

## Mineralization pathways in lake sediments with different oxygen and organic carbon supply

*Martin Maerki*<sup>1</sup>

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland; and ETH, Swiss Federal Institute of Technology, Institute of Biogeochemistry and Pollutant Dynamics, CH-8092 Zurich, Switzerland

*Beat Müller and Christian Dinkel*

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland

*Bernhard Wehrli*

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland; and ETH, Swiss Federal Institute of Technology, Institute of Biogeochemistry and Pollutant Dynamics, CH-8092 Zurich, Switzerland

### *Abstract*

The intensity and pathways of mineralization of sedimentary organic matter were investigated in eutrophic Lake Zug, Switzerland. In a depth transect (25–180 m) from oxic to anoxic bottom water we recorded in situ sediment pore-water concentration profiles of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> with a benthic lander system equipped with both oxygen and ion-selective electrodes. Anaerobic sedimentary mineralization ranged from 13.1 to 34.9 mmol carbon (C) m<sup>-2</sup> d<sup>-1</sup> and increased linearly with water depth, as determined from the NH<sub>4</sub><sup>+</sup> flux rates in the anoxic pore water and the molar C:nitrogen (N) ratio of the surface sediment. A parallel increase of the total organic carbon concentration of the sediment was attributed to lateral transfer of resuspended sedimentary matter. Denitrification was estimated from nitrate profiles and contributed only 1.5–3.2% to the total organic carbon mineralization at any water depth. Aerobic respiration and oxidation of reduced compounds were calculated from O<sub>2</sub> microprofiles and pore-water data of dissolved Mn(II), Fe(II), S(-II), and CH<sub>4</sub>. When the O<sub>2</sub> concentration exceeded 0.15 mmol L<sup>-1</sup> in the sediment overlying water, 41–58%, or 12.4–18.1 mmol C m<sup>-2</sup> d<sup>-1</sup>, was mineralized aerobically, whereas at lower concentrations (<0.04 mmol L<sup>-1</sup>), >92% of organic carbon was mineralized anaerobically. Total benthic mineralization of organic carbon was 26.9–34.9 mmol C m<sup>-2</sup> d<sup>-1</sup>. A budget including particulate as well as dissolved reduced compounds in the sediment indicated that >95% of the anaerobic mineralization was due to methanogenesis. Oxidation of CH<sub>4</sub> consumed 39–56% of the O<sub>2</sub> at the sediment–water interface. Oxygen exposure times for these sediments were estimated to be on the order of weeks to months. These time spans are too short to change the reactivity spectrum of sedimentary organic matter.

Organic carbon burial in sediments is a major sink in the global carbon cycle. The extent of organic matter (OM) mineralization and preservation in marine sediments has been studied extensively and depends on various factors, such as sedimentation rate (Berner 1980), oxygen concentration in the bottom water (Canfield 1994; Hartnett and Devol 2003), oxygen exposure time (Hartnett et al. 1998; Hedges et al. 1999), and the surface area of mineral particles (Keil et al. 1994; Mayer 1994). Mechanisms of OM burial in lake sediments have received similar attention, because inland waters transport and transform a significant fraction of the continental carbon flux to the ocean (Cole et al. 2007). Recent global estimates show that carbon burial in lake sediments could add up to 54 Tg carbon (C) yr<sup>-1</sup>, approaching about 50% of the marine

burial rate (Dean 1998), indicating that lakes may play a significant role in the global carbon cycle at a decadal timescale. In analogy to marine sediments, OM burial efficiency (i.e., the ratio between OM sedimentation and long-term accumulation) has been found to be smaller in oxic as opposed to anoxic conditions (Bastviken et al. 2003, 2004; Müller et al. 2006) (e.g., sediment oxygen exposure time in Lake Baikal has been identified as the crucial factor regulating OM mineralization; Maerki et al. 2006).

The quantitative assessment of benthic mineralization represents a major analytical challenge, especially in sediments with steep concentration gradients at the sediment–water interface. Among various methods tested (Tengberg et al. 1995; Viollier et al. 2003), one of the most promising tools is in situ profiling with microelectrodes (Sweerts and De Beer 1989; Müller et al. 2002), a method providing penetration depths, vertical concentration gradients, and production or consumption rates of substrates and metabolites at submillimeter resolution. However, the in situ applications of microsensors may affect the vertical velocities of the bottom water (Berg et al. 2003), reduce the thickness of the diffusive boundary layer, and thus influence the interstitial O<sub>2</sub> pore-water profile (Glud et al. 1994, 2007). Flux rates derived from pore-water concen-

<sup>1</sup> Corresponding author (martin.maerki@ag.ch).

### *Acknowledgments*

We thank the agencies of Kanton Zug and Betriebsgemeinschaft Dersbach, Hünenberg, for logistical support; Ruth Stierli and Andrea Christoffel for their analytical work in the lab; Peter Keller for providing unpublished data; and René Gächter, John Little, and two anonymous reviewers for their constructive comments on earlier versions of the manuscript.

tration profiles might therefore be overestimated. Alternative methods such as benthic chambers disturb in situ conditions but include an integrated measure of diffusion, advection, and benthic fauna activity (Glud et al. 2003). The new eddy-correlation technique offers nonintrusive measurements of oxygen fluxes above the sediment but is so far limited to  $O_2$  sensors with fast response times (Berg et al. 2003).

In the past, in situ microprofiling revealed fine-scale  $O_2$  concentration profiles across the sediment–water interface (Reimers et al. 1986), the presence of a diffusive sublayer (Archer et al. 1989), its microstructure (Gundersen and Jørgensen 1990), and the coupling of diffuse sublayer thickness with the hydrodynamic conditions in the bottom waters (Lorke et al. 2003; Brand et al. 2007). As a result of the low concentration of interfering ions, freshwater systems allow the application of ion-selective sensors for, for example,  $NH_4^+$ ,  $NO_3^-$ ,  $NO_2^-$ , pH,  $Ca^{2+}$ , and  $CO_3^{2-}$  (Sweerts et al. 1991; Müller et al. 2002; Maerki et al. 2006).

Here we report the first systematic in situ microprofiling study of  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  in surface sediments across a redox gradient in meromictic Lake Zug, Switzerland. This lake represents an ideal setting to study the effects of  $O_2$  availability on autochthonous organic matter accumulation, because little terrestrial input affects the quality and quantity of OM sedimentation, and the lake basin exhibits a gentle slope down to 200 m, for which reason the sediments are exposed to bottom water  $O_2$  concentrations of  $>0.15$  mmol  $L^{-1}$  above 80 m and  $<0.04$  mmol  $L^{-1}$  below 120 m in water depth. Based on 16 sets of  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  benthic microprofiles we quantified the oxic and anoxic degradation of OM under contrasting bottom water  $O_2$  concentrations in order to assess the role of oxygen exposure time for OM burial.

## Methods

**Site description**—Lake Zug, located in Central Switzerland, is a eutrophic hardwater lake with a maximum water depth of 198 m, a surface area of 38.2 km<sup>2</sup>, and an average water residence time of 14 yr. As the water depth increases gently from the shallower North Basin to the deepest site in the South Basin (Fig. 1),  $O_2$  concentrations in the bottom water decrease gradually. Typically, complete mixing of the water column occurs annually to depths of 50–80 m (rarely exceeding 100 m since 1950), resulting in low  $O_2$  concentrations or even anoxic conditions at greater depths. Typical seasonal  $O_2$  profiles in the water column are illustrated in Mengis et al. (1997a). Seven sites along this redox gradient (25 m, 35 m, 50 m, 80 m, 120 m, 160 m, and 180 m) were investigated three times between December 2001 and June 2002 (Fig. 1; Table 1).

Earlier studies on Lake Zug provided background information on mineralization processes and OM preservation. According to Aeschbach–Hertig (1994), the integrated  $O_2$  consumption over the oxic water column (0–130 m) was 29 mmol  $m^{-2} d^{-1}$ , and Mengis et al. (1997b) estimated benthic denitrification in Lake Zug of 1.1 mmol  $m^{-2} d^{-1}$ . Meckler et al. (2004) found a slightly higher sedimentary content of total organic carbon (TOC, 6% dry

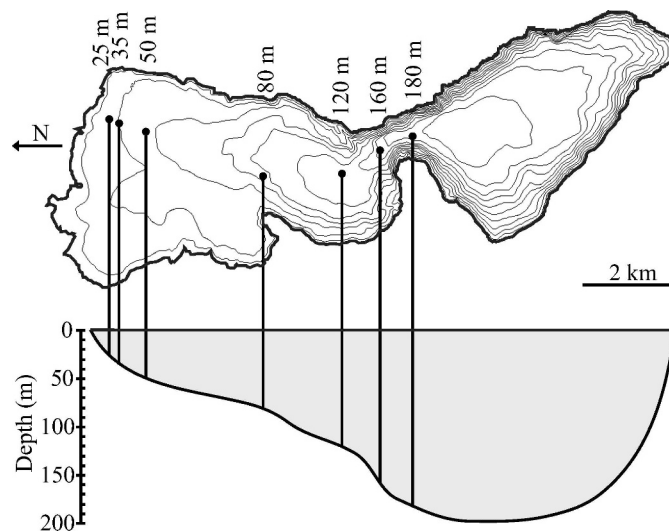


Fig. 1. Map of Lake Zug, Switzerland, and associated depth profile with sampling sites.

weight) at a depth of 120 m compared to 35 m (TOC, 4% dry weight). However, other indicators for OM degradation, such as the amino acid degradation index (Dauwe et al. 2001) and the chlorin index (Schubert et al. 2005), showed little difference, indicating that horizontal transport, rather than different mineralization rates, was probably responsible for the observed difference in TOC burial (Meckler et al. 2004). Benthic macrofauna that may have an impact of sedimentary oxygen uptake (Glud et al. 2003) were investigated in 1994 (P. Keller unpubl.) and showed the highest density ( $\sim 7200$  individuals  $m^{-2}$ ) and variability (13 species) above 33 m in water depth. Below, macrofaunal density and variability decreased drastically to 1000 individuals  $m^{-2}$  and one species below 93 m.

**Lander for ion-selective analysis (LISA)**—In situ measurements were conducted at the lake bottom using a submersible profiling lander system (LISA; Müller et al. 2002) equipped with two to three miniaturized ion-selective electrodes (ISEs) each for  $NH_4^+$  and  $NO_3^-$  and two  $O_2$  microelectrodes (OX-25, Unisense). Briefly, the lander consists of two pressure cases containing power supply, stepping motor control, and data logger units. A sensor rack with up to 18 electrodes is mounted on a stepping motor. In addition, LISA is equipped with a light source and a video endoscope that allow approximate positioning of the sensors near the sediment surface. The stepping motor and data acquisition are controlled on-line from the ship. LISA was deployed onto the lake bottom with a winch, and its gentle landing at a vertical velocity of  $\sim 2$  cm  $s^{-1}$  was ascertained by on-line video observation.

Miniaturized polyvinylchloride (PVC)-based liquid membrane ISEs for  $NH_4^+$  and  $NO_3^-$  were prepared according to the method of Müller et al. (1998). Pipette tips of 10  $\mu L$  volume with a tip diameter of about 0.6 mm were used as electrode bodies, and approximately 1  $\mu L$  of membrane solution was drawn up, resulting in a 0.5-mm-

Table 1. Locations, depths, and dates for in situ profiling with the benthic lander system LISA. Fluxes of O<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> calculated from in situ profiles are given with the number of replicates in parentheses. Positive values indicate flux rates from the water into the sediment (nq, not quantified).

Site, Longitude (°E), latitude (°N)	Water depth (m)	Sampling date	O <sub>2</sub> (μmol L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (μmol L <sup>-1</sup> )	O <sub>2</sub> (mmol m <sup>-2</sup> d <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mmol m <sup>-2</sup> d <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mmol m <sup>-2</sup> d <sup>-1</sup> )
47.1712, 8.5006	25	03 Dec 01	343	nq	29.7±1.5(2)	nq	nq
		11 Mar 02	325	29.1	26.0±0.2(2)	-1.23±0.04(3)	0.59±0.08(3)
		29 May 02	293	23.9	23.0±4.0(7)	-1.13±0.09(3)	0.81±0.08(2)
47.1684, 8.4991	35	05 Dec 01	175	24.8	33.2±0.3(2)	-1.23±0.24(2)	0.85±0.16(2)
		13 Mar 02	318	28.1	14.1±1.8(2)	-1.25±0.04(3)	0.57±0.01(2)
		29 May 02	312	19.0	28.9±2.5(2)	-1.63±0.20(2)	0.63±0.16(3)
47.1639, 8.4969	50	07 Dec 01	203	19.4	36.0±17(2)	-1.01±0.13(2)	0.53±0.03(2)
		13 Mar 02	328	25.7	23.9±7.7(2)	-1.81±0.28(3)	0.71±0.03(2)
		31 May 02	272	19.9	29.1±13(2)	-1.23(1)	0.43±0.05(2)
47.1413, 8.4841	80	07 Dec 01	150	15.5	27.4±6.3(5)	-1.67±0.09(3)	0.71±0.19(4)
		19 Mar 02	181	20.6	28.6±3.2(2)	-1.80±0.28(2)	0.45±0.04(2)
		12 Jun 02	216	19.8	29.2±1.4(4)	-2.01±0.27(4)	0.81±0.22(3)
47.1267, 8.4853	120	07 Dec 01	12	18.3	0.8±0.2(2)	-2.18±0.21(3)	0.82±0.18(2)
		12 Jun 02	37	17.4	3.0±0.2(2)	-3.20±0.37(3)	0.45±0.14(2)
47.1191, 8.4908	160	12 Jun 02	6	15.2	0.9(1)	-3.35±0.19(3)	0.38(1)
47.1123, 8.4962	180	19 Jun 02	0	20.4	0	-3.60±0.10(2)	nq

thick membrane after evaporation. The membrane was conditioned with inner-filling solution for 1 d. A chlorinated silver wire (Ag/AgCl) acted as internal reference, and the potential differences to an Ag/AgCl double-junction cell reference electrode (Metrohm) were recorded using a platinum wire as common ground. Prior to field measurements all sensors were tested in the lab with calibration solutions for several hours in order to eliminate faulty electrodes (Maerki et al. 2006).

*Sensor calibration and data acquisition*—ISEs for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were calibrated on-site with three NH<sub>4</sub>NO<sub>3</sub> solutions ranging from 0.1 to 10 mmol L<sup>-1</sup> at near-in situ temperature. Oxygen sensors were calibrated from the concentration recorded in the bottom water by Winkler titration and the zero reading in the anoxic sediment. Pore-water profiles were obtained from measuring 3–4 cm into the sediment with a vertical resolution of 0.05–0.2 mm. Sixty replicate measurements were recorded at each depth with a frequency of 2 Hz. These averaged records at each depth were used for further calculations. For repeated profiling at the same location, the lander was lifted and re-deployed at an undisturbed sediment area. The sediment–water interface of all profiles was determined from the profiles as the change of the slope from linear to parabolic shape. Nitrate profiles were corrected for interference of HCO<sub>3</sub><sup>-</sup> (~2.6 mmol L<sup>-1</sup>) and Cl<sup>-</sup> (~0.16 mmol L<sup>-1</sup>) and ammonium profiles for the interference of K<sup>+</sup> (0.036 mmol L<sup>-1</sup>), applying the extended Nicolsky–Eisenman equation (Bakker et al. 1994; Müller et al. 1998). Nitrate profiles were adjusted to the observed bottom water concentration determined by standard photometric methods.

*Sediment sampling and analysis*—Bottom water for electrode calibration was sampled from sediment cores taken at each site of LISA deployments using PVC liners

and a gravity corer. Pore water from these cores was sampled from 0.5-cm sections by centrifugation (4000 rounds min<sup>-1</sup>) and subsequent filtration (0.45 μm). If necessary, in situ ammonium profiles were adjusted at 2.75-cm depth by shifting the electrode signal to a reference concentration measured by photometric analysis in the pore water of the sediment section at the lower end of the profile from 2.5 to 3 cm in depth.

Solid sediment material was sampled in 0.5-cm sections by extruding sediment cores from the six sites. Samples were freeze-dried, and total nitrogen (TN) and TOC were determined by thermal combustion with an elemental analyzer (Vario EL, Elementar).

Anaerobic processes were estimated from the data of earlier studies. Pore-water profiles of SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>S, Fe, Mn, and CH<sub>4</sub> were obtained from in situ incubation of dialysis samplers at depths of 97 and 199 m (Mengis et al. 1997b; Schaller and Wehrli 1997). Design, deployment, and analytical procedures were documented by Urban et al. (1997). Direct fluxes of CH<sub>4</sub> were measured with a benthic chamber deployment (Mengis et al. 1997b). Burial rates of Fe, Mn, and iron sulfide were estimated from sediment cores dated with the Cs-137 method (Meckler et al. 2004). Metals were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), and iron sulfides and pyrite were measured by extraction of acid-volatile sulfides and the chromium-reduction method, respectively (Spadini et al. 2003).

*Correcting vertical movement*—The surface sediments of Lake Zug are of high porosity, ranging from 0.90 to 0.96 in the top 4 mm at water depths from 25 to 165 m (Maerki et al. 2004). In spite of the 0.5 m<sup>2</sup> of load-bearing surfaces attached to each of the three legs, the LISA sank slowly into the soft sediments during deployments. This vertical movement had to be taken into account in the interpretation of the pore-water profiles. Analysis of nine O<sub>2</sub> profiles

within 14 h at 35 m (26–27 June 2002) and of four O<sub>2</sub> profiles within 45 min at 25 m (29 May 2002) indicated an exponentially decreasing sinking velocity with time. Because a time lag of 1 h was typically applied between deployment and the start of the profiling, the relevant sinking velocity after 1 h was estimated from the two data sets obtained in June (0.066 mm min<sup>-1</sup>) and May (0.061 mm min<sup>-1</sup>). The good agreement and the similar sediment texture (Maerki et al. 2004) allowed the correction of all pore-water profiles from 25 m to 120 m with this value. In softer sediments at 160 m, a three-times-higher sinking speed (0.20 mm min<sup>-1</sup>) was observed from repeated NH<sub>4</sub><sup>+</sup> profiles and was applied to profiles from 160 m and 180 m.

*Data analysis and calculation of mineralization rates*—Flux rates of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were calculated from pore-water profiles using the zero-order two-sediment layer model of Epping and Helder (1997). For O<sub>2</sub>, Fick's first law for sediments (Bernier 1980) was applied as a result of the extremely steep O<sub>2</sub> concentration gradients characterized by very few data points:

$$J_s = -\frac{D_0}{F} \frac{dC}{dx}, \quad (1)$$

where  $J_s$  stands for the flux rate and  $D_0$  for the diffusion coefficient in pure solution at 5°C (Furrer and Wehrli 1996),  $\frac{dC}{dx}$  represents the concentration gradient, and  $F$  denotes the formation factor ranging between 1 and 1.03 in the top 1 mm of sediment of Lake Zug for depths greater than 25 m (Maerki et al. 2004).

Total mineralization rates of sedimentary organic carbon ( $R_{total}$  in mmol C m<sup>-2</sup> d<sup>-1</sup>), aerobic respiration ( $R_{aerobic}$ ), denitrification ( $R_{denit}$ ), and anaerobic respiration ( $R_{anaerobic}$ ) were quantified from flux rates ( $J$ ) of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and the molar C:nitrogen (N) ratio of the surface sediments. Aerobic respiration (Eq. 2) is calculated as the difference between the measured diffusion rate of oxygen,  $J_{O_2}$ , and an estimate of the reoxidation of the main electron acceptors [Fe(II), Mn(II), S(-II), and CH<sub>4</sub>] diffusing into the oxic sediment layer. In estimating denitrification from NO<sub>3</sub><sup>-</sup> fluxes (Eq. 3), we assume negligible contributions from nitrification and reactions like the anammox process, which oxidizes NH<sub>4</sub><sup>+</sup> with NO<sub>2</sub><sup>-</sup> and therefore does not contribute to organic matter mineralization (Schubert et al. 2006). The flux of NH<sub>4</sub><sup>+</sup> is a measure for the total anaerobic mineralization (Eq. 4) if the following processes do not significantly reduce the NH<sub>4</sub><sup>+</sup> source from anaerobic mineralization: (1) loss of NH<sub>4</sub><sup>+</sup> by nitrification within the thin oxic surface layer, (2) sorption of NH<sub>4</sub><sup>+</sup> on sediment particles, and (3) oxidation of NH<sub>4</sub><sup>+</sup> via processes like anammox. In the following, the areal mineralization rates (mmol C m<sup>-2</sup> d<sup>-1</sup>) were calculated from diffusive fluxes and the relevant stoichiometric factors of the redox reactions, thus:

$$R_{aerobic} = J_{O_2} - J_{reox} \quad (2a)$$

$$= J_{O_2} - \frac{1}{4} \times J_{Fe(II)} - \frac{1}{2} \times J_{Mn(II)} - 2 \times J_{S(-II)} - 2 \times J_{CH_4} \quad (2b)$$

$$R_{denit} = \frac{5}{4} \times J_{NO_3} \quad (3)$$

$$R_{anaerobic} = \frac{5}{4} \times J_{NO_3} + \frac{1}{4} \times J_{Fe(II)} + \frac{1}{2} \times J_{Mn(II)} + 2 \times J_{S(-II)} + 2 \times J_{CH_4} + R_{burial} \quad (4a)$$

$$= f_{CN} \times J_{NH_4} \quad (4b)$$

$$R_{total} = R_{aerobic} + R_{anaerobic} \quad (5)$$

Here, the diffusive transport fluxes are represented by  $J_i$ ,  $f_{CN}$  denotes the measured molar C:N ratio of the top 0.5–2.5 cm sediment layer,  $R_{burial}$  represents the carbon mineralized via the burial flux of minerals containing the reduced electron acceptors Mn(II), Fe(II), and S(-II), and  $J_{reox}$  refers to the flux of O<sub>2</sub> consumed in the reoxidation of reduced compounds.

We based the calculations on one equivalent of C mineralized per equivalent of O<sub>2</sub> (Eq. 2), assuming the production of NH<sub>4</sub><sup>+</sup> instead of NO<sub>3</sub><sup>-</sup>, because none of the concentration profiles indicated a release of NO<sub>3</sub><sup>-</sup> within the thin oxic layer. Estimating  $J_{reox}$ , the fraction of O<sub>2</sub> used in the reoxidation of reduced compounds, was more critical: No comprehensive analysis of high-resolution profiles of Fe(II), Mn(II), H<sub>2</sub>S, and CH<sub>4</sub> was available, but data from earlier studies indicated that  $J_{CH_4}$  was by far the most important flux to be considered for reoxidation. Assuming that variations of the burial rate with depth could be neglected and that the reduced species were quantitatively oxidized in the oxic layer, the fraction of O<sub>2</sub> consumed by these autotrophic processes,  $J_{reox}$ , could be approximated as:

$$J_{reox} \approx R_{anaerobic} - R_{denit} - R_{burial} \quad (6)$$

With this framework the high-resolution profiles of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were used together with C:N ratios to estimate the anaerobic mineralization rate  $R_{anaerobic}$  (Eq. 4b), the denitrification rate  $R_{denit}$  (Eq. 3), and finally the oxic mineralization by combining Eqs. 2 and 6.

## Results

*Oxygen*—O<sub>2</sub> concentrations in the bottom waters exceeded 150 μmol L<sup>-1</sup> at depths of 25–80 m and varied by a factor of two between sampling dates (Table 1). At 120 m and 160 m O<sub>2</sub> was almost depleted (<40 μmol L<sup>-1</sup>). At the sediment–water interface O<sub>2</sub> concentrations decreased sharply, resulting in O<sub>2</sub> penetration depths of less than 0.8 mm at all oxic sites except at the 25-m site, where it penetrated 1.5 mm below the sediment surface (Figs. 2, 3). Mean flux rates calculated according to Eq. 1 were within the range of 23–36 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> at all sites down to 80-m depth, with an average of 27.4 mmol

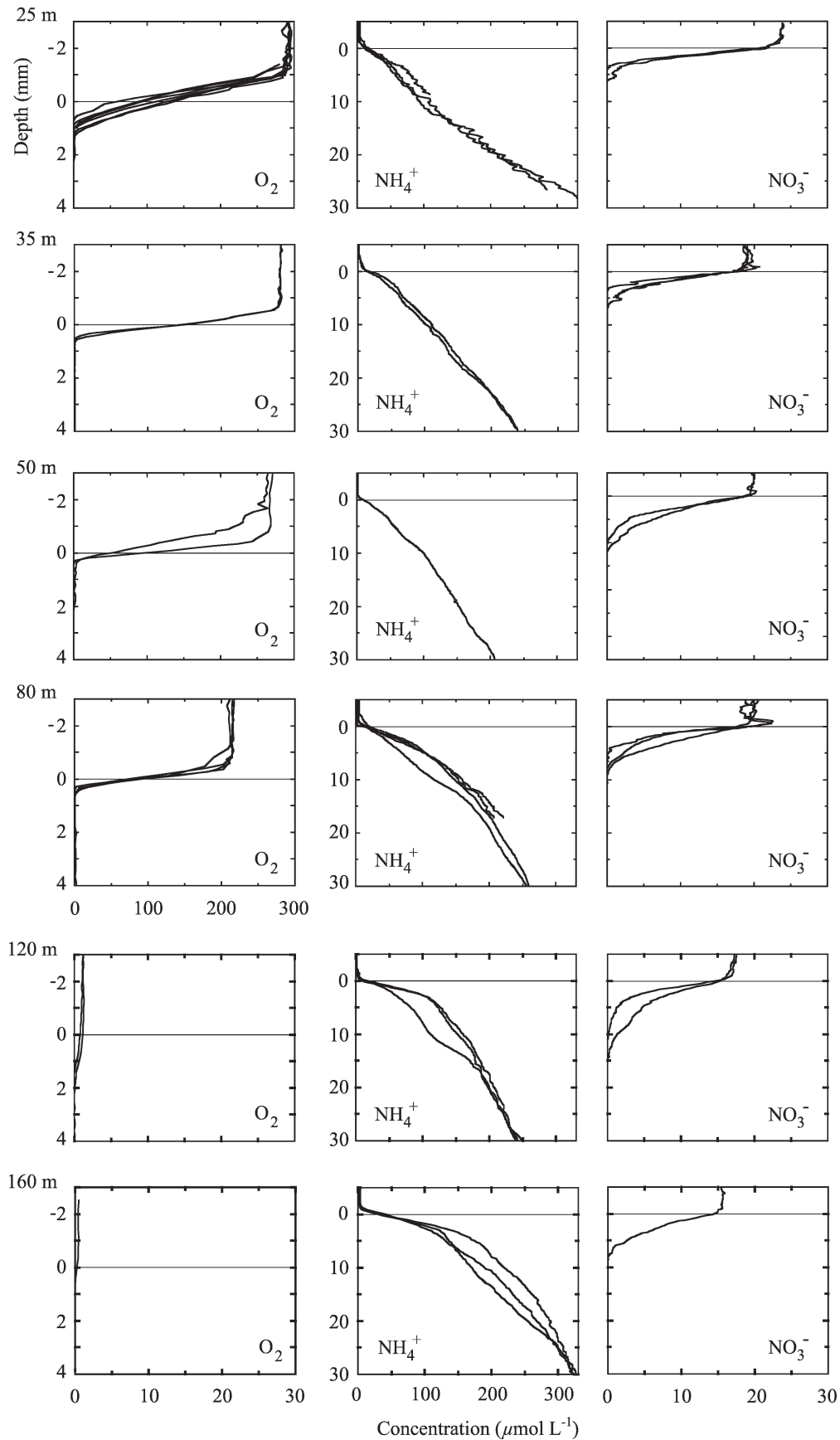


Fig. 2. In situ pore-water concentration profiles for  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  measured with the benthic lander system LISA in Lake Zug: Comparison of profiles from May/June 2002 from different water depths.

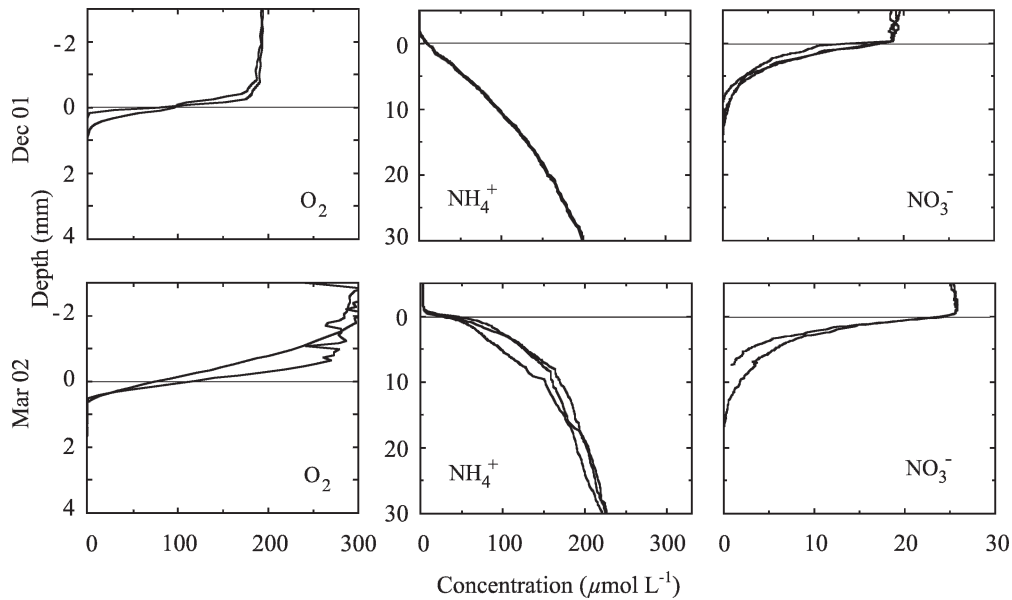


Fig. 3. Seasonal comparison of in situ pore-water concentration profiles for  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  at 50-m water depth.

$m^{-2} d^{-1}$  (Table 1). Flux variations calculated from simultaneously measured profiles were occasionally as high as variations between different sampling dates at the same depth. On 13 March 2002 at 50 m we found the lowest flux among oxic sites, with  $14.1 \text{ mmol } m^{-2} d^{-1}$  coinciding with an extended diffusive boundary layer of  $\sim 2 \text{ mm}$ . The deep stations at 120 m and 160 m were characterized by suboxic conditions ( $< 3 \text{ } \mu\text{mol } O_2 \text{ L}^{-1}$ ) and barely detectable  $O_2$  fluxes ( $< 3 \text{ mmol } m^{-2} d^{-1}$ ). No systematic seasonal variations of  $O_2$  flux rates were evident from the data (Fig. 3). Oxygen flux rates varied by over a factor of two but did not correlate with water depth as long as  $O_2$  was present in the bottom water (Fig. 4). Averages of all three measuring campaigns of sedimentary  $O_2$  consumption were 25–

$30 \text{ mmol } m^{-2} d^{-1}$  (Table 2) and compared well with a depth-integrated consumption rate of about  $29 \text{ mmol } m^{-2} d^{-1}$ , determined with the helium–tritium method in the water column by Aeschbach–Hertig (1994).

*Nitrate*—Nitrate concentrations in the bottom water were slightly higher after lake overturn in March, but during all sampling periods they ranged between  $15.2$  and  $29.1 \text{ } \mu\text{mol } L^{-1}$ , with a slightly decreasing trend with water depth (Table 1). All  $NO_3^-$  profiles were of similar shape, with complete depletion between 4 and 13 mm in sediment depth (Figs. 2, 3). The nitrate sensor analyzed the concentration gradients at the sediment–water interface with adequate precision. The absolute concentrations and

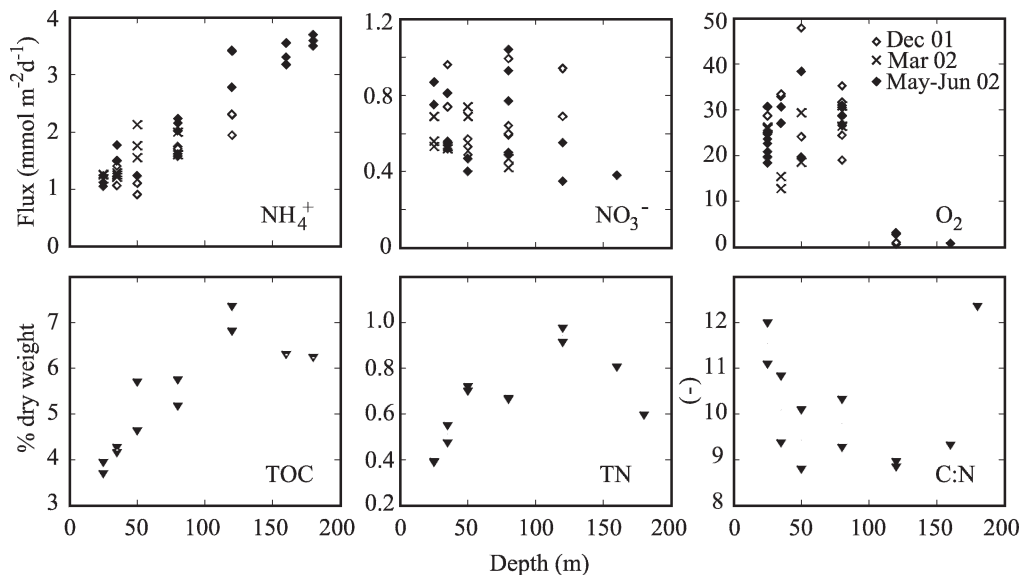


Fig. 4. Fluxes of  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  at various water depths calculated from in situ profiles measured in Lake Zug. The sediment parameters TOC, TN, and C:N were determined in the top 0.5–2.5 cm.

Table 2. Fluxes of  $O_2$ ,  $NO_3^-$ , and  $NH_4^+$  averaged from three sampling campaigns and the mean molar C:N ratio,  $f_{CN}$ , determined in the anaerobic sediments from 0.5–2.5 cm in depth. The rates  $R_{anaerobic}$  and  $R_{denit}$  were calculated via Eqs. 4b and 3, respectively. The rate  $R_{aerobic}$  was estimated by combining Eqs. 2a and 6 and using a constant  $R_{burial} = 0.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (see text) (nq, not quantified).

Depth (m)	$J_{O_2}$	$J_{NO_3^-}$ (mmol $m^{-2} \text{ d}^{-1}$ )	$J_{NH_4^+}$	$f_{CN}$	$R_{anaerobic}$	$R_{aerobic}$ (mmol C $m^{-2} \text{ d}^{-1}$ )	$R_{denit}$	$R_{total}$	Anaerobic (%)
25	26.2±4.4	0.70±0.46	-1.18±0.13	11.5	13.6	14.3	0.88	27.9	48.7
35	25.4±8.6	0.67±0.22	-1.37±0.32	10.1	13.8	13.1	0.84	26.9	51.4
50	29.7±19	0.57±0.43	-1.35±0.42	9.7	13.1	18.1	0.71	31.2	42.0
80	28.4±5.9	0.65±0.28	-1.82±0.35	9.7	17.7	12.4	0.81	30.1	58.7
120	1.9±1.1	0.63±0.29	-2.69±0.72	9.3	25.0	<1.9	0.79	<26.9	>92.9
160	0.9	0.38	-3.34±0.2	9.7	32.3	<0.9	0.48	<33.3	>97.2
180	0	nq	-3.60±0.1	9.7*	<34.9	0	nq	<34.9	100

\* As a result of allochthonous material in the core from 180 m, the molar C:N from 160 m were used for calculations.

the shape of the profiles below the first millimeter were subject to larger errors as the sensors approached their detection limit. Mean flux rates of  $NO_3^-$  varied between 0.38 and 0.85  $\text{mmol m}^{-2} \text{ d}^{-1}$ , with the lowest value measured in summer at 160 m. Averages of all three measuring campaigns at each site revealed remarkably constant denitrification rates with depth (0.6–0.7  $\text{mmol m}^{-2} \text{ d}^{-1}$ ; Table 2).

**Ammonium**—The concentrations of  $NH_4^+$  in the sediment overlying water were very low at all sites (<2  $\mu\text{mol L}^{-1}$ ), they increased markedly at the sediment–water interface, and they remained rather constant below 3 cm in sediment depth (Figs. 2, 3). Concentration measurements of pore waters obtained by centrifugation of the core sections at 2.5–3-cm sediment depth were used as a reference. They varied less than 10% from core to core at a given location and sampling date. In contrast to  $NO_3^-$ , the sensitivity of  $NH_4^+$  sensors was critical at the sediment–water interface, where concentrations approached the detection limit. As a result of the high-resolution measurements the evaluation of gradients could be based on enough data points within the sediment, where concentrations were high enough to be precisely detected. The  $NH_4^+$  release calculated from these profiles ranged from 1.0 to 1.8  $\text{mmol m}^{-2} \text{ d}^{-1}$  at 25–50 m in water depth. Distinctly higher rates were found at 80 m, with 1.7–2.0  $\text{mmol m}^{-2} \text{ d}^{-1}$ , and at 120 m, with 2.2–3.2  $\text{mmol m}^{-2} \text{ d}^{-1}$ . The highest rates were determined at the deepest sites at 160 m and 180 m,

with 3.3 and 3.6  $\text{mmol m}^{-2} \text{ d}^{-1}$ , respectively (Table 1). Thus, derived  $NH_4^+$  fluxes correlated linearly with water depth, as shown in Fig. 4.

**Sedimentation rates and fluxes of reduced species**—The sediment organic carbon content (TOC) in the top 0.5–2.5 cm increased proportionally with the sampling depth to below 120 m and leveled off in the South Basin. The same pattern was observed for TN (Fig. 4). Fluxes of particulate matter in Lake Zug were determined with sediment traps and mass accumulation rates estimated from  $^{137}\text{Cs}$  measurements, yielding rates of 707  $\text{g m}^{-2} \text{ yr}^{-1}$  for the South Basin and an average of 856  $\text{g m}^{-2} \text{ yr}^{-1}$  for the North Basin (Meckler et al. 2004). The annual sedimentation of organic carbon was 7.1–8.3  $\text{mol m}^{-2} \text{ yr}^{-1}$ , corresponding to 19.4–22.7  $\text{mmol C m}^{-2} \text{ d}^{-1}$  (Meckler et al. 2004). Fluxes of reduced species like  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $H_2S$ , and  $CH_4$  as well as solid-phase accumulation rates of Mn, Fe, and S were analyzed in earlier campaigns from benthic chamber and dialysis samples (Table 3).

## Discussion

The first part of this discussion addresses the validation of the new methodology to derive sedimentary mineralization pathways from high-resolution sensor profiles. In the second part of the discussion the governing factors for changes in mineralization pathways with depth in the permanently stratified Lake Zug are identified and assessed.

Table 3. Pore-water and sediment data from earlier measuring campaigns used for estimating anaerobic mineralization and reoxidation rates (see text).

Substrate	Year	Depth (m)	Method	Flux rate (mmol $m^{-2} \text{ d}^{-1}$ )	Burial rate (mmol $m^{-2} \text{ d}^{-1}$ )	$R_{anaerobic}$ (mmol C $m^{-2} \text{ d}^{-1}$ )
$Mn^{2+}$	1993*	97 and 199	Dialysis sampler	~0.03	—	~0.008
$Fe^{2+}$	1993*	97 and 199	Dialysis sampler	~0.03	—	~0.015
$CH_4$	1993†	82	Benthic chamber	7.5	—	15
$Fe(II)$	1997‡	80	Sediment core	—	~0.6	~0.15
$S(-II/0)$	1997‡	80	Sediment core	—	~0.35	~0.6

\* Sampling campaign described by Schaller and Wehrli (1997).

† For flux chamber details, see Mengis et al. (1997b).

‡ Burial rates were estimated from sediment core analysis (FeS: 0.05–0.08  $\text{mmol g}^{-1}$  dry weight; Fe(total): 0.2–0.3  $\text{mmol g}^{-1}$  dry weight; S(total): 0.15  $\text{mmol g}^{-1}$  dry weight; A. Christoffel unpubl.) and sedimentation rates (822–884  $\text{g m}^{-2} \text{ yr}^{-1}$ ; Meckler et al. 2004).

**Aerobic mineralization**—Areal  $O_2$  fluxes to the sediments of Lake Zug calculated from in situ measurements ( $14\text{--}36\text{ mmol m}^{-2}\text{ d}^{-1}$ ) were comparable with rates based on microsensors studies reported from meso-eutrophic Lake Vechten ( $29\text{ mmol m}^{-2}\text{ d}^{-1}$ ; Sweerts et al. 1991) and mesotrophic Lake Alpnach ( $9\text{--}20\text{ mmol m}^{-2}\text{ d}^{-1}$ ; Müller et al. 2002). Oxygen flux rates in Lake Zug above 33 m should be interpreted as lower limits of benthic  $O_2$  consumption because of the high density of benthic macrofauna (P. Keller unpubl.). That means that for 75% of the lake bottom, the effect of macrofaunal activity was of minor importance.

Repeated  $O_2$  measurements during 20 h at a depth of 35 m in June 2002 revealed a temporal variability of a factor of 2.5 in the  $O_2$  consumption rates (Fig. 5). This oscillation of the  $O_2$  fluxes could be caused by the diurnal changes in the hydrodynamic conditions at the lake bottom. Two processes are likely drivers for variable  $O_2$  fluxes: strong and rapid changes of the thickness of the diffusive boundary layer as a function of the bottom water velocity (Lorke et al. 2003) and changing bottom water  $O_2$  concentration due to the advective displacement of water by lake internal seiches (Brand et al. 2008). A detailed interpretation of the pattern in Fig. 5 is not possible, because no data of current velocities and temperature conditions were available. From a practical perspective, the diurnal flux data indicate that averaging over several measurements is necessary to obtain characteristic values for benthic  $O_2$  fluxes.

Quantifying the aerobic mineralization rate ( $R_{\text{aerobic}}$ ) from the  $O_2$  consumption according to Eq. 2 needs an appropriate estimation of the reoxidation rate of reduced compounds that diffuse into the oxic sediment layer from deeper sediment strata. Anaerobic mineralization was mainly driven by methanogenesis, and, thus, the release of  $CH_4$  was the most important reduced component to be considered (Table 3). In comparison, the  $O_2$  consumed for the small flux rates of dissolved  $Mn^{2+}$  and  $Fe^{2+}$

( $\sim 0.03\text{ mmol m}^{-2}\text{ d}^{-1}$ ) was negligible, and free sulfide was not detected in the sediment pore water. If we assume furthermore that the anaerobic mineralization rate related to burial of reduced minerals containing Mn(II), Fe(II), and S(-II) was more or less constant with depth and corresponded to the  $0.8\text{ mmol C m}^{-2}\text{ d}^{-1}$  determined in earlier studies (Table 3), we may estimate that the flux rate  $J_{CH_4}$  at each particular site was close to

$$J_{CH_4} \approx 0.5 \times (R_{\text{anaerobic}} - R_{\text{denit}} - R_{\text{burial}}) \quad (7)$$

Based on the data in Table 2, this relation yields a range of  $6.2\text{--}17\text{ mmol CH}_4\text{ m}^{-2}\text{ d}^{-1}$ . Assuming that all the  $CH_4$  was oxidized at the sediment–water interface, according to the study of Lake Vechten (Sweerts et al. 1991), 39–56% of the  $O_2$  flux into the sediment was consumed by the benthic oxidation of  $CH_4$  at lake depths of  $<120\text{ m}$ . The remaining fraction of the  $O_2$  flux drove aerobic mineralization ranging from  $12.4\text{--}18.1\text{ mmol C m}^{-2}\text{ d}^{-1}$  (Table 2).

Additionally,  $O_2$  may be used for the nitrification of  $NH_4^+$  in the oxic sediment layer. The  $NH_4^+$  concentration profiles in the oxic sediment layer were often linear (Figs. 2, 3), but considering the change of porosity and tortuosity in the top sediment layer of Lake Zug, they actually reflect a net  $NH_4^+$  production (Maerki et al. 2004). As a result of the very low penetration depths of  $O_2$  ( $<1.5\text{ mm}$ ) and the fact that the oxic sediment layer was a source of  $NH_4^+$ , it appears that the diffusion of  $NH_4^+$  from the oxic zone was faster than nitrification, and, thus, sedimentary nitrification was of minor importance. Moreover, investigations with N-isotope tracer experiments with a benthic chamber in eutrophic Lake Baldegg, Switzerland, showed that coupled nitrification–denitrification did not contribute significantly to the total denitrification rate (Mengis et al. 1997b). From these observations we conclude that nitrification occurred mainly in the water column and did not significantly affect the  $O_2$  and  $NH_4^+$  profiles in the oxic sediment layer.

**Denitrification**—Denitrification rates were rather low at all sites ( $0.4\text{--}0.9\text{ mmol NO}_3^- \text{ m}^{-2}\text{ d}^{-1}$ ), as expected, for average bottom water concentrations of only  $15\text{--}30\text{ }\mu\text{mol NO}_3^- \text{ L}^{-1}$ . Denitrification rates obtained from electrode measurements in Lake Baldegg, Switzerland, or from Lake Baikal, Russia, for example, were  $\sim 5$  (Müller et al. 2002) and  $\sim 0.06\text{ mmol m}^{-2}\text{ d}^{-1}$  (Maerki et al. 2006), with corresponding  $NO_3^-$  concentrations in the bottom water of 0.1 and  $0.01\text{ mmol L}^{-1}$ , respectively. These data indicated a close relation between bottom water concentrations and denitrification rates, as discussed by Rysgaard et al. (1994).

A whole-lake mass balance by Mengis et al. (1997b) resulted in a denitrification rate of  $1.1\text{ mmol m}^{-2}\text{ d}^{-1}$  that was in close agreement with the  $NO_3^-$  elimination rates from our in situ electrode measurements (Table 1). Although denitrification was a minor pathway for carbon turnover in Lake Zug, it played a significant role in nitrogen elimination. Denitrification rates were similar to N burial rates in sediments ( $0.6\text{ mmol N m}^{-2}\text{ d}^{-1}$ ; Mengis et al. 1997b).

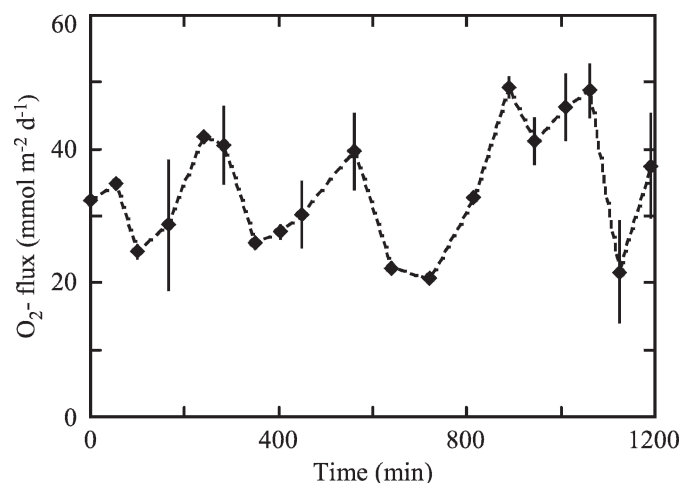


Fig. 5. Variability of  $O_2$  fluxes with 19 sets of consecutive profiles (mostly averaged from two electrode profiles) over a 20-h period at 35-m depth in Lake Zug on 26–27 June 2002.

**Anaerobic mineralization**—In eutrophic lakes, anaerobic mineralization may dominate OM diagenesis even in the presence of high  $O_2$  concentrations in the bottom water (Sweerts et al. 1991; Müller et al. 2002, 2003). In Lake Zug,  $R_{anaerobic}$  always exceeded 40% of the carbon turnover and increased proportionally with depth (13.1–34.9 mmol C  $m^{-2} d^{-1}$ ; Table 2). Estimating  $R_{anaerobic}$  from the flux rate of  $NH_4^+$  and the corresponding molar C:N ratio (Eq. 4) requires an assessment of the quality of such data. Flux rates of  $NH_4^+$  from concentration profiles (1.82 mmol  $m^{-2} d^{-1}$  at 80 m; Table 2) were close to earlier data provided by Mengis et al. (1997b) for Lake Zug at similar depths. These authors reported 1.08 mmol  $NH_4^+ m^{-2} d^{-1}$  at 83-m depth, obtained by dialysis samplers, and 2.67 and 2.53 mmol  $m^{-2} d^{-1}$  with benthic chamber measurements from 1993 at 82-m and 93-m depths. The molar C:N ratio was quite constant in the uppermost 40 cm of anoxic sediments at 35 m and 120 m (Meckler et al. 2004), allowing the conversion of  $NH_4^+$  release into carbon mineralization rates with an average estimate.

An alternative approach to validate the total anaerobic mineralization rate is based on the diffusive transport and burial of all reduced electron acceptors that were released through anaerobic mineralization of OM (Eq. 4a). Pore-water data of  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $H_2S$  ( $\sim 0.003$ ,  $\sim 0.03$ , and close to 0 mmol  $m^{-2} d^{-1}$ , respectively) from dialysis sampler exposures at 97-m and 199-m depths were available, as was the  $CH_4$  flux rate (7.5 mmol  $m^{-2} d^{-1}$ ) from a benthic chamber experiment at 82 m from 1993 (Table 3). Burial rates of Fe(II) and S(-II/0) were estimated from sediment core analysis (FeS: 50–80  $\mu mol g^{-1}$  dry weight; Fe(total): 200–300  $\mu mol g^{-1}$  dry weight; and S(total): 150  $\mu mol g^{-1}$  dry weight) and sedimentation rates (822–884  $g m^{-2} yr^{-1}$ ; Meckler et al. 2004), resulting in  $\sim 0.6$  and  $\sim 0.35$  mmol  $m^{-2} d^{-1}$ , respectively (Table 3). In summary, the corresponding organic carbon mineralization through methanogenesis was  $>15$  mmol C  $m^{-2} d^{-1}$  and for all other anaerobic pathways was less than 0.8 mmol C  $m^{-2} d^{-1}$ . The resulting rate  $R_{anaerobic} \approx 15.8$  mmol C  $m^{-2} d^{-1}$  was in good agreement with the anaerobic mineralization rates calculated from  $NH_4^+$  profiles and molar C:N ratio of the surface sediment, especially at 80 m, the site of  $CH_4$  measurements. These estimates show clearly that anaerobic mineralization was dominated by methanogenesis.

The increase of  $R_{anaerobic}$  and  $J_{NH_4}$  with depth corresponded closely to the increase of TOC and TN content of the sediment (Fig. 4). This was likely due to lateral transport of resuspended sediment particles leading to focusing of organic-rich material at greater depths. The close linear correlation between  $J_{NH_4}$  and the TN and TOC contents of the anoxic sediment (Figs. 4, 6) allowed an estimation of the refractory fractions of TOC and TN from the intercepts in the linear regressions. This indicated the TN concentration at which no further  $NH_4^+$  is liberated. From our data set, we determined refractory TN and TOC contents of 0.06% and 1.81%, which were close to the values of 0.12% and 1.2% determined by Meckler et al. (2004) at 40 cm in sediment depth in cores collected in Lake

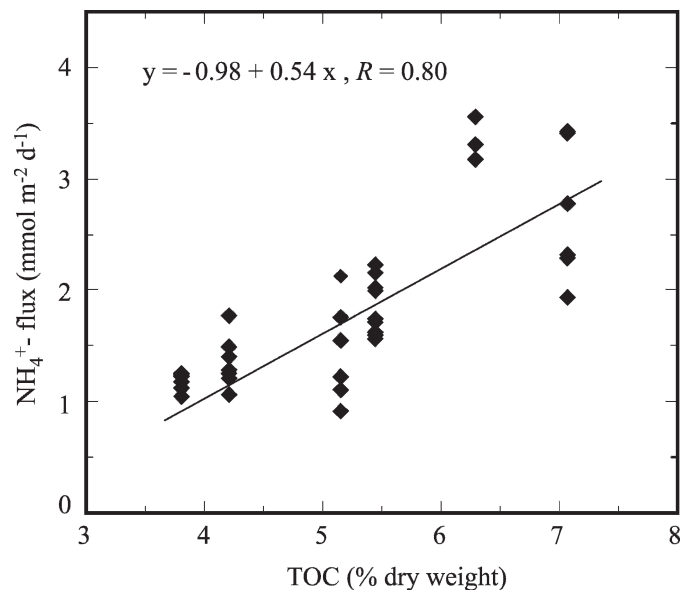


Fig. 6. Correlation between the  $NH_4^+$  flux rate and the TOC concentration of the sediment. Data from 180 m were excluded. TOC data of two sampled cores per depth were averaged.

Zug from depths of 35 m and 120 m. This indicates similar quality of the deposited organic matter at all sites.

**Driving factors of benthic organic carbon mineralization**—The rates of the total benthic organic carbon mineralization  $R_{total}$  (Eq. 5) were quite similar at all sites, ranging between 26.9 and 34.9 mmol C  $m^{-2} d^{-1}$ , with a slight increase at the deepest sites (Fig. 7). However, the mineralization pathways changed dramatically with depth: 41–58% was mineralized aerobically at depths of  $<120$  m, where the  $O_2$  concentration of the water overlying the sediment exceeded 0.15 mmol  $L^{-1}$ . Denitrification was of minor importance (1.5–3.2%). Below 120 m, at suboxic or even  $O_2$ -free bottom water, anaerobic mineralization and specifically methanogenesis dominated the benthic carbon turnover by over 92%. The two drivers for benthic mineralization—oxygen consumption and total organic carbon concentration (Fig. 4)—lead to a pattern of mineralization pathways, which could be separated into three regimes (Fig. 7): (1) Rather constant and equal contributions from aerobic and anaerobic pathways in the shallow sediments above 50-m depth changed to (2) a gradually increasing anaerobic contribution at a constant total mineralization rate in the transition zone from 50 to 120 m and, finally, (3) a slight increase of the total mineralization rate, which was dominated almost entirely by anaerobic processes in the permanently anoxic deep basin below 180 m.

**Oxygen exposure**—The rather constant  $R_{total}$  with decreasing  $R_{aerobic}$  indicates that the quality of organic matter did not change with oxygen exposure time. Calculations of the residence time of organic matter in the thin oxic layers reveal oxygen exposure times in the order of weeks to months, which were apparently too short

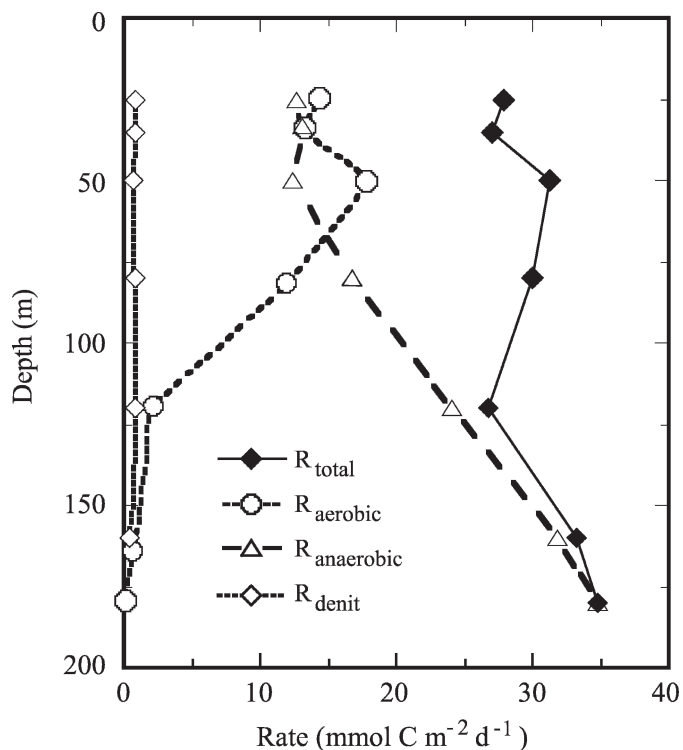


Fig. 7. Rates for different pathways of OC mineralization in sediments of Lake Zug at various water depths.

to influence the bioavailability of carbon substrates. Therefore, the anaerobic pathways were effective enough to keep the total mineralization rate constant below the oxycline at 120 m in water depth (Fig. 7). The oxygen exposure times were short compared to tens of years for the anaerobic mineralization. This is opposite to the highly oligotrophic Lake Baikal, Russia, where oxygen exposure times were 25–2500 yr and, thus, where aerobic mineralization dominated benthic mineralization by far (Maerki et al. 2006). This observation could indicate that significant changes of the reactivity spectrum of sedimentary organic carbon in productive systems will require oxygen exposure times that are longer than months. Quantifying the effects of oxygen exposure on organic carbon burial efficiencies (which are well documented for marine systems: Canfield 1994; Hartnett et al. 1998) will therefore require comparative studies between different lakes.

**Organic carbon input**—In Lake Zug,  $R_{anaerobic}$  was correlated with the TOC concentration of the diagenetically active surface sediment (Fig. 6). TOC concentrations and  $NH_4^+$  fluxes almost doubled from the shallow sites above 50 m to the deep basin below 180 m. While the export production was quite constant in this horizontally well-mixed lake, preferential resuspension and focusing of autochthonous particles along the slopes of the Southern Basin represents a likely mechanism to enrich the surface sediments with reactive organic matter. It is likely that this focusing effect was responsible for the slight increase in

total mineralization rates below 180 m. The concentration of TOC in the top 0.5–2.5 cm proved to be a good predictor for ammonium fluxes and the related anaerobic mineralization rates.

In conclusion, in situ measurements with a profiling lander system are an appropriate tool to resolve the steep gradients at the sediment surface in highly active sediments. Multiple in situ measurements of  $O_2$ ,  $NH_4^+$ , and  $NO_3^-$  allow us to disentangle different pathways of OM mineralization and to constrain their rates with an accuracy similar to that of basin-wide estimates. In the organic-rich sediments of Lake Zug the oxygen exposure time was on the order of weeks to months, which was too short to change the reactivity spectrum of sedimentary organic matter. As a consequence, the total mineralization rate remained rather constant above and below the oxycline in this meromictic system.

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*Edited by: Ronnie Nohr Glud*

*Received: 8 February 2008*

*Accepted: 25 August 2008*

*Amended: 3 November 2008*