The influence of bottom boundary turbulence on sediment solute dynamics

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The influence of bottom boundary turbulence on sediment solute dynamics

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presentd by

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‘Fourty-two!’ yelled Loonquawl. ‘Is that all you’ve got to show for seven and a half million years’ work?’ ‘I checked it very thoroughly,’ said the computer, ‘and that quite definitely is the answer. I think the problem to be quite honest with you, is that you’ve never actually known what the question is.’

(Douglas Adams)
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Summary

The influence of the hydrodynamics in a seiche driven prealpine lake on the oxygen transport into and across the bottom boundary layer and the resulting response of the solute dynamics in the sediment were the main focus of this thesis.

Previous studies have shown that a diffusive boundary layer existed in the investigated lake which correlated well with the turbulence level in the bottom boundary layer. In order to characterize the hydrodynamics in the vicinity of this diffusive sublayer at the last cm above the sediment a novel flow sensor for in situ measurements was used. This sensor could cope with the very low flow velocities close at the sediment water interface. It was thoroughly tested for its suitability as an in situ device. Its signal dependence on pressure, temperature and flow direction was analyzed and the necessary algorithms for the signal postprocessing of the in situ measurements were developed. The recorded flow profiles showed the collapsing turbulence close to the sediment water interface and the transition of the viscous boundary layer into a logarithmic layer. The obtained results compared also well with the horizontal velocities recorded simultaneously with an acoustic Doppler velocimeter.

The temporal variation of the turbulent oxygen transport in the bottom boundary layer due to the oscillating shear was investigated using the eddy correlation technique. The method is based on the simultaneous measurement of the velocity field was measured by an acoustic Doppler velocimeter and the oxygen concentrations close to its measurement volume. This setup was thoroughly tested in a permanently turbulent shallow water system. The obtained data agreed excellently with the sedimentary oxygen uptake during nighttime and showed nicely the oxygen production due to photosynthesis during daytime.

The data obtained in the seiche driven Lake Alpnach showed that the turbulent oxygen flux towards the sediment was highly intermittent. Spectral analysis and thermistor data collected during the field campaign showed that the main reason for this intermittency was the lack of active turbulence which was able to mix oxygen from the lake interior into the bottom boundary layer through its stratified top during flux free periods. This intermittency also explained the slight oxygen depletion of the well mixed part of the bottom boundary layer compared with the lake interior.
The variable oxygen concentration in the bottom boundary layer and the oscillating thickness of the diffusive boundary layer lead to a time dependent oxygen supply of the sediment over a seiching cycle. The potential reaction of the solute dynamics in the sediment on this variable oxygen supply was investigated by recording in-situ high resolution profiles of oxygen and nitrate using microsensors in combination with an analysis of diffusion chamber samples for methane, iron and manganese. These data were used for the calibration of an early diagenetic model. The model calculations showed that the diffusive boundary layer mainly influences the sedimentary denitrification in Lake Alpnach over cycles shorter than 24 hours by acting as a transport resistance while it influences the reoxidation of reduced compounds by controlling the oxygen penetration depth into the sediment.
Zusammenfassung

Die vorliegende Arbeit befasst sich hauptsächlich mit dem Einfluss der Seiche induzierten Strömung auf den Sauerstofftransport in die und innerhalb der Bodengrenzschicht und der daraus resultierenden Reaktion gelöster Stoffe im Sediment in einem Voralpensee.


Die im durch Seiching geprägten Alpnacher See erhaltenen Daten zeigten, dass der Sauerstofffluss zum Sediment nicht kontinuierlich stattfindet. Spekralanalyse und zusätzlich aufgenommene Thermisordaten zeigten, dass das Fehlen aktiver Turbulenz, die den oberen stratifizierten Bereich der Bodengrenzschicht mischen hätte können, der Grund für die beobachteten Unterbrechungen waren. Diese waren auch die Erklärung für die geringe Sauerstoffverarmung der Bodengrenzschicht im Vergleich zum Wasserkörper des Sees.
Chapter 1

Introduction

1.1 Background

The aquatic bottom boundary layer (BBL) is the interface between sediments and the overlying waters in oceans, lakes, wetlands and rivers (Boudreau and Jørgensen 2001). It is the main location (i) of the dissipation of energy of currents and waves as well as (ii) of turbulence and mixing in the stratified interior (Wüest and Lorke 2003). This transport in the BBL can even dominate the basinwide vertical transport of solutes in small lakes (Goudsmit et al. 1997).

The BBL in lakes can be subdivided into three zones by their nature of momentum and solute transport (Fig. 1-1). The logarithmic layer starts at a height of several meters over the sediment surface. It devolves into the viscous sublayer (VBL), which starts at about 1 cm above the lake floor. It includes the diffusive sublayer (DBL) at about 1 mm above the sediment. The horizontal velocity $u$ increases linearly with depth in this layer (Boudreau and Guinasso 1982) (Fig. 1-1 right). The transitions between these layers are smooth and their thickness depends on the regime of the currents in the aquatic environment. The structure of the BBL is created by shear flow, waves and turbulence, each of which can be broadly classified in terms of their characteristic time and space scales (Dade et al. 2001). The mean flow represents the conditions which are relatively steady over a period of several hours or longer (Dade et al. 2001). Typical values for such flow speeds in the oceans lie between 1 - 25 cm/s in deep sea BBL (Dade et al. 2001). The values in lakes are expected to be even lower. Each layer can be classified by the importance of different momentum and solute transport mechanisms based on the classical boundary layer theory. Momentum is not only transported by the mean flow and molecular transfer but also by turbulence. A diffusion constant, which is called eddy viscosity $K_m$ can be assigned to this latter mechanism of momentum transfer (Boudreau 1997). Far above the stationary surface, the turbulent flow determines the momentum transfer and $K_m$ is much larger than the molecular viscosity $\nu$. In this region, the flow velocities follow the characteristic logarithmic profile described by the law of the wall (Wüest and Lorke 2003). Close to the sediment surface, turbulent fluctuations...
are dampened and molecular forces dominate momentum transfer as the velocity decreases to zero (Fig. 1-1 left). The upper limit of this so called viscous boundary layer is defined at the location where the molecular viscosity equals the eddy viscosity. In the upper part of the viscous sublayer, very small eddies still suffice to mix dissolved substances. These eddies almost disappear very close to the surface and molecular diffusion dominates the solute transport. The upper end of the diffusive sublayer is given by the relation $D = K_c$ where $K_c$ is the eddy diffusion coefficient for solute transport and $D$ the molecular diffusion coefficient (Boudreau 2001).

Since molecular diffusion is much slower than turbulent or advective transport, the DBL mainly acts as a bottleneck for the transport of solutes from the open waters to the sediment. Fluxes across the boundary layer are therefore governed by molecular diffusion, by the thickness of the boundary layer and by a quasi linear concentration gradient across the boundary.
In the last 20 years, many laboratory investigations concentrated on the importance of the DBL on the oxygen dynamics in the sediment. (Jørgensen and Revsbech 1985) used oxygen microelectrodes in order to analyze the structure of the DBL in a laboratory flumes. They found that the DBL can limit the oxygen uptake rate in the sediment if its reactivity is high enough. Kelly-Gerreyn et al. (2005) showed that fluxes of nitrate, ammonium and sulfate can vary heavily with changing DBL thickness using a steady state model in which oxygen was only used by mineralization and ammonium oxidation. They also showed that the degree of these changes increases with increasing reactivity of the particulate organic material.

In contrast to these laboratory studies and the modeling study, we cannot expect a permanently uniform BBL in small lakes, since the bottom currents can vary due to internal waves with a low frequency $f \sim \sqrt{\frac{g \Delta \rho}{\rho} \frac{H}{2L}}$ where $g$ is the gravitation constant, $\Delta \rho$ is the difference in density between epilimnion and hypolimnion, $H$ the depth of the lake and $L$ its length (Gloor 1995).

This seiching influences the thickness of the diffusive boundary layer in the sediment. Lorke et al. (2003) showed that the thickness of the DBL depends on the turbulence level and therefore controlled the oxygen uptake of the sediment in Lake Alpnach.

Gloor et al. (2000) observed in the same lake that the well mixed part of the BBL on the lake bottom is relatively constant in periods with pronounced seiching, whereas its nature is much more dynamic and the presence of a mixed layer is highly intermittent on the sloping sediments. In addition, some lakes with low flow velocities parallel to the sediment can not produce enough shear to keep a permanently well mixed BBL against the background stratification. This is for example the case if the buoyancy flux from the sediment due to the release of dissolved mineralization products leads to the development of stratified boundary layer if the turbulence is too weak to transport the solutes from the sediment. This process has been observed e.g. in Lake Zug (Wüest and Gloor 1998).

1.2 Goals and outline of this thesis

In the context of these previous findings by Gloor et al. (2000) and Lorke et al. (2003), the presented work aims to address three open questions concerning the transfer processes at the interface of the BBL to the lake interior on the upper and the sediment on the lower side:
(I) Even though the dynamics of the DBL has been characterized using oxygen microelectrodes, no one has analyzed the properties of the viscous boundary layer in lakes with low shear flow. Until recently, there existed no in situ device which could measure very low flow velocities at the required spatial resolution.

(II) Many physical measurements of the structure, turbulence regime and flow dynamics of the BBL in seiche driven lakes have been conducted. Nevertheless, no direct measurements of oxygen fluxes into and across the BBL have been performed. Therefore, the underlying processes of the oxygen dynamics in the whole bottom boundary layer were not adequately addressed.

(III) The third question is how the non-stationary oscillating DBL thickness affects the mass transfer between the sediment and lake water and early diagenetic processes in the sediment in lakes. Many reactions like denitrification and reoxidation of reduced compounds are directly coupled with the oxygen dynamics in the sediment. It is still unclear to which extent how the DBL influences these processes.

To address these questions, following studies were carried out within this dissertation:

Microsensor for in-situ flow measurements in benthic boundary layers at sub-millimeter resolution with extremely slow flow (Chapter 2): A novel flow sensor which was capable to measure very low flow velocities was adapted and characterized for in situ measurements at the bottom of Lake Alpnach. The sensor enabled us to investigate the VBL above the sediments of a lake with low shear velocities for the first time.

Local oxygen flux estimates from eddy correlation in shallow freshwater: towards routine application and analysis (Chapter 3): A novel eddy correlation setup for the measurement of turbulent oxygen transport in aquatic systems was developed and thoroughly tested in a system with permanently turbulent shallow water system. The obtained data agreed excellently with the sedimentary oxygen uptake during nighttime and showed nicely the oxygen production due to photosynthesis during daytime.
Intermittent oxygen flux from the interior into the bottom boundary of lakes as observed by eddy correlation (Chapter 4): As a next step the variability of the oxygen flux on the sloping sediments of Lake Alpnach was investigated with the eddy correlation method. The turbulent oxygen flux was highly intermittent due to periods of low flow velocity which could not produce enough turbulence to mix oxygen through the stratified top of the BBL.

Influence of the diffusive boundary layer on the solute dynamics in a seiche driven prealpine lake - a model study (Chapter 5): The response of the solute dynamics in lake Alpnach on the variability thickness of the DBL and oxygen concentrations in the overlying waters was investigated using numerical modeling. The study shows that the diffusive boundary layer mainly influences the short term sedimentary denitrification by acting as a transport resistance while it influences the reoxidation of reduced compounds by controlling the oxygen penetration depth into the sediment.
1.3 References


Chapter 2

Microsensor for in-situ flow measurements in benthic boundary layers at sub-millimeter resolution with extremely slow flow

Andreas Brand, Beat Müller, Alfred Wüest, Christian Dinkel, Niels Peter Revsbech, Lars Peter Nielsen, Ole Pedersen, Lars Riis Damgaard, Lars Hauer Larsen, Bernhard Wehrli

Abstract

The currents in the lowest few mm of the bottom boundary layer of lakes are highly important for the dissipation of kinetic energy and for chemical processes like oxygen transfer into the sediment. So far, no high resolution flow velocity profiles close to the sediment water interface have been reported for such systems because a suitable flow meter was lacking. This paper introduces a novel sensor for the measurement of extremely low flow velocities. The sensor is based on a gas transducer which is surrounded by a gas reservoir. It measures the change in the partial pressure of a tracer gas on the outside of the reservoir tip due to advective transport. The sensor is suitable for measurements of velocities smaller than 1 mm s\(^{-1}\) with a spatial resolution of 100 to 250 µm. The flow measurements prove to be insensitive to temperature changes between 5 and 15 °C. The sensor is robust against relative pressure changes, and angular differences in the sensitivity can be calibrated. We present high resolution in situ measurements at the bottom of a pre-alpine lake with shear velocities as low as 0.13 ± 0.02 cm s\(^{-1}\). The velocity profile resolves nicely the transition zone between the viscous and the logarithmic boundary layer.
2.1 Introduction

The aquatic benthic boundary layer (BBL) is the interface between sediments and the overlying waters in oceans, lakes, wetlands and rivers (Boudreau and Jørgensen 2001). It is the main location (i) of the dissipation of energy of currents and waves as well as (ii) of turbulence and mixing in the stratified interior (Wüest and Lorke, 2003). Below this interface early diagenetic processes of settled particulate matter cause chemical concentration gradients in the pore water (Boudreau and Jørgensen 2001). Processes on both sides of the interface have been shown to influence the exchange of dissolved substances between the sediment and the overlying water. While the role of the BBL in biogeochemical processes has been extensively investigated (Boudreau and Guinasso 1982; Jørgensen and Revsbech 1985; Jørgensen and Marais 1990; Lorke et al. 2003), studies on properties of currents in the few mm immediately above the sediment are scarce (Caldwell and Chriss 1979; Chriss and Caldwell 1982; Chriss and Caldwell 1984a; Chriss and Caldwell 1984b). To our knowledge, Caldwell and Chriss (1979) performed the only in situ measurements in the viscous boundary layer (VBL) in the ocean. No comparable measurements have been reported for lakes where deep-water flow velocities are much lower than in the ocean, and so far no probe of suitable sensitivity and size has been developed and applied.

A variety of methods exist for the measurement of flows in natural waters close to the sediment (Khalili et al., 2001). One of the more widely used methods is laser Doppler anemometry which measures with high precision and with fast response times, making it suitable for the characterization of vortices and turbulent environments (Nelson et al. 1995). In situ applications have a typical spatial resolution in the range of several millimeters (Agrawal and Belting 1988). Hot film anemometry and hot wire anemometry (HWA) have also been applied e.g. in studies of shear stress and flow profiles over surfaces in oceanic systems (Gust 1988). Caldwell and Chriss (1979) were able to investigate the viscous boundary layer on the continental shelf at 185 m depth using a heated thermistor. These probes are sturdy and have a fast response, but due to the induced thermal convection, their detection limit is in the range of 1 cm s⁻¹ (Khalili et al. 2001). Very slow flow velocities of < 1 mm s⁻¹, however, can be observed by particle image velocimetry (PIV). This method has recently been used to describe the flow in diffusive boundary layers above sediments in the laboratory (Røy et al. 2002) and in the coastal ocean (Bertuccioli et al. 1999, Nimmo Smith et al. 2002; Nimmo Smith et al. 2005). Nevertheless, using PIV in situ demands a very
sophisticated experimental setup and in situ measurements in the lowest region of the VBL have not yet been reported.

Fig. 2-1: A) Overview of the main parts of the sensor. The tracer gas reservoir (2) is flushed through the steel in- and outlets (3 and 4). The gas reservoir is situated around the gas transducer (1) and sealed with epoxy resin (5). B) Concentration profiles in the setup at two different flow velocities. A constant partial pressure is applied in the reservoir. At steady state, tracer gas diffuses through the membrane with a constant flux into the environment. The concentration outside of the tip is high at low flow (solid curve). If the flow velocity increases, the diffusion sphere is eroded more efficiently and the hydrogen concentration decreases (dashed line). C) Detailed sketch of the tip. The tracer gas diffuses from the reservoir (7) through the silicone membrane (8) and forms a diffusion sphere (9) around the sensor. Concentration changes are measured in the membrane by the transducer (6).

In order to study low velocities in the BBL of lakes we have developed and applied a new type of miniaturized flow sensor with an extremely low detection limit and a fine spatial resolution for the in situ application on a benthic bottom lander. The detection limit is in the sub mm range since the probe does not induce any convective currents. It can be used with many existing lander systems equipped with amperometric channels. The novel flow velocity
microsensor is based on the principle of the diffusivity sensor presented by Revsbech et al. (1998). The design and principle of the sensor are illustrated in Fig. 2-1A. Tracer gas is continuously diffusing through the membrane of the reservoir and a sphere of tracer gas builds up at the tip of the microsensor (Fig. 2-1C). At steady-state, the diffusive loss of tracer gas leads to a linear decrease in partial pressure across the membrane reservoir. In stagnant fluids, the partial pressure gradient builds up, causing a high signal from the gas transducer, whereas high flow rates in the fluids erode the gas sphere (Fig. 2-1B). This erosion decreases the partial pressure of the tracer at the sensing tip, thereby resulting in low signals from the gas transducer. In our case we used hydrogen as a tracer gas and a Clark type sensor as the transducer, which measures a current caused by the reduction of hydrogen at the anode. The maximum reduction current is therefore measured under stagnant conditions. The tracer must be inert within the measurement volume but may be any gas that the transducer is able to detect.

2.2 Materials and Procedures

2.2.1 Sensor design

We applied hydrogen as a tracer gas and a hydrogen microsensor (Unisense A/S) as a transducer within the flow sensor (Fig. 2-1A). Otherwise it was constructed as described by Revsbech et al. (1998), except that the tip diameters were 40 to 50 µm and thus considerably smaller than the typical diffusivity sensors they described. The two thin steel capillaries in contact with the otherwise sealed hydrogen reservoir allowed a constant flushing with hydrogen gas. The outflow capillary had a much smaller diameter than the inflow capillary so that the pressure within the reservoir at high gas flows almost corresponded to the pressure within the inlet line.

2.2.2 Sensor calibration

We used the setup shown in Fig. 2-2 for all calibrations and tests of the sensor in the laboratory. A polyurethane disc (1) with a water-filled 4 mm wide and 10 mm deep groove with a radius of 51 mm was mounted on a modified peristaltic pump (2) (Gilson Minipulse). The disc was kept in a perspex container under water saturated atmosphere in order to avoid currents induced by air draught and thermal convection due to evaporative cooling of the water surface. The air was moisturized by bubbling air through water in a container (6). The sensor was then positioned in the water-filled groove using horizontal and vertical
micromanipulators. Hydrogen gas flow was controlled with a standard pressure reducer for outlet pressures of up to 1 MPa. The sensor signal was recorded with a commercially available picoamperemeter (UNISENSE PA 2000) after A/D conversion (ADC 100 A/D converter). Data acquisition, evaluation and remote controlling of the peristaltic pump were performed using LabVIEW scripts.

Fig. 2-2: Setup for the sensor calibration. A plastic disc (1) with a groove is mounted on a modified hosepump (2). The sensor (3) is fixed in a Lab stand (4) and inserted into the water-filled groove. The gas inlet of the sensor is connected to a gas bottle with a standard pressure reducer (5). The disc is contained in a box flushed with water-saturated air produced by bubbling air though water in the plastic container (6). The reduction current of the sensor is recorded using a picoamperemeter (8). The control of the hosepump and data acquisition is performed automatically.

Before each calibration the groove of the disc was filled with fresh water. After filling completely, a small portion of the water was removed until the curvature of the meniscus in the groove remained constant. The sensor was inserted 2 mm deep into the water and allowed to equilibrate for 10 min under stagnant conditions. Calibrations were performed in the range of 14 mm s\(^{-1}\) down to 0.2 mm s\(^{-1}\). Velocities were regulated by setting the hose pump to the corresponding rotation speed. The motor speed stability of the pump is 0.5 %. Each interval of
constant speed was recorded for 60 s and an average of the last 15 s was used to calculate calibration curves. The response was calculated as the ratio of maximum reduction current at \( u = 0 \) mm s\(^{-1}\) and the actual current.

### 2.2.3 Sensor performance

Calibrations were performed in the temperature range of 5 to 22 °C at a reservoir pressure of 0.2 MPa in order to investigate the influence of temperature on the sensor response. The whole setup was operated in a climate chamber which was sequentially working at 5, 7, 10, 15 and 22 °C. The system was allowed to adapt completely to the new temperature for at least 5 h before the sensor calibration procedure was applied. The influence of pressure variation on the signal was investigated by performing standard calibrations under 0.2, 0.3, 0.4 and 0.5 MPa pressure in the hydrogen reservoir. Two different methods were used in order to determine the response times of the sensors. In a first attempt, four different flow velocities were applied after stagnant conditions. After that, the flow was stepwise decelerated from 1.8 mm s\(^{-1}\) to 0.2 mm s\(^{-1}\) and then accelerated stepwise again. To determine the sensitivity of the sensor signals to flow direction, standard calibrations were performed for different orientations of the sensor. One position of the sensor was arbitrarily marked as the zero orientation. Successive calibrations were performed every 15 degrees.

### 2.2.4 In-situ measurements

In situ measurements were carried out in May 2005 in Lake Alpnach, a medium-sized mesotrophic subbasin of Lake Lucerne in Central Switzerland. It has an elliptical shape of approximately 5 by 1.5 km, a surface area of 4.2 km\(^2\), and a maximum depth of 34 m. The lake is well known for its persistent basin-scale deep-water seiching of several cm s\(^{-1}\) amplitude with a period of more than 8 hours in length (Gloor et al., 1994; Lorke et al., 2003) which results from the lake’s physical dimensions, stratification and the regular wind forcing.

To conduct field measurements, we expanded our benthic lander system LISA (Müller et al. 2002) with an amperometric channel for the flow sensor. A compass was built into LISA to determine the sensor orientation. A 3.5 L hydrogen tank with a high precision pressure reducer (Tescom) was used as a hydrogen supply. The pressure reducer was adjusted for a constant pressure difference of 0.15 MPa, which resulted in a reservoir pressure of 0.45 MPa at the investigated location in 30 m depth. The sensor was calibrated before each measurement campaign using water from the investigated lake at 7 °C. Profiles were recorded
starting at approximately 1.5 cm above the sediment, which consisted of fine silty material. A
time series of 120 s was recorded at 3 Hz at each depth. The first 30 s were omitted in the data
evaluation in order to avoid artifacts caused by the sensor response time. Thus, averages were
calculated in the time interval of 30 to 120 s. For comparison of flow direction and velocities,
an acoustic doppler velocity meter (ADV; Nortek) was installed stationary 11 cm above the
sediment approximately 10 m apart from LISA. All errors for the values calculated by
regression were estimated using the methods described in Bronstein et al. (1997) at a
probability value of 0.1. Linear error propagation was used to estimate uncertainty of
interpolated and extrapolated variables.

2.3 Assessment

2.3.1 Sensor performance

Fig. 2-3 shows typical calibration curves at temperatures between 5 and 22 °C. We
approximated the velocity \( u \) [mm/s] using the empirical function

\[
u(S) = A \exp(k (S - B)) + C S^D - E \tag{2-1}
\]

of the relative signal \( S \) [%] (Fig. 2-3) with \( A, B, C, D, E \) and \( k \) as fit parameters. We chose this
function for its flexible structure and because the observed calibration values are very well
approximated. Eq. 2-1 is not based on physical reasoning and many different combinations of
parameter values describe the observed data with the same quality.

The relative signals of the calibrations between 5 and 15 °C were almost identical. A
substantial difference in the calibration was only observed at 22 °C. In the following analysis
of the method’s accuracy; we use the data obtained at 5 to 15 °C. The inset of Fig. 2-3 shows
the effect of the difference in the signals on the velocities. Eq. 2-1 was fitted to the results
recorded at 7 °C. The actual velocities are in good agreement with the calculated ones. The
error bars show the uncertainty of the velocities \( \Delta u(S) \) estimated by

\[
\Delta u = \frac{du(S)}{dS} \times \sigma_S \tag{2-2}
\]
Fig. 2-3: Calibration curves of a sensor at different temperatures. The inset compares the applied velocities to the velocities calculated from the calibration at 7 °C. Error bars indicate the deviations estimated from the sensitivity of the calibration curve and the standard deviation calculated from the signals recorded at 5, 7, 10 and 15 °C.

using the local sensitivity of the calibration function $\frac{du(S)}{dS}$ and the standard deviation $\sigma_s$ of the relative signals recorded between 5 and 15 °C. The error is small for slow flow, but at a velocity of 9 mm s$^{-1}$ the relative error exceeds 10%. Due to the decreasing sensitivity of the sensor for increasing velocities, the uncertainty increases with the flow.

A calibration performed at a reservoir pressure of 0.5 MPa is compared with the calibrations performed at 0.4, 0.3 and 0.2 MPa. Fig. 2-4 shows that, although the absolute signals differ from each other (see inset), the relative signals are close to the 1:1 line, indicating almost identical signals. Thus, a calibration recorded in the laboratory for a reservoir pressure of e.g. 0.2 MPa can be used for in situ measurements at up to 30 m depth since the relative sensor signal does not depend on the pressure in the reservoir for at least up to 0.5 MPa.
Fig. 2-4: Influence of reservoir pressure on the signals. The relative signals recorded at different reservoir pressures are compared with those recorded at 0.5 MPa. The solid line represents the 1:1 relation. Although the absolute signals increase with increasing pressure (inset) the relative signals agree very well with each other.

Both tests show that the fitting parameters are independent of pressure and temperature in the range relevant for our in situ measurements. The calibration curve varies only between sensors. The 90 % response time varied from 8 to 15 s, depending on the individual sensor.

The spatial resolution of the sensor is not well defined, since it depends upon the size of the diffusion sphere of the tracer gas, which is affected by the flow of the surrounding medium. However, a rough estimation can be performed based on the size of the tracer gas sphere under stagnant conditions. According to Crank (1983) the steady state concentration $C(r)$ at a given distance $r$ of such a gas sphere can be calculated as

\[
C(r) = C_\infty + (C_R - C_\infty) \frac{R}{r}
\]  

(2-3)
assuming that the tracer is diffusing from a sphere equal to that of the reservoir membrane with a radius $R$. $C_\infty$ is the tracer concentration at infinite distance (in our case, $C_\infty = 0$). The radius $r$, where the concentration is still 10% of the maximum concentration at the sensor tip is 10 times the tip radius which is typically 7.5 to 15 $\mu$m. Consequently, $r$ is between 75 and 150 $\mu$m depending on the size of the sensor. Nevertheless, the size of the diffusion sphere decreases dramatically at the presence of even small flow velocities in the surrounding media, and the spatial resolution can be assumed to be much higher if the water is flowing. Therefore we recommend the use of Eq. 2-3 as a worst case estimate.

2.3.2 Angular dependence

The dependence on angle ($\alpha$) of the flow sensor signal $S(u, \alpha)$ followed an empirical sinusoidal relationship

$$S(u, \alpha) = O(u) + (m * u + t) * \sin(\alpha + \beta).$$  \hspace{1cm} (2-4)

where $m$, $t$ and $\beta$ are fit parameters independent of $u$. Fig. 5 compares experimental sensor signals to functions of Eq. 2-4, which were fitted to the measured signals. As is obvious from Fig. 5, the fit parameter $O(u)$ depends on the velocity.

Since we have a formal description of the signal dependence on flow direction (second term in Eq. 2-4) and a unidirectional calibration curve $O(u)$ (first term in Eq. 2-4), we can calculate the velocity in any given situation as long as we know the flow direction $\alpha$.

For the special case of $\alpha = 0$, Eq. 2-4 reads

$$S(u,0) = O(u) + (m * u + t) * \sin(\beta).$$  \hspace{1cm} (2-5)

By combining Eqs. 2-4 and 2-5, the $\alpha$-independent term $O(u)$ is eliminated by

$$S(u,0) = S(u,\alpha) - (m * u + t) * (\sin(\alpha + \beta) - \sin(\beta)).$$  \hspace{1cm} (2-6)

This elimination permits us to reduce the amount of velocity steps significantly when we examine the direction dependence of the sensor. Otherwise we would have to determine $O(u)$ for every flow velocity. In order to calculate the flow we use the calibration performed at a current direction of $\alpha = 0$:  

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Fig. 2-5: Angular dependence of the sensor: Relative signals of the flow velocities were recorded at different current angles. The lines represent fitted sinusoidal functions (Eq. 2-4)

\[ u = B \exp(k(S(u,0) - A)) + C S(u,0)^D - E. \]  

(2-7)

The two unknown variables \( S(u,0) \) and the flow \( u \) can be calculated iteratively using Eqs. 2-6 and 2-7.

The parameters of the calibration curve and the angle dependence are determined from the characterization of the sensor in the laboratory. The flow direction \( \alpha \) has to be determined from an additional measurement (see below). The flow sensor measurement will give us a signal \( S(u, \alpha) \): This value is used in Eq. 2-7 as an initial estimate for \( S(u,0) \). The resulting \( u \) is used in Eq. 2-6 in order to calculate an improved estimate of \( S(u,0) \). This process is repeated until the difference in the successively calculated velocities \( u \) changes less than a given value (here \( 10^{-7} \) mm/s).
Fig 2-6: In situ profile recorded in Lake Alpnach on 13 May 2005. It reflects the transition between the linear boundary layer (squares) and the logarithmic boundary layer (diamonds) at approximately 8 mm above the sediment. The bars represent the standard deviations of the velocity due to flow fluctuations during the 90 s recording time and do not reflect measurement errors. The inset shows a detail of the raw data plotted against the distance covered by the sensor. The sediment surface was detected as the point where the kink in the signal was observed. The signal value at the kink was taken as the zero flow reading.

2.3.3 In-situ measurements in Lake Alpnach

The inset of Fig. 2-6 shows the behavior of the raw signal when the sensor crosses the sediment water interface (SWI). It increases strongly as the sensor approaches the sediment. Since the thickness of a Brinkmann layer in the silty sediment is less than 10 µm (Dade et al. 2001) it can be neglected and the velocity can be assumed to be zero at the SWI. The significantly slower increase in the signal as the sensor penetrates the sediment can be attributed to the decreasing porosity and diffusivity with depth (Revsbech et. al. 1998). The
SWI is identified as the position where the kink is observed in the profile. The absolute signal at this position was used as the reference for the calculation of relative signals.

Fig. 2-6 shows a typical velocity profile recorded during the field campaign. The average horizontal velocities are plotted as a function of the distance from the sediment. The velocity fluctuations are described by the standard deviation of horizontal velocities and are represented by error bars. The transition from the linear zone in the VBL (squares) to the logarithmic layer above (diamonds) (Dade et al. 2001) is reflected in the flow profile. The increase in velocity fluctuations with height also reflects the expected behavior of flow at the transition between the VBL and the logarithmic region.

The grey solid line shows the linear fit to the data in the VBL. It is obvious that this region between the SWI and 7.5 mm above the sediment follows the linear form expected in the VBL. The shear stress \( \tau \) in the VBL

\[
\tau = \rho u \frac{du}{dz}
\]  

(2-8)

with the water density \( \rho \) and the temperature-dependent kinematic viscosity \( \nu \) (e.g. Caldwell and Chriss (1979)) can be calculated to \( 1.70 \pm 0.02 \times 10^{-3} \) N m\(^{-2}\). The shear velocity \( u_* \) is defined as

\[
 u_* = \sqrt{\frac{\tau}{\rho}}
\]  

(2-9)

which corresponds to \( 0.13 \pm 0.01 \) cm s\(^{-1}\). This value was used to calculate the logarithmic profile (dark line)

\[
 u(z) = \frac{u_*}{\kappa} \ln \left( \frac{z}{z_0} \right).
\]  

(2-10)

The roughness parameter \( z_0 \) was taken from the intercept of the linear fit as \( z_0 = 0.6 \pm 0.2 \) mm. We used the usual value of the von Karman constant \( \kappa \) of 0.41 (e.g. Chriss and Caldwell 1984b).

To compare the ADV measurements with the results of the flow sensor, we extrapolated the velocity profile as described by the law-of-the-wall (Eq. 2-10) to the height of the measurement volume of the ADV 11 cm above the sediment. The calculated velocity of
1.7 ± 0.1 cm s\(^{-1}\) is in excellent agreement with the measured velocity of 1.6 ± 0.1 cm s\(^{-1}\) considering the fact that we are extrapolating over the range of 10 cm.

The flow sensor works properly only if vertical flows are negligible. The ADV measurements reveal that less than 10% of the recorded vertical velocities exceeded one fifth of the horizontal velocity 11 cm above the sediment. Since we can assume that vertical velocities are even more dampened close to the sediment surface, their influence on the flow sensor signal can be safely ignored.

The current direction was relatively constant with a standard deviation of ± 7° during profile recording. Therefore, we can exclude the existence of depth-dependent flow directions in the investigated scale and conclude that the estimation of the flow direction using the ADV 11 cm above the sediment water interface is sufficient in our case.

### 2.4 Discussion

The new flow sensor was characterized in the laboratory and tested for its applicability at 27 m depth in a lake with very low flow at the sediment water interface. Due to its high sensitivity at low currents and fine spatial resolution, the sensor provides an excellent tool for the study of very slow flow in the ultimate proximity to sediment boundaries of natural water bodies with extremely weak shear. This instrument fills the gap left by other methods like ADV (low spatial resolution) and HWA (higher speed is necessary).

The use of relative signals makes the sensor quite resistant to changes in environmental conditions like pressure and temperature differences between calibration and application. This robustness to intrinsic environmental variabilities facilitates the use of the sensor.

Since the sensor is based on a gas transducer, most lander systems which are equipped with amperometric channels can easily be extended for its use. This enables simultaneous measurements of chemical parameters and flow velocities at high spatial resolution which helps to gain insight into the processes occurring at the sediment water interface.

### 2.5 Comments and Recommendation

Although the relative signals are quite insensitive to changes in the environment, we recommend performing calibrations as close as possible to field conditions. Monitoring flow conditions in the field with additional devices to determine flow direction and vertical flow velocities is also advised as the sensor is also sensitive to vertical velocities. Therefore, it
should only be used in systems with negligible vertical components of flow. The sensor could be used to measure flow velocities in systems that have vertical components as well. However, this would require additional calibrations for several inclination angles of the sensor. The direction dependence of the flow sensor demands a simultaneous monitoring of the flow direction. If the direction is constant or changes very slowly, a measurement of the direction at a fixed position is sufficient. If the current directions change very rapidly, the data must be interpreted more carefully. Another critical point is the decrease in sensitivity of the sensor with increasing flow and large errors have to be taken into account for high velocities. For our sensors the critical threshold was around 12 mm s\(^{-1}\). Under such conditions thermistors offer a preferable option for flow measurements. The technique introduced here performs best at low velocities. In waters with high particle concentrations, particles may adhere to the sensor tip and lead to increased signals and therefore to an underestimation of the flow. If the sensor is applied in such systems, a cleaning system should be integrated in the measurement setup. The strengths of this sensor are the high sensitivity to very low velocities, high spatial resolution and small tip size. It allowed us to perform a detailed study of the structure of the flow profile in the last few mm above the sediment. Provided that adequate calibration procedures are developed, the sensor opens opportunities for many more potential applications such as flow measurements in capillaries or porous media.
2.6 References


Measurements of eddy correlation oxygen fluxes in shallow freshwaters: Towards routine applications and analysis

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Abstract

Benthic fluxes of dissolved oxygen are measured in a shallow reservoir using the eddy correlation technique. Their variation shows the diurnal production-consumption cycle, with daytime oxygen release following the solar radiation trend. The average nighttime uptake of \(-40 \pm 11 \text{ mmol m}^{-2} \text{ d}^{-1}\) is in excellent agreement with the rate of \(-35 \pm 3 \text{ mmol m}^{-2} \text{ d}^{-1}\) derived from sediment oxygen microprofiles. Separating large-scale advective and turbulent fluctuations becomes a crucial and uncertain component of the flux computation and the largest source of error. To compensate for the 2.25 s oxygen sensor response time, the oxygen flux calculations are corrected by only \(~5\%\) using a first-order spectral enhancement. This work demonstrates that only a slightly faster oxygen sensor would be needed to resolve the entire flux spectrum. The 18 hours of data are the first measurements obtained in a freshwater reservoir that captures the diurnal oxygen production-consumption cycle.
3.1 Introduction – Eddy Correlation Method

In lakes and reservoirs, a prime question concerns the flux of dissolved oxygen (DO) through the sediment-water interface. In this study, DO fluxes 15 cm above the sediment are directly measured using the eddy correlation (EC) technique. While this method has been previously implemented for measuring constituent fluxes in the atmosphere (Lee et al., 2004) and heat fluxes in the ocean (Shirasawa et al., 1997), the application of the EC technique for measuring DO fluxes in stratified waters is novel, with only four measurement studies reported so far; three from marine systems (Berg et al., 2003; 2007; Kuwae et al., 2006), and one from a freshwater lake (Brand et al., 2008).

The EC technique has several distinct advantages over traditional DO uptake measurement methods (e.g. in situ chambers, DO sediment microprofiles) (Berg et al., 2003). The most obvious advantage is that the EC technique does not disturb the sediment and natural hydrodynamics. Another important advantage lies in the temporal resolution, as we now have the possibility to measure fluxes continuously on the time scale of minutes.

The EC instrumentation consists of a DO sensor deployed simultaneously with an acoustic Doppler velocity meter (Fig. 3-1 - left) as first proposed and implemented by Berg et al. (2003; 2007). We applied the technique in a shallow, run-of-river reservoir (Lake Wohlen, Switzerland). To our knowledge, the 18 hours of data presented here are the first such measurement obtained in freshwater that captures the diurnal benthic oxygen production-consumption cycle. Given the obvious benefits of the EC technique, we ultimately strive for an easily deployable EC instrument combined with routine protocol for data analysis.

Below, we first describe the EC instrumentation, then the data processing and spectral DO response-time corrections (section 2). The subsequent presentation of the application to the run-of-river reservoir and resulting flux estimates (section 3) includes a discussion of analysis requirements and appropriate data treatment. Finally, we show that our 2.25 s DO sensor response results in only a 5% loss of the DO flux estimates.

3.2 Methods

The DO flux is expressed as \( w \text{DO} \), where \( w \) (vertical velocity) and \( \text{DO} \) (concentration) can be broken down into the mean and fluctuating components, \( w + w' \) and \( \text{DO} + \text{DO}' \) (Reynolds, 1895; Berg et al., 2003). For DO fluxes towards the sediment, the typical DO
fluctuation (DO’) is higher than the mean when the vertical velocity fluctuation (w’) points towards the sediment and visa versa (see Fig. 3-1 – center).

3.2.1 Eddy Correlation Device

The EC device consists of a velocimeter (Vector, Nortek, www.nortek-as.com) and a Clark-type oxygen microelectrode from Unisense (www.unisense.com; 90% response time < 0.3 s) that allow simultaneous measurements of near-sediment velocity and DO concentrations (Fig. 3-1 - center). The electronics amplifying the microelectrode signal consist of a precision pico-amplifier in series with a guard circuit. A sampling volume location device (c in Fig. 3-1 – left) is used to position the DO sensor tip (b) close to the velocimeter measurement volume and is removed before deployment.

![Fig. 3-1. Left: Eddy correlation instrument. (a) Three-beam Nortek Vector with (b) Unisense dissolved oxygen (DO) sensor and (c) artificial measurement volume for positioning the DO sensor (removed during deployment). Center: Nine minutes data collected at Lake Wohlen: vertical velocity (top) and DO (bottom). Black lines indicate running averages, grey lines are data (smoothed for clarity). Right: Covariance as a function of shifting DO time series ahead the velocity data series. The maximum negative correlation is ~2.25 s.]

3.2.2 Data Analysis

(i) Time Corrections: The main factor affecting the DO response time is the amplifier response (~2 s), and to a much lesser extent, the travel time (lag) between the DO sensor tip and velocity sampling volume (distance is ~1 cm). Because the DO signal reacts slower than the velocimeter, the DO data series are shifted back in time relative to the velocity series (Fig. 3-1 – right) until the maximum flux (correlation) is obtained. To verify this approach, the cross correlation is calculated to obtain the maximum (negative for consumption, positive for
production) correlation between DO and velocity (Fig. 3-1 – right). Both procedures suggest an ~2.25 s time correction.

The DO spectra and calculated cospectra of $w'$ and DO' are then corrected for the frequency-dependent damping (Eugster and Senn, 1995; Gregg, 1999). Basically, high-frequency DO spectral contributions are “enhanced” to correct for that part of the signal that is lost due to response times. For linear damping, the correction function is

$$S_{DO, \text{corr}}(f) = \left(1 + f^2 \tau^2\right)S_{DO, \text{meas}}.$$

where $S_{DO, \text{corr}}$ ($\mu$M$^2$ s) is the DO power spectrum corrected for response time $\tau$ (s) from the measured $S_{DO, \text{meas}}$, and $f$ is frequency (Hz). The cospectra are enhanced by the same procedure. By integrating the enhanced cospectra, we determined that <5% of the flux signal is lost due to the finite DO sensor response time (Fig. 3-2 – left).

(ii) Eddy flux calculations: The DO fluxes are calculated from raw velocity and DO data using the software package EddyFlux Version 1.3 beta. It uses three independent
methods to remove the means from raw data (mean removal, linear detrending, and filtering by running averaging; see for example Lee et al. (2004)) to extract $w'$ and $DO'$. 

(iii) Sediment flux calculations: Flux estimates were obtained from DO microprofiles (Fig. 3-2 – right) measured in the top few mm of the sediment by a simultaneously deployed lander (Müller et al., 2002). The vertically well-resolved profiles allow to calculate the DO flux at the sediment-water interface from the concentration-depth profile (Berg et al., 1998) and from the vertically integrated DO depletion rate (see Müller et al., 2002).

3.2.3 Study Site and Campaign

The study was conducted at Lake Wohlen, a run-of-river reservoir located on the Aare River (Bern, Switzerland). Lake Wohlen has a surface area of 3.65 km$^2$ and a maximum depth of 20 m. From 5 to 7 September 2006, EC measurements were performed in ~3 m water depth, 15 cm above the sediment with a sampling rate of 32 Hz. The EC device was deployed on a rigid aluminum tripod with two legs orthogonal to the main flow direction and the third leg downstream from the sensors. Our two deployments spanned an ~38-hr time range: deployment 1 from 5 Sept 14:00 to 6 Sept 06:00 and deployment 2 from 6 Sept 09:30 to 7 Sept 02:00, 2006 (CEST). The oxygen sensor was calibrated in the laboratory before and after the deployment and showed negligible drift.

3.3 Results and Discussion

In this section, we firstly present the eddy flux results. Next, we discuss the determination of the running average window size. We then analyze the spectral contribution of the eddies. Using the DO spectra, we illustrate that there is no clear spectral gap between large-scale advective fluxes and the smaller scale turbulent fluxes, emphasizing the importance of appropriate mean removal determine the fluctuations. Finally, we address DO response time compensation.

3.3.1 Overview of Flux Estimates

Figures 3-3A, B, and C show the measured horizontal velocity, vertical velocity and DO values used for the flux estimates. Fig. 3-3D gives individual fluxes calculated from ~0.25 to 1 hr time intervals (depending on quality of time series). The dark-grey line on Fig. 3-3D (right-axis) shows the global radiation (data: MeteoSwiss). Parts of the time series were omitted from the analysis shown on Fig. 3-3D due to corrupted data, probably caused by floating debris or electrical interference.
The DO fluxes convincingly demonstrate the effect of photosynthesis on the benthic DO exchange. The fluxes are high during the day, with peak releases of $54 \pm 13$ (SD) mmol m$^{-2}$ d$^{-1}$ on 5 Sept (clear sky) and $36 \pm 22$ (SD) mmol m$^{-2}$ d$^{-1}$ on 6 Sept (cloudy sky), following the trend in global solar radiation. Nighttime DO uptake varies from $-47 \pm 14$ (SD) mmol m$^{-2}$ d$^{-1}$ during the first night, to $-34 \pm 6$ (SD) mmol m$^{-2}$ d$^{-1}$ during the second night (measurement locations were about 3 meters apart), with the overall average nighttime flux for both nights of $-40 \pm 11$ (SD) mmol m$^{-2}$ d$^{-1}$. This value is in very good agreement with the $-35 \pm 3$ (SD) mmol m$^{-2}$ d$^{-1}$ estimated from the nearby lander DO microprofiles (Fig. 3-2 – right).

### 3.3.2 Sensitivity of Spectral Flux Contributions

When extracting the fluctuations using running mean, it is an intrinsic difficulty to determine the appropriate averaging window length. The number of data points used must be long enough to encompass all of the flux contributing eddy sizes, but not too long as to include artifacts such as sensor drift or non-turbulent (reversible) changes. Fig. 3-4 (left)
illustrates the sensitivity of the flux estimations as a function of averaging window size. The averaging window analysis is initiated with a flux calculation based on a narrow window for the running averages (1 data point gives a flux of zero on Fig. 3-4 (left) and proceeds from right to left along horizontal axis as averaging window size increases). The averaging window is expanded step-wise and the flux is recalculated. By increasing the averaging window size and repeating the flux calculation, the outcome is basically the cumulative addition of the value of the spectral contributions. For comparison, the cumulative cospectra of \( w' \) and DO' are calculated. As shown in Fig. 3-4 (left), the calculated cumulative cospectra yield the same flux as the averaging window-size analysis.

The results of the two described analyses indicate that both methods can be used to determine the frequency cutoffs for the eddy spectral contributions. As shown on Fig. 3-4 (left), fluxes reach nearly their maxima at \( \sim 17 \times 10^{-3} \) Hz (\( \sim 60 \) s) during the day and \( \sim 4 \times 10^{-3} \) Hz (\( \sim 250 \) s) at night, before they level off (indicated by solid vertical lines in Fig. 3-4). At the other end of the spectrum, the maximum frequency of eddies contributing to the flux appears to be at 0.2 to 0.3 Hz (\( \sim 3 \) to 5 s; point at which curve begins to diverge from horizontal) for both methods and does not vary significantly between daytime and nighttime.

In the so-called “variance-preserving” plot of the DO spectrum (frequency \( \times S_{DO} \), where \( S_{DO} \) is the DO power spectrum), the area under the curve is proportional to the contribution of the total DO variance (Gregg, 1999). The variance-preserving plot on Figures 4 (right) indicate from which spectral range most of the DO contributions are to be expected for both the daytime and nighttime data (grey line shows corrected spectra). The solid vertical lines correspond with the minimum frequency of spectral contributions shown in Fig. 3-4 (left). At the lower frequencies (\( < 1 \times 10^{-2} \) Hz), the effects of basin-scale waves (both surface and internal seiche) can be seen, which have a frequency around \( \sim 5 \times 10^{-4} \) to \( 5 \times 10^{-3} \) Hz (\( \sim 3 \) to 33 minutes) in Lake Wohlen (from thermistor data, not shown).

From Fig. 3-4, it is not always clear where to place the low frequency cutoff when defining the averaging window, as there is no obvious spectral gap between the large scale, advective contributions, and smaller-scale eddies. This is particularly visible from the daytime variance-preserving spectral plot. We view this as the biggest challenge in eddy correlation flux extractions and therefore conclude that the largest uncertainties associated with the technique are rooted here.
Fig. 3-4: Left: Normalized DO fluxes for ~30-min long time series (points) during day- and nighttime, as estimated for different lengths of the averaging window. These DO fluxes compare well to those calculated from the cumulative cospectra (solid line). Vertical lines represent estimates of low frequency cutoffs for turbulent contributions. Figure is read from right- to left-side along x-axis. Right: Variance-preserving DO spectrum (frequency x spectral density (SDO)) for entire day- and nighttime data series. The grey curve represents the variance-preserving spectra corrected for response time of DO sensor. Basin-scale waves (both surface and internal) have a frequency of ~5 x 10^{-4} to 5 x 10^{-3} Hz (~3 to 33 minutes) in Lake Wohlen.

### 3.3.3 Time Scales

The eddy time scales contributing to the signal range from ~3 to 60 s during the day and from ~3 to 250 s at night. During the day, Lake Wohlen may slightly stratify and suppress larger eddies. However, at night the water column is completely well-mixed, resulting in the maximum eddy size being limited only by the depth of the water.

For comparison, the smallest expected eddy size can be estimated by the Kolmogorov length scale, $L_K = \left(\frac{\nu^3}{\varepsilon}\right)^{\frac{1}{4}}$. Using a kinematic viscosity of $\nu = 1.5 \times 10^{-6}$ m$^2$ s$^{-1}$ and a turbulent dissipation estimate of $\varepsilon = 1 \times 10^{-7}$ W kg$^{-1}$ yields minimum eddy sizes $L_K$ in the range of ~2 mm with a minimum time scale $\left(\frac{L_K^2}{\varepsilon}\right)^{\frac{1}{3}}$ of ~4 s (Wüest and Lorke, 2003).

### 3.3.4 Noise

Fig. 3-4 (right) indicates peaks at around 1 Hz for DO. Higher frequency noise is present in both the velocity and DO data. It is suspected that this noise may be caused by the ~1 Hz internal compass readings (ENU coordinates), which will be disabled during future...
measurements. However, as expected, the noise of w and DO are uncorrelated and do not significantly contribute to the fluxes.

3.4 Summary

The eddy correlation dissolved oxygen (DO) fluxes (-40 ± 11 mmol m⁻² d⁻¹) compare well with the lander microprofile DO fluxes (-35 ± 3 mmol m⁻² d⁻¹). To determine the most accurate eddy correlation fluxes, it was necessary to account for the DO response time by both (i) shifting the DO data back in time, and (ii) enhancing the damped spectral contributions due to the ~2 s response time of our amplifier by a first order linear correction. We found that shifting the DO time series 2.25 s backwards maximized the fluxes, and that only a slightly faster sensor would be needed to obtain the entire signal. However, the entire signal can also be closely estimated by enhancing the spectra theoretically.

Selection of the appropriate time-averaging window for the running mean must be done to ensure that all of the turbulent flux contributions are included, and all reversible (e.g. basin scale internal waves) motions are excluded. However, the absence of distinct spectral gaps makes this task more uncertain, and leads to some overlap (and hence uncertainties) from these two categories of contributions. For the data presented here, we estimate that the spectral-gap uncertainties potentially cause the largest errors in flux estimates, possibly up to 10% based on sensitivity analyses and how well the spectral gap can be resolved. We have further shown that even for the same locations, the length of the averaging window can substantially vary between day- and nighttime. The different averaging time scales are associated with changing spectral contributions related to the water column stability (i.e. larger eddies are suppressed during daytime stratification).

Overall, the results show that the eddy correlation technique is a promising method for determining DO fluxes in natural water bodies. With this unique data set collected over ~38-hr, we were able to demonstrate the diurnal benthic DO production-consumption cycle. The DO production fluxes relate well with the nearby measured solar radiation while nighttime consumption was relatively constant and agrees with results obtained from DO sediment microprofiles. With the eddy correlation technique, we are now able to resolve the high temporal variability (minutes) of the sediment DO fluxes, which until now could only be resolved on the time scale of hours to days using traditional measurement techniques. Furthermore, the measurement and analysis of eddy correlation data have the added advantage of resolving many bottom-boundary layer hydrodynamic properties.
The eddy correlation technique is limited to constituents that can be measured with relatively fast sensors. However, in this work we have demonstrated that sensors with response times of (several) seconds could potentially be used. Currently, instrument deployment lengths are limited to internal memory and battery capacities, and DO sensor fouling considerations.

Taken together, the analysis described here allows a controlled and consistent protocol to estimate the DO flux, spectral contributions and potential errors. The procedure is still in the early stages of application in aquatic systems, and many more data must be collected and analyzed to reveal the full capability of this new technique.
3.5 References


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Intermittent oxygen flux from the interior into the bottom boundary of lakes as observed by eddy correlation

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Abstract

Turbulent oxygen transport from the overlying stratified water column into the bottom boundary layer (BBL) on the slope of a mid-sized lake was investigated using the eddy correlation (EC) technique. The seiche-induced oscillatory flow of the BBL, with a period of ~1 day, was identified as the mechanism driving turbulent oxygen transport. Sporadic short-term EC vertical oxygen fluxes exceeded the sedimentary oxygen uptake of 13 ± 2 mmol m$^{-2}$ d$^{-1}$ calculated from sediment oxygen profiles by more than a factor of 3. The average EC flux over half of a seiching period was 9.2 mmol m$^{-2}$ d$^{-1}$ similar in range as the flux into the sediment; however, these two fluxes do not have to coincide spatially and temporally. The EC oxygen flux was only significant when the deep basin-scale currents exceeded a velocity of 2 cm s$^{-1}$ and the corresponding bottom shear was sufficient to produce active turbulence. Below this threshold, decaying turbulence resulted in oxygen fluxes lower than 3.5 mmol m$^{-2}$ d$^{-1}$, with an even lower average flux of 0.8 mmol m$^{-2}$ d$^{-1}$ observed during reversals of the seiching. At low velocities, the weak turbulence is insufficient to transport dissolved oxygen through the stratified top of the BBL (stability $N^2 \approx 2.4 \times 10^{-4}$ s$^{-2}$), even though turbulence was found in the inertial subrange and periodical bottom convective mixing was still present. The EC technique provided valuable data on the temporal variability of oxygen transport related to the BBL hydrodynamics and flux pathways.
4.1 Introduction

The eddy correlation (EC) technique is a well-established method to determine atmospheric fluxes of water vapor, carbon dioxide, nitrous oxide and others between water and air or soil and air (e.g., Famulari et al. 2004; Lee et al. 2004). This method is based on the simultaneous measurements of the fluctuations of turbulent velocity ($u'$) and concentration ($c'$): The product of both variations results in the momentary turbulent fluxes of a substance in horizontal and vertical direction ($u'c'$ and $w'c'$), respectively. The net turbulent flux is obtained by averaging this fluctuation product over a given time span. Berg et al. (2003) were the first to determine sedimentary oxygen uptake in aquatic systems with an EC approach in fluvial and coastal marine sites. The resulting oxygen flux estimates agreed well with those determined with traditional techniques, like flux chambers and the evaluation of oxygen profiles in the sediment. Kuwae et al. (2006) recorded time series between 12 and 40 minutes over a tidal mudflat during day- and nighttime and showed that the EC method could also be used to investigate photosynthesis. McGinnis et al. (2008) recorded the diurnal cycle of photosynthesis and respiration in a run-of-the-river hydropower reservoir in Switzerland. These studies revealed the excellent potential of the EC technique for quantifying solute dynamics under turbulent conditions.

Here we use the EC technique to examine oxygen flux in a turbulent system that demonstrates strong intermittency. Specifically, we examined the bottom boundary layer (BBL) of lakes where there is strong variability due to sporadic energy input. Lake Alpnach, a pre-alpine lake with regular, non-steady basin-scale deep currents was chosen as the study site, because convective winds from the surrounding mountains force the lake-internal seiching which generates regular BBL dynamics (Gloor et al. 2000). Two different seiche modes were observed in Lake Alpnach: the first horizontal, first vertical seiche mode with a typical period of 8 to 12 h and the first horizontal second vertical seiche mode with a period of approximately 1 day (Münnich et al. 1992).

BBLs influence the exchange of momentum, heat, solutes, and particles with bottom sediments and the turbulent dissipation of energy from currents and waves (Wüest and Lorke 2003). In addition, BBL dynamics affect bottom regions which provide habitat for benthic microorganisms and invertebrates and are sites of biogeochemical activity in lakes (Maerki et al. 2006) and oceans (Boudreau and Jørgensen 2001). It is, therefore, important to explore the
From a microscale perspective, it is already known that BBL turbulence near the bottom has been shown to influence sediment oxygen uptake (Lorke et al. 2003) since the thickness of the diffusive boundary layer (DBL) correlates with shear and physically limits oxygen transport at the sediment water interface (Jørgensen and Marais 1990). Here we explore the link between turbulent dynamics and solute exchange at larger scales within the BBL (typically up to several meters above the sediment surface). We also investigate the required conditions for applying the EC technique under non-steady conditions, caused by seiches typical of the near bottom environment.

4.2 Methods

4.2.1 Study site

Measurements were conducted at 27 m water depth over the sloping sediment on the south-east side of Lake Alpnach (46° 57' 51" N, 8° 18' 13" E) starting on 14 September 2005 at 16:00 h and ending 15 September 2005 at 04:00 h. The lake is a medium-sized mesotrophic sub-basin of Lake Lucerne in Central Switzerland. It has an elliptical shape of approximately 5 by 1.5 km, a surface area of 4.2 km², and a maximum depth of 34 m. Lake Alpnach is separated by a 3 m deep sill from the rest of Lake Lucerne. For most of the time, inflowing water merges into the surface layer, as it consists of warm epilimnetic water from an upstream lake. However, the measurements were conducted three weeks after a flood event discharging warm and highly turbid water into the hypolimnion of Lake Alpnach.

4.2.2 Experimental setup

The experimental arrangement consisted of three devices. A densely spaced vertical thermistor array was used for measuring continuous temperature profiles 4 m above the bottom sediments in order to observe the macroscopic development of the BBL at the slope. Sixteen TR-1000 thermistors (RBR Oceanographic Instrumentation, Canada) were fixed on the tripod with 0.25 m spacing. Temperature was logged every 3 seconds. Prior to the measurements, the sensors were simultaneously calibrated in a 7025 Benchtop Calibration Bath (Hart Scientific, USA), which reduced the sensor-to-sensor differences to \( \sim 1 \times 10^{-3} ^\circ C \) (Lorke et al. 2005).
Sedimentary oxygen consumption rates were calculated from oxygen microprofiles recorded in the top few mm of the sediment using the lander system LISA (Müller et al. 2002) equipped with two Clarke-type oxygen electrodes (Unisense, Denmark). Their output signals were processed with a custom built electronics package consisting of a low-noise current-to-voltage converter with a precision instrumentation amplifier in series with a guard circuit. The signal was filtered with a 50 Hz low-pass filter. The profiles were recorded with 0.1 mm vertical resolution and 300 data points were acquired at 3 Hz for each vertical sensor position. The electrodes were calibrated by Winkler titration, performed on samples taken at 27 m depth using a Niskin bottle. The fluxes were used for comparison with the results provided from the EC technique.

A fast-response miniature Clark-type oxygen microsensor with 10 µm tip diameter (Ox-10 fast, Unisense, Denmark; < 0.3 s for 90% signal response), was mounted next to an acoustic Doppler velocimeter (ADV, Vector, Nortek, Norway) for the EC measurements. The tip of the oxygen probe was positioned approximately 2 mm from the measurement volume of the ADV installed 11 cm above the sediment. Signal acquisition and amplification were performed at 8 Hz using the same electronics as in the lander system but without a low-pass filter. The setup was installed on a tripod and was deployed in the main current direction to avoid flow obstruction by the legs of the tripod.

4.2.3 Flux calculation

Vertical velocities and oxygen concentrations were time lag corrected. The cross correlation between oxygen and vertical velocities showed the typical maxima at ~2 to ~3 s. This inferred time lag was then used for shifting the data series accordingly. Thereafter, the time series were subdivided into 15 minutes subsets. Fluctuations of velocities and concentrations and their standard deviations were calculated after linear detrending.

Sediment oxygen consumption was obtained from sediment oxygen microprofiles, and were calculated using the software PROFILE (Berg et al. 1998).

4.2.4 Spectral analysis

Power spectral densities of vertical velocities ($S_w$) and co-spectral densities ($C_{owc}$) were calculated using the Welch (1967) method. The resulting spectra, which consisted of $N = f \times T$ (frequency × period length) data points were subdivided into $A_{Nr} = 50$ intervals.
The bandwidths $b_k$ were calculated using $b_k = \exp\left(\frac{k \times \ln(N)}{A - N r}\right)$ for each interval number $k$ (from 1 to 50). The spectral values were averaged over the resulting intervals and plotted against the central frequencies (Kaimal and Gaynor, 1983).

For detailed analysis, the $C_{wc}(f)$ of the vertical velocity ($w$) and oxygen concentration ($c$) were subdivided into positive and negative contributions prior to band averaging. Since the sum of the two subdivided and band-averaged co-spectral densities is identical to the band-averaged full co-spectral densities, we concluded that the data separation was logically consistent.

The normalized ogives

$$Og(f) = \frac{\int_{f_{\min}}^{f_{\max}} C_{wc}(f) df}{\int_{f_{\min}}^{f_{\max}} C_{wc}(f) df}$$

(4-1)

were calculated from the co-spectral densities without prior band-averaging. The ogive is a measure of the relative contribution of the frequencies above $f$ (Oncley et al. 1996) to the covariance $\overline{wc}$ between $w$ and $c$ (Stull 1988). This integral term in the denominator also represents the average of the solute flux in the investigated time interval. If $f_{\min}$ is small enough to catch all relevant fluctuations that contribute to the flux, the ogive should reach the plateau value of 1 as $f$ decreases towards $f_{\min}$ (Desjardins et al. 1989).
Fig. 4-1: Baroclinic structure of the BBL in Lake Alpnach during the measurements. (a) Schematic seiching motion of the BBL as observed from the temperature data. The vertical solid line represents the thermistor chain mounted in the south west (SW) of the basin. (b) Temperature (°C) development during the 12-hour measurement from the sediment surface to 4 m above the ground. (c) 5-minute averaged vertical temperature profiles at 1, 6, and 10 h of the measurement. The BBL has its highest extent over the north east (NE) slope of Lake Alpnach during the first hour of measurement. The reversal of the seiche after the movement towards the SW with the highest extent over the south west margin can be observed between the 6th and 7th hour. After, the BBL moves back towards the north east.
Fig. 4-2: Time series of 15 min averages of (a) absolute horizontal velocity at 0.11 m height above the sediment. The right y-axis denotes the corresponding Reynolds numbers calculated for a length scale equal the distance of 0.11 m from the sediment. The horizontal line marks the threshold above which turbulent oxygen transport was observed. The arrow to the right indicates flow direction to SW, the arrow to the left indicates flow direction to NE. (b) Standard deviation of vertical velocity and (c) vertical oxygen flux determined by the eddy correlation technique (bars) in comparison with the sedimentary oxygen consumption rate (solid line) and its uncertainty (dotted line). The arrows in panel (c) mark highly positive fluxes that were identified as artifacts of the measurement during transition periods from low to highly turbulent regimes. The roman numerals I to VII mark different periods of turbulent mixing as discussed in the text.

4.3 Results

The following section demonstrates that the turbulent oxygen flux is highly variable in time as a consequence of the internal seiching. Therefore we start with a short description of the BBL dynamics, before we present the observed turbulent fluxes and their spectral characteristics.
Fig. 4-3: (a, b): 10-minute time series of vertical velocity. (c,d): corresponding oxygen concentration fluctuations. (e, f): integrated turbulent oxygen flux from 0 to 10 minutes. (a, c and e) for time t = 7.5 h (Fig 2; turbulent flux); and (b, d and f) for time t = 6.25 h (Fig 2; no significant flux).

4.3.1 BBL dynamics

The oscillatory motions and the variable extent of the well-mixed BBL reflect the seiching of Lake Alpnach during the investigated time span (Fig. 4-1). The high temperatures at the bottom of the lake were the consequence of a flood event which flushed the entire basin with warm, particle-rich river water three weeks prior to the measurements. The stratified upper-boundary of the BBL was close to the sediment at the beginning of the campaign (Fig. 4-1 b and c). It ascended until the well-mixed part of the BBL reached a maximum height of 1.5 m
above the bottom around $t \approx 6.5$ h (Fig. 4-1b). During the same period, the vertical velocity decreased. After, the current changed direction at $t \approx 6.75$ h and accelerated (Fig. 4-2a). Simultaneously, the well-mixed portion of the BBL decreased until it vanished almost completely at $t \approx 10$ h (Fig. 4-1b). This oscillating motion of the BBL along the SW-NE axis is illustrated in Fig. 4-1a. Obviously, we observed approximately half of the first horizontal, second vertical mode seiche period (~1 day) during the 12 h campaign (Münnich et al. 1992).

Tab. 4-1: Time periods classified by different conditions of turbulent transport. The temperature gradient was calculated for the lowest 0.5 m above the sediment. The standard deviations of the vertical velocities were used as an indicator for the turbulence level. Periods during which turbulence decays steadily are marked with *.

<table>
<thead>
<tr>
<th>Section</th>
<th>Time (h)</th>
<th>Temperature gradient ($^\circ$C m$^{-1}$)</th>
<th>Vertical velocity fluctuations (mm s$^{-1}$)</th>
<th>Oxygen flux (mmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0 to 0.75</td>
<td>0.306 ± 0.143</td>
<td>0.5 ± 0.2</td>
<td>-0.8 ± 3.4</td>
</tr>
<tr>
<td>II</td>
<td>1 to 3.75</td>
<td>0.242 ± 0.147</td>
<td>1.0 ± 0.3</td>
<td>-19.5 ± 12.1</td>
</tr>
<tr>
<td>III</td>
<td>4 to 5.5</td>
<td>0.027 ± 0.044</td>
<td>0.6 ± 0.2*</td>
<td>-0.3 ± 2.3</td>
</tr>
<tr>
<td>IV</td>
<td>5.75 to 6.75</td>
<td>-0.001 ± 0.005</td>
<td>0.5 ± 0.2</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>V</td>
<td>7 to 8.5</td>
<td>0.059 ± 0.040</td>
<td>1.3 ± 0.3</td>
<td>-9.3 ± 5.2</td>
</tr>
<tr>
<td>VI</td>
<td>8.75 to 9.5</td>
<td>0.058 ± 0.021</td>
<td>0.9 ± 0.3*</td>
<td>-3.5 ± 2.6</td>
</tr>
<tr>
<td>VII</td>
<td>9.75 to 11.75</td>
<td>0.293 ± 0.130</td>
<td>1.1 ± 0.3</td>
<td>-13.9 ± 6.8</td>
</tr>
</tbody>
</table>

4.3.2 Turbulent oxygen flux

The turbulent oxygen flux was extremely variable over the measurement period (Fig. 4-2c). Intervals with no significant flux were observed as well as periods with fluxes exceeding 40 mmol m$^{-2}$ d$^{-1}$. This was 3 times the sediment consumption of 13 ± 2 mmol m$^{-2}$ d$^{-1}$ (mean ± standard deviation) as determined from seven microsensor oxygen profiles (data not provided). Vertical turbulent oxygen transport in the range between 3.5 mmol m$^{-2}$ d$^{-1}$ and 45 mmol m$^{-2}$ d$^{-1}$ were only observed when the turbulence level (indicated by the standard deviation of the vertical velocities in Fig. 4-2b) was sufficiently high and when the mean horizontal velocity was faster than ~2 cm s$^{-1}$.

The difference in turbulence between periods with and without measurable turbulent fluxes can be readily seen by comparing recorded time series. During conditions with high turbulent flux, the vertical velocity fluctuations exceeded 2 mm s$^{-1}$ and oxygen fluctuations were larger than 1.5 mmol m$^{-3}$ (Fig. 4-3a), yielding a cumulative flux of 14 mmol m$^{-2}$ d$^{-1}$. In
Fig. 4-4: Spectral analysis of a time interval from period V during which significant turbulent transport is observed. (a) Power spectral density $S_w$ of vertical velocity $w$. The black line indicates the slope of the inertial range. (b) Co-spectral densities of $w$ and oxygen concentration $c$. (c) Ogive calculated from the co-spectral densities, and (d) Plot of the split co-spectral densities (circles: contribution to the flux towards the sediment, triangles: contributions to the flux away from the sediment).

In situations without significant turbulent flux, the vertical fluctuations rarely exceeded 1 mm s$^{-1}$ and concentration fluctuations were far below 0.05 mmol m$^{-3}$ (Fig. 4-3b). The extremely low concentration fluctuations also indicate that the oxygen concentration gradient was close to zero. This is in agreement with the results of the temperature measurements, which indicate a well-mixed BBL at $t = 6.25$ h.

We subdivided the EC time series into seven periods which differ in flux, turbulence level and stratification (Fig. 4-2 and Table 4-1). Significant turbulent oxygen fluxes were observed in the periods II, V, and VII, where vertical velocity fluctuations around 1 mm s$^{-1}$ and temperature gradients above 0.03°C m$^{-1}$ were simultaneously present; whereas there was no measurable turbulent flux during the periods I, III, and IV when horizontal velocities were below 2 cm s$^{-1}$. During period VI, when the average horizontal velocity just drops below 2 cm s$^{-1}$, the oxygen transport to the sediment simultaneously decreased with the decaying
turbulence. The flux during this period was comparably low (approximately 3.5 mmol m$^{-2}$ d$^{-1}$) even though a relatively strong temperature gradient also suggests a pronounced oxygen gradient. Overall, we observed that significant fluxes only occurred when the standard deviation of the vertical velocity was at least 1 mm s$^{-1}$, whereas no significant fluxes were detected when the standard deviation was less than 0.5 mm s$^{-1}$.

### 4.3.3 Spectral content of the turbulent fluxes

In order to investigate the characteristics of the turbulent oxygen fluxes, we compared the $S_w$ and $C_{ow_c}$ for the period IV without significant flux (Fig. 4-5) with those of period V in which a larger flux was observed (Fig. 4-4). $S_w$ of period V (Fig. 4-4a) contained more energy than in period IV (Fig. 4-5a). In period V, the inertial dissipation range extended between $f \approx 0.02$ Hz and $f \approx 0.15$ Hz. The ogive (Fig. 4-4c) and $C_{ow_c}$ (Fig. 4-4b) show that only 25% of the flux was driven by frequencies in the inertial dissipation range whereas lower frequencies characteristic for active turbulence were responsible for 75% of the flux. The plot of the
Fig. 4-6: Vertical velocities during transitions between periods with high and low turbulence. (a) Almost complete decay of turbulence at \( t = 5 \) h (Fig. 4-2) during the 15 min data series. (b) Starting production of turbulent kinetic energy at \( t = 6.25 \) h (Fig. 4-2). The arrows indicate the distinct transition from laminar to turbulent flow.

Subdivided \( C_{ow} \) (Fig. 4-4d) shows that positive and negative contributions to the flux balanced above \( f \approx 0.15 \) Hz. This frequency also denotes the start of the viscous dissipation range which is indicated by the characteristic drop-off in \( S_w \) (Gibson and Schwarz, 1963). Fluctuations towards the sediment prevailed only at lower frequencies.

The inertial subrange of \( S_w \) in period IV (Fig. 4-5a) extended over frequencies between \( f \approx 0.01 \) Hz and \( f \approx 0.05 \) Hz followed by the viscous dissipation range at higher frequencies. \( C_{ow} \) showed no contributions to the flux for frequencies above 0.003 Hz (Fig. 4-5b). Positive and negative contributions balanced mainly in the considered frequency range (Fig. 4-5d). The ogive (Fig. 4-5c) does not increase as steady as the one calculated for period V. This was typical for ogives calculated for periods with no observable turbulent fluxes.

The stepwise change from low to high vertical velocity fluctuations marked the inception of the highly turbulent regime (Fig. 4-6b), whereas the transition from higher down to lower turbulence levels was rather smooth (Fig. 4-6a). The decay of turbulence occurred when horizontal velocities fell below a threshold value around 2 cm s\(^{-1}\). This could be visualized in spectra calculated for subsequent time steps during such a period of decaying
Fig. 4-7: Power spectral density of vertical velocity fluctuations $S_w$ at $t = 4.0$ h (open circles) and 4.5 h (open triangles) during a period of decaying turbulence. The solid line shows the slope of the inertial subrange.

Turbulence which nicely demonstrated the gradual loss of turbulent kinetic energy (Fig. 4-7).

The $S_w$ calculated at $t = 4$ h, however, still revealed a significant amount of turbulent kinetic energy. The inertial subrange was found between $f \approx 0.02$ Hz and $f \approx 0.15$ Hz. In the spectrum at $t = 4.5$ h, the inertial subrange shifted towards lower frequencies between $f \approx 0.015$ Hz and $f \approx 0.07$ Hz and a significantly lower energy level was observed (Fig. 4-7). The decay of turbulence was also reflected in the standard deviations of the vertical fluctuations from 1 mm s$^{-1}$ to 0.75 mm s$^{-1}$ (Fig. 4-1). Such examples of decaying turbulence were observed in the periods III and VI.

### 4.4 Discussion

An oxygen uptake of $13 \pm 2$ mmol m$^{-2}$ d$^{-1}$ calculated from sediment profiles is typical for Lake Alpnach and lies within the range of $\sim 6$ to $\sim 13.2$ mmol m$^{-2}$ d$^{-1}$ determined in a previous study (Lorke et al. 2003). In contrast, EC measurements in Lake Alpnach have shown that the turbulent transport at the BBL did not always match the sediment oxygen consumption rate determined from the sediment micro profiles and was highly intermittent.
4.4.1 Reynolds number as an indicator for turbulent transport

Turbulent oxygen transport was only observed for horizontal velocities higher than 2 cm s\(^{-1}\). In addition, the transition from a low level of turbulence to a high level at the end of period IV occurs almost instantaneously (Fig. 4-6b). Both observations suggest the existence of a threshold for the production of turbulence. If no density gradients are present and the Reynolds numbers (\( \text{Re} = \frac{\text{Lu}}{\nu} \), where \( L \) is the characteristic length scale which corresponds to the ADV measurement volume height above the sediment \( L = z_{\text{meas}} = 0.11 \text{ m} \) and \( \nu \) is the kinematic viscosity) exceeds a critical value \( \text{Re}_c \), the shear must only overcome the viscous forces in order to generate turbulence. In this context, turbulent oxygen flux was only observed for Reynolds numbers above \( \sim 1700 \) (Fig. 4-2a). This value is consistent with a critical Reynolds number of \( \sim 1500 \) for the fluid flow of a stationary lower and a moving upper plate at a height \( L \) (Fox et al. 2004), a situation that is similar to the flow dynamics in Lake Alpnach. Therefore, oxygen transport by eddies was only observed if turbulence was produced actively against viscous forces.

4.4.2 Turbulent mixing through the stratified top of the BBL

Another important variable of turbulent transport through the BBL is the height (\( h_{\text{mix}} \)) where shear still produces turbulence, which results in transport between the BBL and stratified lake interior. The temperature gradient of the stratified part of the BBL from the thermistor data ranged between 0.18 and 0.35°C m\(^{-1}\), which corresponds to a stability range of \( N^2 \) between \( 1.6 \times 10^{-4} \) and \( 3.1 \times 10^{-4} \text{ s}^{-2} \). The criterion for the production of active turbulence against a density gradient is given by Stillinger et al. (1983) and has been applied by Wüest and Gloor (1998) to BBLs in lakes:

\[
\varepsilon > C \nu N^2
\]  

(4-2)

where \( C \) is a dimensionless constant in the range between 15 and 25. The dissipation rate \( \varepsilon \) is estimated for BBL turbulence by (Caldwell and Chriss 1979)

\[
\varepsilon = \frac{u^3}{\kappa z}
\]  

(4-3)

where \( \kappa = 0.41 \) is the von Karman constant and \( u^* \) is the shear velocity. Therefore, we find a critical shear velocity \( u^* > \sqrt{20 \nu N^2 \kappa} \) for the production of active turbulence at any elevation.
Fig. 4-8: Mixing height at an average stability $N^2 = 2.4 \times 10^{-4} \text{ s}^{-2}$ of the stratified top of the BBL as a function of the horizontal velocity 0.11 m above the sediment (solid line). Turbulent BBL mixing is shown by the shaded area. The dashed line denotes the mixing height for the critical velocity of 0.02 m s$^{-1}$ below which no shear-induced turbulence was observed.

$z$ above the sediment by combining Eq. 4-2 and 4-3 and using $C = 20$. Consequently, $h_{mix}$ can be calculated as

$$h_{mix} < \frac{u_*^3}{20
u N^2 \kappa} \quad (4-4)$$

at constant shear and stratification. $u_*$ can be estimated from the ADV measurements at 0.11 m height from the law-of-the-wall (LOW): 

$$u_{meas} = \frac{u_*}{\kappa} \ln \left( \frac{z_{meas}}{z_0} \right) \quad (4-5)$$

The roughness height $z_0$ is taken as 0.002 m (Brand et al. 2007). Lorke et al. (2002) showed that the LOW is valid in Lake Alpnach as long as $u > 0.01 \text{ m s}^{-1}$. Figure 8 shows the $h_{mix}$ as a function of the $u$ in 0.11 m height calculated by combining Eqs. 4-4 and 4-5. For example,
Fig. 4-9: One hour averages of displacement length (symbols) and temperature profiles (dashed line) at (a) \( t = 1 \) h (period with oxygen flux) and (b) \( t = 6 \) h (period without oxygen flux) determined from the thermistor vertical array. Bars denote the standard deviations.

\[ u = 0.02 \text{ m s}^{-1} \] produces active turbulence up to \( z = 3.5 \) m above the sediment for an average stability \( N^2 = 2.4 \times 10^{-4} \text{ s}^{-2} \) (Fig. 4-8).

The \( h_{\text{mix}} \) also explains the long time spans of approximately 1000 s which are necessary to resolve the entire spectral content of the solute fluxes, as shown in the ogives of period V (Fig. 4-4c). The stability in this period was \( 1.9 \times 10^{-4} \text{ s}^{-2} \) and the average \( u = 0.025 \text{ m s}^{-1} \), which corresponds to \( u^* = 0.0026 \text{ m s}^{-1} \) (Eqs. 4-3 and 4-5). This results in \( h_{\text{mix}} = 7.1 \text{ m} \) (Eq. 4-4). The timescale for the largest eddy during this period can be estimated by \( h_{\text{mix}}/u^* \approx 2700 \text{ s} \). Nevertheless, the contributions of fluctuations of such long timescales are almost negligible due to their low frequency and the ogive reaches its plateau for shorter times scales (500 to 1000 s).
4.4.3 The nature of weak turbulence during periods with no measurable flux

The difference between weak and actively sheared turbulent regimes is shown in Fig. 4-9. Intense mixing occurs at $t = 1$ h against the strong temperature stratification ($N^2 \sim 2.2 \times 10^{-4}$ s$^{-2}$) whereas the weak turbulence at $t = 6$ h can mix the lower part of the BBL but not the stratified top.

Decaying turbulence and shear-induced convection drive this weak turbulence during the flux-free periods. Even if the shear forces are too low to overcome the viscous forces, turbulence can be generated by convective mixing. Lorke et al. (2005) observed that seiching in Lake Alpnach can cause inverse temperature gradients that result in bottom convective mixing. Figure 10a shows that $N^2$ falls below zero several times during the flux-free periods III and IV. Convective mixing occurs only if the density anomaly $\Delta \rho$ caused by a temperature anomaly $\Delta T < 0$ is able to overcome viscous forces and thermal diffusion. This is the case if the Rayleigh number, which is the ratio of $Ra = g\Delta \rho h_{Ra}^3 / \rho K_T V$ where $g$ is the gravitational acceleration, $K_T$ is the thermal diffusivity and $h_{Ra}$ is the height of the unstable layer, exceeds a
critical value of $\sim 10^3$ (Turner 1973). The Rayleigh number, shown in Fig. 4-10b for the flux-free period, indicates that intermittent convection is present, which can also cause turbulence during shear-free periods. Nevertheless the typical height of the unstable layer was $h_{Ra} = 0.5$ m above the sediment and BCM contributed only to the internal mixing of the BBL. The weak nature of the BCM is also reflected in the low values of the Rayleigh numbers that never exceeded $3 \times 10^6$, in contrast to the values around $10^8$ observed in previous studies (Lorke et al. 2005). These low numbers can be explained by the significantly lower $h_{Ra}$ in our study compared to $h_{Ra} \approx 2.5$ m observed by Lorke et al. (2005). They conducted their measurements at a depth of 32 m where the well-mixed part of the BBL extends further above the sediment and BCM becomes a more important process.

Another source for weak turbulence, which can be observed during flux-free periods, is the dissipation of residual turbulence generated by previous shear. Lorke et al. (2002) showed that there is a phase lag of about 1.5 h between the law-of-the-wall shear and the observed dissipation in Lake Alpnach. This explains the turbulence in the inertial subrange that we observed during shear-free period III and is also reflected in the decreasing energy level in the velocity spectra at 4.0 and 4.5 h in Fig. 4-7. Nevertheless, this remaining turbulence is also too weak to mix against the density gradient.

**4.4.4 Conceptual model**

The nature of the observed turbulent oxygen transport above the sediment on the slopes of Lake Alpnach can be described by a conceptual model. The time series can be subdivided into three periods: (a) upflow, (b) deceleration and seiche flow reversal, and (c) downflow of the BBL. The conceptual steps can be visualized in Fig 1 where the upflow occurs between 1 h and 6.5 h, followed by the downflow. First, the BBL moves up the slope. The upper part of the BBL is characterized by a significant temperature gradient. The intense oxygen fluctuations during these stratified periods suggest that an oxygen gradient is also present even close to the sediment. Turbulent kinetic energy is produced by the shear from the seiching, which maintains active turbulence throughout the BBL. Oxygen-rich water is transported towards the sediment whereas oxygen-depleted water is transported towards the interior water column. As the horizontal velocities decrease to less than 2 cm s$^{-1}$ (seiche reversal) the flow is too weak to produce sufficient turbulent energy to transport oxygen through the stratified top of the BBL and only weak turbulence in the inertial dissipation range and low bottom convective mixing are present. At the same time the well-mixed part of
the BBL overlays the margin at 27 m depth and no macroscopic oxygen gradient is present. The constant oxygen profile and the low turbulence lead to the observed intermittency of turbulent oxygen transport. After the stagnation of the flow, the BBL moves downslope and the shear is again high enough to induce turbulent mixing against the density gradient of the BBL.

Until now, eddy correlation studies in aquatic systems have been mainly used to determine oxygen fluxes into or from the sediment. To relate our work with these previous studies it is necessary to discuss the difference in the interpretation of previous eddy correlation studies and our work. The turbulent transport of oxygen in the water column can be described by the 2-dimensional transport equation for scalar quantities:

\[
\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \bar{w} \frac{\partial \bar{c}}{\partial z} = \left( \frac{\partial J_x}{\partial x} + \frac{\partial J_z}{\partial z} \right) + S_c
\]

(4-6)

where \( J_x \) and \( J_z \) are horizontal and vertical fluxes, \( S_c \) is the source-sink term of the oxygen concentration \( c \), and \( \bar{u}, \bar{w} \), and \( \bar{c} \) denote time averaged quantities. Term (i) represents the change of the averaged concentration over time \( t \), (ii) denotes the advective transport of the oxygen by mean flow, (iii) the divergence of the flux in horizontal and vertical direction and (iv) the sink or source \( S_c \) of oxygen in the water column.

In most EC studies, steady state and a non-divergent horizontal turbulent transport are assumed. Term (ii) reduces to zero if there is no horizontal concentration gradient and the average vertical velocity is zero. Under all these assumptions, Eq. 4-6 reduces to

\[
\frac{\partial J_z}{\partial z} = -S_c = 0 .
\]

(4-7)

If we assume that \( S_c \) in the water column is equal to 0 and neglect diffusion, we can directly use the vertical turbulent flux \( \bar{w}'c' \) measured at a certain elevation to determine the flux into the sediment \( J_{sed} \):
Eq. 4-8 was a reasonable assumption for studies conducted under highly turbulent, steady-state conditions (Berg et al. 2003, McGinnis et al. 2008). However, these conditions do not hold for systems like Lake Alpnach with dynamic and intermittent turbulence. The EC technique measures the turbulent flux of a solute through a horizontal plane which can not necessarily be interpreted as the sediment oxygen uptake (Fig. 4-2). Therefore we must interpret the short-term vertical fluxes more carefully in highly intermittent systems. Both the stagnant and actively sheared phases must be resolved to estimate oxygen budgets that reflect the sediment oxygen uptake.

In this study, measurements conducted over half a seiching period demonstrated both mixing phases. The averaged turbulent exchange of oxygen between the BBL and lake interior was 9.2 mmol m$^{-2}$ d$^{-1}$ which was somewhat lower than the oxygen uptake of 13 ± 2 mmol m$^{-2}$ d$^{-1}$ determined from the oxygen profiles. The discrepancy between sediment oxygen uptake and turbulent oxygen transport also explains the observed oxygen depletion in the BBL of ~25 mmol m$^{-3}$ compared with the lake interior. A flood replaced most of the bottom water of Lake Alpnach and established a rather homogenous oxygen distribution 24 days before our study. This event allows us to estimate roughly the time that was necessary to establish the observed oxygen depletion in the BBL. If we assume a typical thickness of the BBL of ~3 m, we can calculate the oxygen deficit of the BBL roughly by 25 mmol m$^{-3}$ × 3 m = 75 mmol m$^{-2}$. Since the difference between the sediment oxygen flux and the turbulent oxygen flux in this study was 5 mmol m$^{-2}$ d$^{-1}$, our calculation predicts that 15 d (75 mmol m$^{-2}$ × (5 mmol m$^{-2}$ d$^{-1}$)$^{-1}$) were necessary to establish the observed oxygen deficit. This is reasonable given that the flood occurred 24 d previously. The flux determined by the EC technique may also contain some systematic error, since we can not be sure whether we have captured all properties of the seiching system such as the harmonics of the BBL oscillations with period lengths of 6 and 8 h (Münnich et al. 1992). Measurements over several seiche periods are necessary for representative flux estimates and more insight in the long-term variability of these fluxes.

Whereas the dynamics of internal mixing processes of the BBL (Gloor et al. 2000; Wüest and Gloor 1998) are becoming better understood and the processes occurring at the sediment-water interface have been closely investigated with respect to momentum (Brand et
al. 2007; Caldwell and Chriss 1979) and solute exchange (Jørgensen and Boudreau 2001), little research has been undertaken to understand the solute transfer between the BBL and the interior of lakes. These transport processes are crucial for the solute exchange between the water column and the sediment of the lake. Moreover, slopes are important factors for the increased efficiency of the basin-wide solute transport by the BBL in lakes as has been observed by Goudsmit et al. (1997). The EC technique has therefore proven to be an excellent tool for the study of turbulent oxygen exchange between the BBL and the lake interior.
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Influence of the diffusive boundary layer on the solute dynamics in the sediments of a seiche-driven lake - a model study

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Abstract

The diffusive boundary layer (DBL) plays an important role for mineralization and oxidation processes in highly reactive sediments. We used transient numerical modelling in order to identify the different effects of the DBL on solute dynamics in the sediments of Lake Alpnach. Our model study shows that the DBL mainly influences the short term sedimentary denitrification by acting as a transport resistance while it governs the reoxidation of reduced compounds by controlling the oxygen penetration depth in the sediment. An increase of the DBL thickness from 0.25 to 1.5 mm decreased the oxygen uptake into the sediment by more than 30 % from 15 to 9.5 mmol m⁻² d⁻¹ and had different effects on the reoxidation of reduced solutes released in the anoxic sediment layers: While the rates of Fe(II) and Mn(II) oxidation decreased by up to 80 % the oxidation of methane changed by only 3 % when an upper limit of the DBL thickness of 2 mm was applied. Still, the contribution to the total oxygen uptake by these redox processes never exceeded 40 %. Denitrification rates under steady state conditions were 11 % slower at a DBL thickness of 2 mm. We also found that processes in the deeper layers of the sediment which are inhibited by the presence of oxygen show a low sensitivity to a changing DBL thickness under steady state conditions. However, fluxes of nitrogen species periodically deviate by more than 60 % when an oscillating DBL thickness with periods of less than 6 h was modeled.
5.1 Introduction

The importance of the diffusive boundary layer (DBL) for the solute dynamics in the sediment has been subject to research for a long time (Jørgensen and Revsbech 1985, Boudreau and Guinasso 1982). The DBL denotes the region right above the sediment water interface (SWI) where turbulence is dampened and molecular diffusion becomes the dominant transport of solutes to and from the sediment (Boudreau and Guinasso 1982). Since molecular diffusion is much slower than turbulent or advective transport, the DBL mainly acts as a bottleneck between the open waters and the sediment. Fluxes across the DBL are governed by molecular diffusion, by the thickness of the DBL and by the concentration differences across the DBL.

Jørgensen and Revsbech (1985) used oxygen microelectrodes in order to analyze the structure of the DBL in laboratory flumes. They found that the DBL can limit the oxygen uptake rate in the sediment if its reactivity is high enough. The thickness of the DBL varies with sediment topography and bulk flow velocity (Gundersen and Jørgensen 1990; Jørgensen and Marais 1990). The first in situ investigations of the relevance of the DBL were performed using indirect methods. Santschi et al. (1983) estimated the DBL thickness at a measurement site in the Pacific by recording the mass loss of gypsum plates laid out at the ocean floor. The first direct in situ measurements of the DBL using oxygen electrodes were reported for the Santa Catalania Basin in 1989 (Archer et al. 1989). Steinberger and Hondzo (1999) and Hondzo et al. (2005) investigated the velocity dependence of the DBL thickness in the laboratory under steady state conditions and found that it increases with decreasing shear velocity following the proportionality relation $\delta_{DBL} \sim u^{-1}$.

The first systematic in situ investigation on the variability of the DBL thickness due to variable flow velocity has been performed in seiche-driven prealpine Lake Alpnach (Lorke et al. 2003). They showed that the thickness of the DBL is described very well by the Batchelor length scale

$$L_B = 2\pi \left( \frac{vD^2}{\varepsilon} \right).$$

(5-1)

where $\varepsilon$ is the dissipation rate of turbulent kinetic energy. This indicates that the thickness of the DBL depends on the turbulence rather than on the actual shear stress, since a time lag
between $\varepsilon$ and the oscillating, seiche-induced shear of about 1.5 hours was observed under transient conditions (Lorke et al. 2002).

The extent of the influence of the DBL on the dynamics of oxygen and other solutes in the sediment depends on the nature of the prevailing reactions in the sediment. Jørgensen and Boudreau (2001) illustrated the potential influence of the DBL on the oxygen uptake into the sediment by discussing the analytical solutions for two extreme cases: In reactive sediments, the DBL can influence the consumption of oxygen where mineralization of organic matter acts as the primary oxygen sink. However, the oxygen flux is completely independent of the DBL thickness, if oxygen is used only for the instantaneous oxidation of dissolved reduced compounds (RC) like sulfide. Even so, the penetration depth of oxygen into the sediment varies in both cases. These findings were confirmed recently in more detailed numerical studies. Glud et al. (2007) used a dynamic model to show that the DBL has only a minor influence on the oxygen flux at Aarhus Bay where oxygen is mainly consumed by secondary reactions like ammonia and manganese oxidation. In contrast, Kelly-Gerreyyn et al. (2005) found that fluxes of oxygen, nitrate and sulfate can vary heavily with changing DBL thickness. In their model, they assumed that oxygen was only used by mineralization and ammonium oxidation. Highly reactive particulate organic matter showed more sensitivity to changing DBL than refractory material. Both studies were conducted in marine environments.

The first systematic in situ investigation on the dynamic variability of the DBL thickness due to variable flow velocity has been performed in seiche-driven prealpine Lake Alpnach (Lorke et al. 2003). The DBL thickness varied between 0.16 and 0.84 mm during one seiching period. Our modeling study will concentrate on the implications of the variable DBL and seiching on the mineralization and reoxidation dynamics as they occur in this lake.

We were also interested in a more detailed analysis of the response of denitrifying processes, since nitrate is the most energy efficient electron acceptor after oxygen and most likely to be effected by the DBL variation. This has already been suggested by Höhener and Gächter (1994). They found that the sedimentary nitrate uptake and ammonium release determined from benthic chambers correlated well with the stirring velocity of the water.

Baumann et al. (1997) investigated the dynamic behavior of denitrification under alternating aerobic and anaerobic conditions. They studied the response of microbes like Paracoccus denitrificans and microbial communities under alternating aerobic-anaerobic
conditions in batch cultures and found that the efficiency of nitrogen production and the composition of the intermediates depended highly on the duration of the time intervals. When the anaerobic period was 24 hours, the cultures reached stable denitrification activities and N₂ was the only denitrification product released. If the duration of the anaerobic periods was short, a semi steady-state was reached after some cycles and nitrite accumulated as the dominant denitrification product. Such changes in reaction pathways were expected based on earlier kinetic modeling. Wild et al. (1995) showed that denitrification rates under varying oxygen conditions could be explained by including the oxygen dependent formation and degradation of denitrifying enzymes.

In this paper we will focus on the effects of seiche-induced variability of oxygen concentration and DBL thickness on mineralization and reoxidation processes in mesotrophic Lake Alpnach (Switzerland). We used high resolution oxygen and nitrate profiles recorded in the uppermost sediment in combination with concentration profiles of manganese, methane and iron in order to estimate the kinetic parameters for oxygen consumption and denitrification. Different scenarios with increasing complexity were implemented and analyzed in order to answer following questions:

(I) How do oxygen fluxes respond to variable DBL thickness? Is the observed behavior adequately explained by simple mineralization or do reduced dissolved species (such as ferric iron, dissolved manganese and methane) govern oxygen dynamics in the sediment? (II) How are fluxes of these reduced compounds influenced by a variable DBL thickness and how does denitrification respond on these changes? (III) How do short-term fluctuations influence oxygen and denitrification dynamics? Do they also influence long term average values?

5.2 Study Site and Measurements

5.2.1 Study site

Lander and temperature measurements were conducted on the south-east slope of Lake Alpnach (46° 57' 51" N, 8° 18' 13" E) on the 14 and 15 September 2005 in a depth of 27 m. The lake is a medium-sized mesotrophic subbasin of Lake Lucerne in central Switzerland. It has an elliptical shape of approximately 5 by 1.5 km, a surface area of 4.2 km², and a maximum depth of 34 m (Gloor et al. 1994). Lake Alpnach is separated by a 3 m deep sill from the rest of Lake Lucerne. It is well known for its persistent basin-scale deep-water seiching of several cm s⁻¹ amplitude with a period of more than 8 hours in length (Gloor et al.,
resulting from the physical dimensions, stratification and the regular wind forcing of the system. For most of the time, inflowing water merges into the surface layer, because the major river input of warm epilimnetic water from an upstream lake. However, the measurements were conducted three weeks after a flood event which disturbed some characteristics of the system by discharging warm and highly turbid water into the hypolimnion.

5.2.2 Data acquisition

Solute microprofiles were recorded using our in situ lander system LISA (Müller et al. 2002), which was equipped with amperometric Clarke type oxygen electrodes (Unisense) and potentiometric ion selective electrodes (ISE) for nitrate. The ISEs were made using 10 µl plastic pipette tips with an average tip diameter of about 0.6 mm as electrode bodies and membrane solutions based on tridodecylmethylammonium nitrate (Wegmann et al. 1984).

The oxygen microelectrodes were calibrated using the signal readings in the water column and in the anaerobic part of the sediment. Samples for the oxygen determination by Winkler titration were taken using a Niskin bottle close to the sediment surface every two hours. The potentiometric electrodes were calibrated and corrected as described in Maerki et al. (2006). Supernatant water from sediment cores was sampled for nitrate measurements. A two-point calibration was performed for the nitrate profiles assuming a concentration of zero at the sediment depth below which the measured nitrate concentration stayed constant.

In order to monitor the seiching of the bottom boundary layer (BBL), sixteen TR-1000 thermistors (RBR Oceanographic Instrumentation) were fixed on the tripod over a 4 m depth range at 25 cm spacing after sensor-to-sensor calibration (Brand et al. in press) and temperature was logged every 3 seconds.

Iron and manganese were measured in July 2005 with a diffusive chamber sampler, inserted into the sediment in the middle of Lake Alpnach over a week. Iron was determined using the phenantroline method (Tamura et al. 1974) and manganese was analyzed by ion chromatography. Methane concentrations were also determined from diffusion chamber samples taken in May 2006 and analyzed by headspace gas chromatography with a flame ionization detector (McAullife 1971).
### Tab. 5-1: Reactions included in the model study.

<table>
<thead>
<tr>
<th>Reaction Nr.</th>
<th>Scenario used in</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-1</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>R-2</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>½ N₂ + 5/4 CO₂ + 7/4 H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-3</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>R-4</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
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<td>x</td>
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<td>x</td>
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<td>R-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>R-9</td>
<td>Built up of enzyme activity</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>R-10</td>
<td>Decay of enzyme activity</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

### Tab. 5-2: Reaction rate parameterizations applied in the model study

<table>
<thead>
<tr>
<th>Reaction Nr.</th>
<th>Rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-1</td>
<td>( R_1 = k_1 \frac{[O_2]}{K_{S,O2} + [O_2]} )</td>
</tr>
<tr>
<td>R-2</td>
<td>( R_2 = k_2 \frac{[NO_3^-]}{K_{S,NO3^-} + [NO_3^-]} \frac{K_{J,NO3^-,O2}}{K_{J,NO3^-,O2} + [O_2]} )</td>
</tr>
<tr>
<td>R-3</td>
<td>( R_3 = k_3 [O_2] [CH_4] )</td>
</tr>
</tbody>
</table>
### Reaction Nr. Rate law

<table>
<thead>
<tr>
<th>Reaction Nr.</th>
<th>Rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-4</td>
<td>( R_4 = k_4 \left[ O_2 \right] \left[ Mn^{2+} \right] )</td>
</tr>
<tr>
<td>R-5</td>
<td>( R_5 = k_5 \left[ O_2 \right] \left[ Fe^{2+} \right] )</td>
</tr>
<tr>
<td>R-6</td>
<td>( R_6 = k_6 \frac{[NO_2]}{K_{S.NO2} + [NO_2]} \frac{K_{I.NO2-NO2}}{K_{I_NO3-NO3} + \left[ O_2 \right]} + \frac{K_{I_NO3-NO2}}{K_{I_NO3-NO2} + [NO_2]} )</td>
</tr>
<tr>
<td>R-7</td>
<td>( R_7 = k_7 \frac{[NO_2]}{K_{S.NO2} + [NO_2]} \frac{K_{I.NO2-NO2}}{K_{I_NO2-NO2} + \left[ O_2 \right]} + \frac{K_{I_NO2-NO2}}{K_{I_NO2-NO2} + [NO_2]} )</td>
</tr>
<tr>
<td>R-8</td>
<td>( R_8 = k_8 \frac{[N_2O]}{K_{S.NO2} + [N_2O]} \frac{K_{I.N2O-NO2}}{K_{I_NO2-NO2} + \left[ O_2 \right]} + \frac{K_{I_NO2-NO2}}{K_{I_NO2-NO2} + [NO_2]} )</td>
</tr>
<tr>
<td>R-9</td>
<td>( R_9 = k_9 \frac{[NO_3] [NO_2]}{K_{S.NO2-E} + [NO_3] + [NO_2]} + \frac{[NO_2]}{K_{S.NO2-E} + [NO_3] + [NO_2]} )</td>
</tr>
<tr>
<td>R-10</td>
<td>( R_{10} = -k_{10} E )</td>
</tr>
</tbody>
</table>

### 5.3 Model setup

#### 5.3.1 Model structure

One-dimensional model calculations were performed using the sediment module implemented in the software AQUASIM (Dittrich et al. 2003; Reichert 1994). Since we were mainly interested in the influence of the DBL on the dynamics of oxygen and nitrate over the diurnal cycle, we used a simple diffusion-reaction model:

\[
\frac{dC_i}{dt} = D'_i \frac{\partial^2 C_i}{\partial z^2} + R_i, \quad (5-2)
\]

where \( C_i \) is the concentration of the solute \( i \), \( D'_i \) stands for the effective diffusion coefficient in the sediment and \( R_i \) represents the reaction term of the processes affecting solute \( i \).
Four different models with an increasing number of biogeochemical processes were implemented in order to investigate the response of aerobic mineralization, RC reoxidation, and denitrification on DBL thickness variations (Table 5-1). The kinetics are formulated as Monod-type rate laws with inhibition terms (Wang and VanCappellen 1996). The simplest model describes only Monod-type oxygen consumption (scenario 1) and allows testing whether a single set of Monod Parameters (R1 in Table 5-2) is sufficient to describe the oxygen profiles recorded under different oxygen regimes in the surface waters.

The interaction between oxygen and RC was implemented as second order reactions (Wang and VanCappellen 1996). Since our study was restricted to the zone of aerobic mineralization and denitrification, we did not include a detailed model for methanogenesis, sulfate reduction and reductive dissolution of solid iron and manganese phases. In a simplified approach, we modeled the release of the RC as sources \( S_i \) starting at a certain depth \( z_{min,i} \) below the sediment (scenario 2):

\[
R_{rel,i} = \begin{cases} 
S_i & \text{if } z > z_{min,i} \\
0 & \text{if } z < z_{min,i}
\end{cases}
\]  

(5-3)

The response of the denitrification on the variable DBL was analyzed by fitting a Monod-type reaction law for nitrate consumption which was inhibited by oxygen (scenario 3). The potential dynamics of intermediates produced during the denitrification process was modeled using the structured Biomass approach described by Wild et al. (1995) (scenario 4).

### 5.3.2 Implementation of the DBL

The flux of a solute \( J_i \) across a DBL is given by

\[
J_i = -\beta_i (C_{i,B} - C_{i,S}) = -\frac{D_i}{\delta_{DBL}} (C_{i,B} - C_{i,S}).
\]  

(5-4)

where \( \beta_i \) is the mass transfer coefficient defined as the ratio between the molecular diffusion coefficient \( D_i \) of solute \( i \) and the thickness of the DBL, \( \delta_{DBL} \), and the concentrations \( C_{i,B} \) and \( C_{i,S} \) refer to the solute in the bulk water and at the sediment surface. The sediment module of AQUASIM allows only the specification of solute concentrations on the upper end of the domain. The DBL was represented by a \( \delta_{domain} = 250 \) \( \mu \text{m} \) thick region above the SWI in the
Fig. 5-1: a) Development of temperature and oxygen concentration above the sediment. a) Isolines of temperature during the 25 hour measurement campaign. b) Temperature (solid line) and oxygen concentrations (circles) measured 50 cm above sediment. Grey bars denote the time span during which oxygen and nitrate microprofiles were measured. The vertical line marks the time when the oxygen electrode was right at the SWI.

modeled domain. It was assumed that the reaction rates of the considered solutes were negligible above the SWI and therefore molecular diffusion was the only relevant process in this zone. We used $C_{i,B}$ as the upper boundary condition and an effective diffusion coefficient $D_{eff,i}$ was calculated by

$$D_{eff,i} = D_i \frac{\delta_{DOM}}{\delta_{DBL}}.$$  \hfill (5-5)
for the corresponding DBL thickness $\delta_{\text{DBL}}$. At steady state, the effective diffusion coefficient generates the same flux in the implemented system as would be calculated in a system with variable boundary layer thickness.

## 5.4 Results

### 5.4.1 Adequateness of DBL implementation

We compared our implementation with an analytical steady state solution of Equation 1 where oxygen reacts following a first order rate law with reaction constant $k = 20 \text{ h}^{-1}$. The analytical expression for the concentration at the sediment surface is:

$$C_{i,s} = C_{i,b} \left(1 + \sqrt{kD_i} \frac{\delta_{\text{DBL}}}{D_i}\right)^{-1}.$$  

(5-6)
Fig. 5-3: Oxygen flux and oxygen concentrations at the sediment surface as functions of DBL thickness calculated with the Monod model.

The results of the AQUASIM implementation were in excellent agreement with the analytical model and deviated by less than 1.5 % for DBL thicknesses between 0.25 and 2 mm. Therefore we conclude that our implementation is adequate.

5.4.2 Seiching dynamics and modeling of oxygen profiles

Lake Alpnach demonstrated typical seiching behavior during the field campaign (Gloor et al. 1994 Brand, in press). The oscillating BBL with the relatively cold interior and stratified top moved up the slope until $t = 12$ h and then moved slowly back thereafter (Fig. 5-1a). The concentration of oxygen followed the trend of the temperature (Fig. 5-2b) because the well-mixed part of the oscillating BBL was depleted in oxygen compared to the lake interior (see Brand et al, in press). During the campaign, 3 oxygen profiles with different concentrations of oxygen in the supernatant water (Fig. 5-1b) were recorded and the Monod parameters ($k_I = 285$ mmol m$^{-3}$ h$^{-1}$, $K_{S,O_2} = 4.12$ mmol) for steady-state oxic respiration were determined based on scenario 1. The fitted results agreed very well with the measured profiles (Fig. 5-2a) and the kinetic parameters were used to assess the influence of a variable thickness of the DBL. In the model, the oxygen concentration at the sediment surface varied between 120 and 50 mmol m$^{-3}$ if the DBL thickness changed from 0.25 mm to 1.5 mm. Simultaneously, the oxygen penetration depth – defined as the depth where the oxygen concentration drops below 10 mmol m$^{-3}$ - decreased from 1.7 mm to 1.2 mm (Fig. 5-2b). The oxygen uptake dynamics
Fig. 5-4: Measured and fitted concentration profiles of a) manganese, iron and b) methane. c) Detailed modeled depth profile of these solutes and oxygen in the aerobic zone at a DBL thickness of 1.0 mm and d) 0.5 mm.

were sensitive to changes in the DBL thicknesses (Fig. 5-3). An increase of the DBL thickness from 0.25 to 1.5 mm decreased the oxygen uptake into the sediment by more than 30 % from 15 to 9.5 mmol m$^{-2}$ d$^{-1}$ (Fig. 5-3).

5.4.3 Dynamics of dissolved reduced compounds

Scenario 2 of the model was designed to study the simultaneous response of reduced compounds and oxygen governed by variable DBL thickness. The source terms and release zones for iron(II), manganese(II) and methane (Eq. 5-3) were adjusted in order to reproduce the fluxes towards the sediment obtained from the diffusion sampler measurements ($S_{Fe} = S_{Mn} = 0.11$ mmol m$^{-3}$ h$^{-1}$, $S_{CH4} = 1.4$ mmol m$^{-3}$ h$^{-1}$, $z_{min,Mn} = 20$ mm, $z_{min,Fe} = 30$ mm,
Fig. 5-5: left: concentrations of manganese, iron and methane at the SWI. right: relative oxidation rate of the reduced compounds in the aerobic zone of the sediment as a function of the DBL thickness.

$z_{min,CH_4} = 20\text{mm})$. A negligible lake water concentration was implied as upper boundary condition. Methane fluxes contributed most to the flux of RIC in the sediment ($J_{CH_4} = 1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$) while iron and manganese fluxes were significantly smaller ($J_{Fe} = 0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $J_{Mn} = 0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$). We used published rate constants for the reoxidation of methane, ferrous iron (Wang and VanCappellen 1996) and manganese (Morgan 2005) their numerical values are documented in the appendix.

The modeled concentration curves of RC were linear until the solutes diffused into the aerobic zone where they were oxidized (Fig. 5-4 a, b). Methane was oxidized almost completely in the sediment, whereas about 45% of the Fe(II) and 95% of the Mn(II) were released to the overlying water. Especially the concentration profile of methane reacted significantly to changes in the DBL thickness. When the DBL thickness was expanded, the lower boundary of the reaction zones for the solutes migrated closer to the sediment surface (Fig. 5-4 c, d) the surface concentrations of the RIC increased (Fig. 5-5a) and their reoxidation rates changed. The influence of the DBL thickness on the methane oxidation was small compared to the Fe and Mn oxidation (Fig. 5-5). The methanotropic rate slowed down only by 2.5% when the DBL size expanded because CH$_4$ was almost completely consumed before reaching the sediment-water interface. Iron and manganese oxidation showed a much higher sensitivity (40 and 80% change) to the DBL thickness since the reaction rate of these compounds was slower and a deeper penetration depth of oxygen increased their residence time in the aerobic zone (Fig. 5-5).

The DBL thickness also controls the proportion of aerobic mineralization and reoxidation. The contribution of RC to the total sedimentary oxygen flux increases from 22 to
Fig. 5-6: (a) and (b): Comparison between measured (dots) and fitted (line) nitrate profiles at (a) 5 hours. (b) at 16 hours. The measured DBL thickness was 0.5 mm in both cases. The error bars denote the standard deviations between several electrodes and reflect the spatial heterogeneity. (c) Modeled nitrate profiles at three different DBL thicknesses. (d) Modeled nitrate profiles at oxygen concentrations which correspond to the surface concentrations at the three DBL dimensions.

36 % if the DBL thickness is raised from 0.25 to 2.0 mm. At the same time, the oxygen uptake itself changes from 13 to 8 mmol m\(^{-2}\) d\(^{-1}\).

5.4.4 Influence of variable DBL thickness on denitrifying processes

Similar to oxygen, nitrate shows the typical behavior of a terminal electron acceptor which is consumed in the sediment (Fig. 5-6 a and b). The measured penetration depth of nitrate was \(\approx 14\) mm and the thickness of the DBL was \(\approx 0.5\) mm during the recording of both profiles. No evidence for nitrification was found in the aerobic zone of the sediment. Therefore, we considered only a denitrification rate which was inhibited by oxygen in the
Fig. 5-7: Influence of the DBL on nitrate reduction in Lake Alpnach. Circles denote the increase of the nitrate flux by oxygen inhibition; squares denote the overall decrease of the nitrate flux due to increasing DBL thickness. Note that the corresponding surface oxygen concentration intervals shown on the upper axis are not equidistant.

model scenario 3 (Table 5-2). Even though the difference in the modeled surface concentrations of oxygen was 11 mmol m$^{-3}$ between the recordings at $t = 5$ and $t = 16$ h, the calculated nitrate profiles were almost identical and fitted the measurements well. The similarity between both profiles can be explained by the almost identical DBL during the measurements. Modeled nitrate profiles differed clearly from each other at variable boundary layer thickness (Fig. 5-6 c), but a change in the concentration of surface oxygen at constant nitrate produced almost identical profiles (Fig. 5-6 d). Still, the decrease of oxygen inhibition at lower oxygen concentrations leads to an increase of the nitrate flux of up to 8 % (Fig. 5-7). The inset of Fig. 5-6 d shows the change of the oxygen gradient in the sediment when less oxygen is present and the denitrification zone is closer at the sediment surface. The DBL influences denitrification in two ways: It reduces oxygen inhibition and still it compensates for this enhancement of denitrification by imposing a transfer resistance for nitrate. Therefore, we observed a net decrease of the nitrate flux by up 5 % under the presence of a DBL (Fig. 5-7).
In order to investigate the potential behavior of the other nitrogen species nitrite and nitrate, we implemented a sequential denitrification model in scenario 4 which also included the build-up and decay of enzymes catalyzing the denitrification (Wild et al. 1995). The development of enzyme activity was modeled as a Monod-type process which was limited by the presence of nitrate and nitrite and inhibited by oxygen. The synthesis would stop at an enzyme activity of 1. Nevertheless, this value was never reached due to the permanent decay of enzymes. The model for nitrate reduction was fitted to the measured profiles, whereas we had to use the Monod parameters for nitrite and nitrous oxide reduction for activated sludge (Wild et al. 1995), due to the lack of data for sediments. Nevertheless, the calculated values for the nitrous oxide flux of $\sim 4.8 \times 10^{-4} \text{ mmol m}^{-2} \text{ d}^{-1}$ were of the same magnitude as the benthic flux of $21.6 \times 10^{-4} \text{ mmol m}^{-2} \text{ d}^{-1}$ determined by Mengis et al. (1997) using a mass balance approach. The modeled nitrite profile showed a maximum of 6 mmol m$^{-3}$ at $\sim 10$ mm depth and a penetration of more than 60 mm (Fig. 5-8). The modeled concentration of nitrous oxide in the sediment reached around 11 $\mu$mol m$^{-3}$ with a slightly higher penetration depth than nitrite. Maximum enzyme activity was found around 3 mm, right below the zone where no oxygen was available and nitrate concentrations were around 6.5 mmol m$^{-3}$. The peak
concentrations of nitrite and nitrous oxide were far below the zone of oxygen depletion at around 6.5 and 6.8 mm. The local maximum of nitrous oxide at 2 mm was due to the relatively high sensitivity of the nitrous oxide reduction to the presence of oxygen in comparison with the sensitivity of its production from nitrite.

In order to investigate the response of the denitrification on the DBL thickness, we varied it between 0.25 to 0.75 mm. The average fluxes of nitrous oxide and nitrite were $\sim 4.8 \times 10^{-4}$ mmol m$^{-2}$ d$^{-1}$ and 0.130 mmol m$^{-2}$ d$^{-1}$ respectively. The variation between these fluxes due to the variable DBL thickness never exceeded 1%.
5.4.5 Effects of the oscillating BBL

The solute dynamics of Lake Alpnach are mainly governed by internal seiching and the resulting variability of the DBL. In order to investigate the influence of this dynamic condition, we investigated two scenarios. In the first, we applied a sinusoidal DBL thickness between 0.25 and 0.75 mm at different periods (T) between 0.5 and 24 h. In a second scenario we varied only the corresponding surface concentration of oxygen by 113 ± 19 mmol m\(^{-3}\) (mean ± amplitude). At T < 6 h, the relative amplitude (the ratio between the absolute amplitude and the average value) of the fluxes of all solutes was highly sensitive to the variation frequency of the DBL thickness. It increased from 45 to 62 % at T = 0.5 h to 20 % at T = 6 h (Fig. 5-9 a). The relative amplitude for oxygen remained constant at T > 6 h, whereas those for the nitrogen species drop below 10 % for T > 24 h. In contrast, a decrease of the amplitude of solute fluxes was observed when only the surface oxygen concentration was changed. In this case, oxygen fluxes varied over 350 % of the average flux and even oxygen fluxes from the sediment were observed during times when oxygen concentration was decreasing at the sediment surface. Nevertheless, the fluxes of the nitrogen species varied only up to 7 % of the average flux (Fig. 5-9 b). The decrease of the amplitude of nitrite and nitrate can be explained with the decreased variability of the penetration depth of oxygen at lower frequencies. Only nitrous oxide shows a slight maximum at T = 3 h. Even though the fluxes of all species can vary highly during an oscillation period, the influence of the transient variability of the DBL thickness or oxygen surface concentration on the average fluxes is less than 1 % for all solutes.

5.5 Discussion

The main purpose of our model study was the investigation of short-term effects of variable near-sediment flow velocities and oscillating DBL on the solute dynamics in the uppermost sediment. The model results allow addressing the research questions brought forth in the introduction.

5.5.1 Response of oxygen fluxes

In a first attempt, we attempted to identify zones in the sediment with different zero-order reaction rates using the method of Berg et al. (1998). Two reaction zones with lower rates at greater depth were necessary to fit the profiles adequately. This pattern differs from frequently observed higher reaction rates in the lower part of the oxic zone which was explained by the reoxidation of highly reactive RC in marine systems (Jørgensen and...
Boudreau 2001; Rasmussen and Jørgensen 1992). Still, these pathways play a less important role in our system, since RC reoxidation contributed less than 40% of the sediment oxygen demand in this study of Lake Alpnach.

In order to describe the different profiles under variable conditions, the reaction rates had to be varied by more than 30% in each zone. By contrast, all three profiles could be modeled with a single set of Monod parameters by only varying the oxygen concentration at the sediment surface. The Monod model for oxygen consumption was therefore more applicable under dynamic conditions and was used in the further scenarios.

The calculated response of oxygen uptake in the sediment to DBL dynamics by more than 30% was similar to the 25% reduction of oxygen flux reduction calculated for Aarhus Bay during late autumn (Glud et al. 2007) and to the 22% for highly reactive organic carbon (Kelly-Gerreyn et al. 2005). This comparison indicates that the DBL plays an important role in the oxygen dynamics of mesotrophic lakes because the settled organic material is still highly reactive. An even higher sensitivity of oxygen uptake to DBL changes could be expected in sediments of eutrophic lakes such as Lake Zug (Maerki et al. 2008) if enough oxygen is present and if it is mainly consumed via mineralization of organic matter.

This last condition is questionable because Jørgensen and Boudreau (2001) showed in a theoretical model that the sensitivity of the oxygen flux on the DBL thickness can be strongly damped if the oxygen demand is mainly caused by reduced dissolved compounds. Our calculations for Lake Alpnach showed a significant decrease of oxygen flux with increasing DBL thickness even if aerobic reoxidation of RC was included in the model. The proportion of RC to the sediment oxygen uptake of less than 40% was apparently too low to act as a “buffer” against DBL dynamics. Eutrophic lakes could well show a different behavior: A recent microsensor study in eutrophic Lake Zug indicated that about 50% of the oxygen flux was consumed by reoxidation of RC (Maerki et al. 2008)

5.5.2 Mechanisms and extent of DBL control on other solutes fluxes

The DBL mainly acts as a transfer resistance at the sediment-water interface. The modeled fluxes of the solutes diffusing into the sediment like oxygen and nitrate therefore showed the highest sensitivity towards a change of the diffusion distance caused by a variable DBL. This sensitivity decreased with the distance of the reactive zone from the sediment surface and with slower reaction rates. In the model, the oxygen flux adjusted to 47% when a
2 mm thick DBL was imposed, whereas the nitrate flux varied by only 11%. The influence of the DBL on dissolved RC like methane, manganese and ferrous iron was twofold. In addition to acting as a diffusion resistance, it also controlled the penetration depth and flux of oxygen into the sediment which affected the oxidation of these compounds by defining the location and extension of the reaction zone for RC. As a consequence, expanding the DBL shifted the portion of oxygen uptake by RC from 22 to 36%. Similar results were obtained by Glud et al. (2007) in their study of Aarhus Bay where the contribution of RC to the sedimentary oxygen uptake was over 70%.

The model scenario of the denitrification process and its intermediates suggested that the inhibition effect of oxygen as controlled by the DBL was negligible under steady-state conditions. Nevertheless, this indirect effect via inhibition became more important under dynamic conditions with timescales of less than one day. These results are in contrast with findings of Kelly-Gerreyn et al. (2005) which implied that denitrification was mainly influenced by the variable oxygen penetration depth. The main reason for this discrepancy was the exclusion of nitrification in our model since the available data allowed to exclude this process in the top millimeters of Lake Alpnach sediments.

5.5.3 Implications of short-term variations

The fluxes averaged over a dynamic model for the full seiching period deviated by less than 1% from the steady state solutions. Still, temporary deviations from steady state profiles can be higher than 20% for oxygen and 10% for other nitrogen species for oscillation periods in Lake Alpnach which are shorter than 24 h (Münnich et al. 1992). Such large short-term variations have been reported by Lorke et al. (2003) who observed variable oxygen fluxes between 6 and 13.2 mmol m$^{-2}$ d$^{-1}$ during a 24 h campaign in Lake Alpnach.

This result highlights that single profiles recorded in the upper few mm of the sediments must be interpreted carefully if the solutes are highly sensitive to DBL variations and the investigated system is highly dynamic. In this case, microprofiles can only represent the state of the sediment at a certain time interval. The combination of non-invasive flux measurements (eddy correlation technique) which integrate over larger areas at high temporal resolution (Brand et al. 2008; McGinnis et al. 2008) with profiling at high spatial resolution in the sediment can improve the understanding of these highly dynamic processes. The eddy correlation method which has been developed for the determination of oxygen fluxes close to
the SWI seems to be a promising tool for these flux measurements which integrate over a certain surface area (Berg et al. 2007).

By contrast, reduction processes which occur several cm below the aerobic zone like methanogenesis or reductive iron dissolution are mainly unaffected by DBL dynamics. This decoupling of processes in anoxic sediment layers simplifies both the measurement and interpretation of gradients and diffuse fluxes of reduced compounds below the aerobic zone.
5.6 References


## 5.7 Appendix: Transport and reaction constants used in the model study

<table>
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<th>Scenario</th>
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<th>Unit</th>
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</table>

[a]: set arbitrarily

[f]: fitted

[1]: Boudreau (1997)

[2]: Wang and VanCappellen (1996)

[3]: Wild et al. (1995)

[4]: Morgan (2005)
Chapter 6

Synopsis and outlook

6.1 Conclusions

The presented work contributes mainly to the understanding of solute transfer processes at the interfaces of the BBL with the sediment on the lower and the lake interior on the upper side. As a conclusion, I will give concise answers to the questions posed in chapter 1.2:

(I) The novel flow sensor was successfully applied in situ in lake Alpnach. Similar to the DBL, we could also observe a VBL which was assumed in theory but has never been observed before. It merges into a logarithmic layer at the bottom of the sediment even at a shear velocity was as low as 0.13 cm s\(^{-1}\). Using the novel flow sensor, we also measured the gradual decay of velocity fluctuations close to the sediment. Therefore, the developed flow sensor proved to be a promising tool for the investigation of flow at high resolution close to the sediment water interface when velocities are extremely low.

(II) The turbulent oxygen flux on the sloping sediments of Lake Alpnach showed an high intermittency which seems to line in with the intermittent presence of a well mixed BBL described by (Gloor et al. 2000). Surprisingly, it was found that turbulent oxygen transport did not coincide with the presence of a pronounced, well mixed BBL. In contrast, turbulent oxygen transport was generally present when the stratified top of the BBL was close to the sediment and horizontal bulk velocities exceeded \(\approx 2\) cm s\(^{-1}\). We concluded that a certain bottom shear is necessary to induce turbulent oxygen transport across the stratified top which separates the BBL from the lake interior. This turbulent oxygen exchange is - in contrast to permanently turbulent systems as investigated by Berg et al. (2003) – not always sufficient to cover the sedimentary oxygen demand during a full seiching period. Therefore the well mixed part of the BBL can be depleted in oxygen relative to the lake interior. This leads to a variable oxygen concentration in the water above the sediment. A variation of more than 1.5 mg l\(^{-1}\) was measured in our study. In addition to the variable DBL thickness (Lorke et al. 2003), this concentration change can also influence the solute and mineralization dynamics in lake sediments.
(III) Still, the model study of solute dynamics in the sediments of Lake Alpnach showed that the DBL influences mainly the mineralization, denitrification and reoxidation of reduced compounds by imposing a diffusion resistance at the sediment water interface. This is in contrast to the model study performed by Kelly-Gerreyn et al. (2005) who found that nitrification-denitrification dynamics are mainly influenced indirectly by the DBL thickness due to the variability of the surface oxygen concentration. This difference in the results between both studies is due to the exclusion of nitrification in our study since this process has not been observed in Lake Alpnach.

6.2 Outlook

These results can be the starting point for further investigations which intend to lead to the further understanding of the mass transfer in the BBL and its implication for early diagenetic processes. In the following, I will first outline the new questions and problems which should be tackled in future work and will discuss potential applications of the new methods which were used during the thesis after.

6.2.1 New problems and open questions

We showed that the newly introduced flow sensor is a promising tool to study flow processes for low flow velocities at high spatial resolution. Nevertheless, it is still not clear whether the sensor works reliably under all conditions. Comparative measurements between the flow sensor and e.g. particle image velocimetry in laboratory flumes should help to increase the confidence in obtained in situ data and to distinguish between fact and artifact in critical situations. For example, some of our in situ measurements suggested the development of a density gradient right on top of the sediment water interface under very low shear due to the release of solutes from the sediment. This layer could cause a change in momentum transfer and consequently a deviation from the VBL in the lowest parts of the flow profile. Simultaneous high resolution measurements of oxygen, conductivity and flow velocity can help to substantiate the existence of such a layer.

The EC measurements in Lake Alpnach were performed only at the sloping sediments. The investigation of the driving forces of turbulent oxygen transport at the bottom of the lake is certainly an interesting task for future projects. The quantification of the contribution of different sources to turbulence in Lake Alpnach is still an unresolved problem. Until now it is not possible to separate the contributions of the shear induced convection and the production
of turbulence by shear (Lorke et al. 2005). The comparison of simultaneous measurements of flow velocity and temperature profiles at the deepest location and the sloping sediments of the lake could help to solve this problem.

The model study on the influence of the diffusive boundary layer on the solute dynamics in the sediment also revealed the need for additional measurements. The accuracy of flux estimates based on solute profiles decreases as the reactivity of the sediment increases due to the limited spatial resolution of the microsensors and the spatial heterogeneity of the investigated system. In addition, commercially available ion selective electrodes have a limited applicability due to their high detection limits and high bias by interfering ions (Müller et al. 1998). Recent attempts to modify these classical ion selective electrodes (Radu et al. 2007, Chumbimuni-Torres et al. 2006) might improve the quality of these sensors in the future. Reliable flux measurements can also help to calibrate transient early diagenetic models. During the model study in chapter 5 we found that the database for the kinetic description of microbial growth and enzyme induction is quite scarce. The investigation of these processes in batch and chemostat cultures in combination with modeling of microbial growth dynamics (Panikov 1995) is required to substantially improve this database.

6.2.2 Potential applications for the novel methods

The novel flow sensor opens opportunities for many more potential applications because of its high spatial resolution, its relatively small size and its high sensitivity to very slow flow. The main requirement for the application of the sensor in different systems is a thorough calibration in a setup which is similar to the investigated system. Recent attempts include the measurement of flow in capillaries (UNISENSE, pers. comm.) and in burrows of chironomidae (Roskosch, pers. comm). Flow measurements in porous media might also be possible.

It was shown that EC measurements are useful tools to determine turbulent flux over long time periods at high temporal resolution directly. The application is by far not limited to oxygen measurements as long as appropriate sensors are available. Simultaneous measurements of velocity fluctuations and temperature can help to quantify the turbulent heat flux and mass exchange of water between lake interior and well mixed BBL. If the density of the water is controlled by temperature, it is also possible to determine the buoyancy flux.
First attempts of EC flux measurements were also attempted for nitrate (Barry, pers. comm.) using a recently developed, fast responding microelectrode. The microsensor is based on ultraviolet spectroscopy ((Johnson and Coletti 2002) and has a low response time (< 1 s) and a low detection limit (1.5 mmol l\(^{-1}\)). If these measurements can be conducted successfully, they can help to improve the conceptual understanding of nitrate uptake dynamics a high spatial and high temporal resolution. Nevertheless, it is sometimes difficult to check the quality of the measured data. The interpretation of EC measurements in the context of the turbulence properties of the investigated system as we did in chapter 3 and 4 can be the starting point for the establishment of a standardized quality check protocol which ensures the reliability of flux data determined by the ECT. These data can help to improve transient early diagenetic models as they were set up in chapter 5.
6.3 Literature


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Ich möchte mich bei allen bedanken, die mich während der letzten vier Jahren unterstützt haben und mir halfen, auch turbulente Zeiten zu überstehen. Besonders erwähnen möchte ich:

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Curriculum vitae

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2002-2003 Research Associate, Chair of applied mathematics, University of Erlangen, Germany
2003-2007 PhD thesis at Swiss Federal Institute of Aquatic Science, Kastanienbaum and Swiss Federal Institute of Technology, Zurich, Switzerland
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