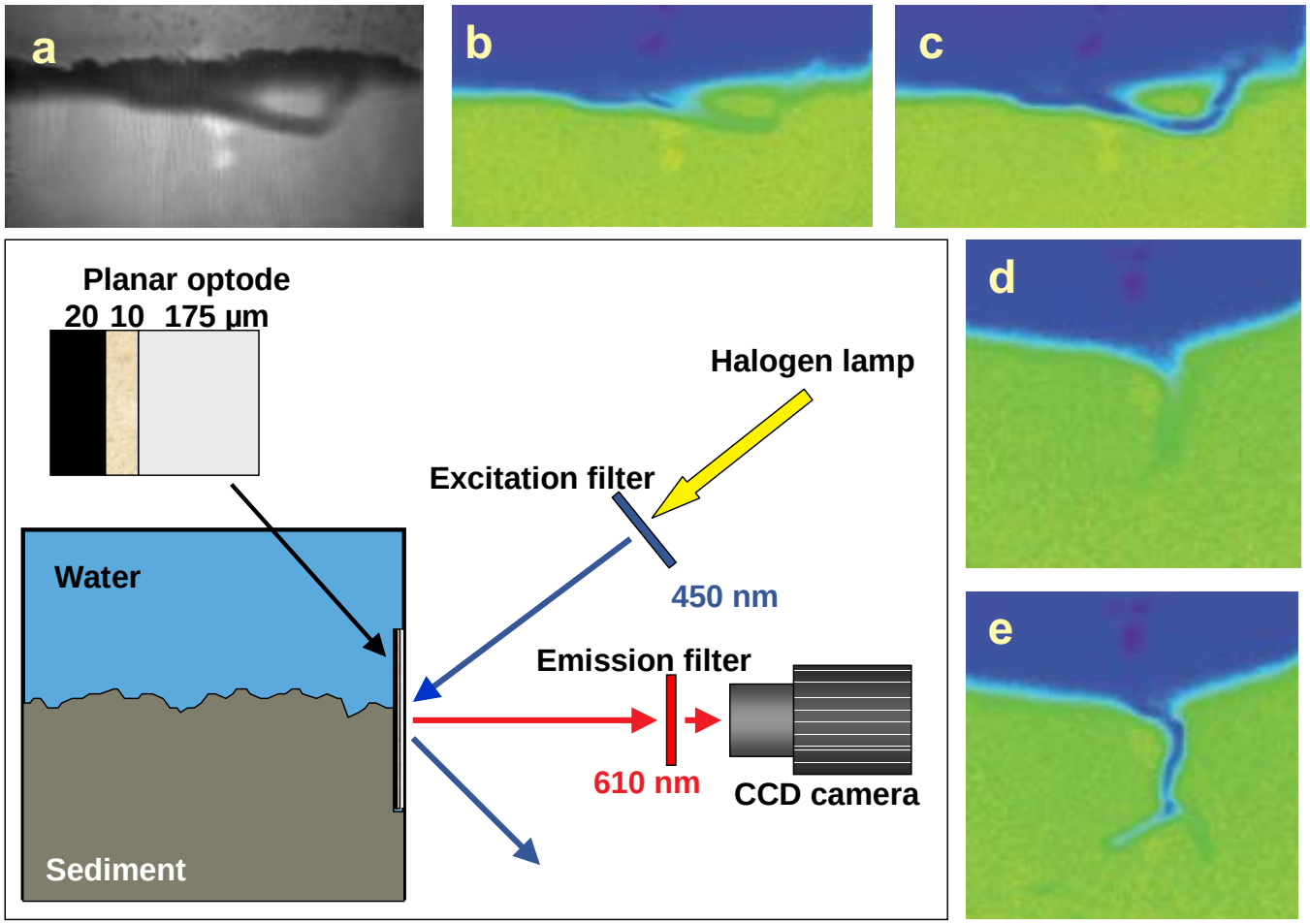


For many sediments this square cosine correction is moderate (e.g. 1.13 for α=10° and 1.7 for α=20°), whereby a mean slope of 20° is already steeper than most sediment surfaces. A field survey of surface topographies is still needed to relate the steadily growing database on chemical microprofiles to the effective 3-D diffusion field.

High-resolution mapping of oxygen microgradients across the sea floor can be done semiautomatically using computer controlled micromanipulators and online data aquisition. A linear transect was measured in the same sediment as in Fig. 1 and the results demonstrated that the oxygen flux is very heterogeneous and related to the activity of benthic invertebrates (Fig. 2). Due to the defecation by small deposit-feeding oligochaetes, hot-spots of reduced sediment were maintained on the sediment surface in the laboratory flume. Such few millimeter wide fecal spots had oxygen consumption rates up to 3-fold higher than the ambient sediment, but the oxygen flux was very dynamic and dropped within hours after the worms stopped their activity, partly due to the reoxidation of reactive iron-sulfur minerals.

Progress in the study of spatial distributions of chemical species has often come with the development of novel analytical techniques. The mapping of oxygen from individual vertical profiles tends to be a low-capacity approach, frequently interrupted by frustrations of the experimenter due to breakage of the fine electrode tip. A different sensing principle based on dynamic fluorescence quenching has in recent years opened exciting new possibilities for the analysis of oxygen in aquatic environments by optical microsensors, so called microoptodes (Klimant et al., 1995). A fluorophore such as $Ru(diph)_3$ (Ruthenium(II) tris-4-7-diphenyl-1, 10-phenanthroline perchlorate) dissolved in a liquid polymer such as polystyrene or sol-gel can be applied to the 30 µm tip of a tapered optical silica fiber by simple dip-coating and

Figure 3. Two-dimensional oxygen distribution in sediment inhabited by burrowing fauna. A planar optode was glued to the inside of a sea water aquarium half filled with marine sediment. The optode consists of a 175 µm thick supporting plastic foil, a 10 µm film with the sensing chemistry, and 20 µm black silicone (redrawn from Glud et al., 1996). The optode is excited by blue light and emits orange-red flourescence which is photographed by a CCD camera. Oxygen diffuses into the O_2-sensitive film and reversibly quenches the fluorescence, whereby the light intensity can be calibrated to oxygen concentration at the ambient temperature. By using modulated light, the planar optode can be made without the light-shielding black silicone and sediment structures may be observed through the semi-transparent film (frame a). The images show: (a-c) a shallow U-shaped burrow of the amphipod, *Corophium volutator,* and (d-e) an inverse Y-shaped burrow of the polychaete, *Nereis diversicolor.* The O_2 scale goes from air saturation (dark blue) to zero (yellow-green) and the light blue color thus delineates the extension of the DBL and oxic sediment. The sediment sections are ca. 3 cm across. (U. Franke and G. Holst, unpublished data).



drying. The fluorophore has a large Stoke shift with absorption maximum in blue light at 450 nm and emission in the red-orange at 610 nm. The blue excitation light from a light-emitting diode is guided through the fiber out to the tip and the resulting red-orange flourescence emission is guided back up through the same fiber and detected by a sensitive photomultiplier. Oxygen from the ambient water diffuses through the solidified polymer at the sensor tip and reversibly quenches the fluorescence. More oxygen causes less emission of orange light, and the sensor can thereby be calibrated against oxygen concentration at a given temperature.

When used in continuous mode, the sensor must be shielded from ambient light which would otherwise interfere with the measured flourescence. The fluorophore may, however, also be excited with modulated light whereby, for example, the exponential decay of light emission after each excitation pulse is monitored. In this mode the sensor needs no shielding from ambient light. This fluorescence life-time is also a function of oxygen quenching and can similarly be used to determine its concentration. The dynamic life-time mode of detection has the great advantage that it is independent of geometry, and the polymer-embedded fluorophore may thus be arbitrarily distributed and will still report the oxygen concentration correctly after initial calibration (Holst et al., 1998, Holst and Grunwald, 2001).

As an example, an oxygen-sensing planar optode can be constructed by coating the polymer over a plastic foil which then reports the adjacent oxygen concentration. Glud et al. (1995) first glued such a piece of foil to the inside of an aquarium and filled it half with sediment in order to measure the oxygen penetration (Fig. 3). It was later found that the natural fauna may reestablish in the mud and build burrows which are sometimes positioned directly up against the planar optode. By imaging the optode fluorescence with a CCD camera (Charge Coupled Device producing a digital video) at regular intervals, the two-dimensional oxygen distribution can thus be continuously recorded by a million pixels at a resolution ranging from 2 µm to 100 µm per pixel. Such time-lapse recordings provide a wealth of information about the oxygen transport in relation to the burrowing and ventilation activity of benthic invertebrates (Fig. 3). It is now possible to make transparent planar optodes, whereby the oxygen dynamics can be related to the observed sediment structures and animals behind the optode (Fig. 3a). An *in situ* instrument was recently developed which enables observations directly in the sea floor of the two-dimensional vertical oxygen distribution in sediments concurrent with photography of the same sediment section of ca 10x10 cm.

The analysis of the three-dimensional oxygen distributions in water is also becoming possible through the application of optical sensing techniques. A first step in this direction was made by the development of fluorescent nanoparticles which are suspended in the water and report the oxygen concentration at any point which can be reached by the excitation light and observed by a CCD camera (G. Holst, unpublished results). By illuminating the water with a thin laser curtain of blue light, the oxygen distribution is analyzed in a <1-mm thick vertical section. Consecutive sections may allow the construction of a 3-D image which, however, is a composite of non-synchronous sections and is therefore likely to require many repetitive images. As computers rapidly increase in capacity, this requirement should not limit the application of such 3-D techniques. The sensing chemistry is also well developed for pH and temperature, and further chemical species and parameters are expected to enter the program. In the future, the possibility of combining concurrent digital photographic recordings of sediment structures and organisms with optical analyses of chemistry and flow will open new dimensions, both in space and time, and in the concepts of aquatic ecology.

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