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Sulfide and methane evolution in the hypolimnion of a subtropical lake: a three-year study

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Abstract The differential impact of microbial sulfate reduction and methanogenesis on the mineralization of particulate organic carbon (POC) in warm monomictic Lake Kinneret (LK), Israel was studied during three consecutive lake cycles. The hypolimnetic accumulation of total sulfide and dissolved methane was examined in relation to the physical forcing of the water column and the settling flux of particulate matter. With the on-set of thermal stratification in spring, both solutes increased concomitantly with the depletion of oxygen, first in the benthic boundary layer, followed by the upper hypolimnion. Methane production was restricted to the sediments as emphasized by the persistently linear concentration gradient in the hypolimnion. Sulfate reduction occurred both in the sediments and the water column as revealed by the hypolimnetic distribution of sulfide and recurring metalimnetic sulfide peaks. Annual differences in the accumulation pattern of both solutes appeared to be primarily linked to the settling flux of POC and the length of the stratified season. Relatively lower hypolimnetic concentrations of dissolved methane during the stratified season of 2000 coincided with increased ebullition of gaseous methane, likely as the result of a nearly a 2 m drop in the lake level. Overall, sulfate reduction accounted for more than 60% of the POC settling flux, a finding that differs from similar studies made in temperate lakes where methanogenesis was shown to be the primary mode of terminal carbon mineralization. Intensive organic carbon turnover at the sediment water interface and comparatively high sulfate concentrations in LK are the most likely reason.

Keywords Methane · Total sulfide · Particulate carbon · Hypolimnetic accumulation · Lake Kinneret

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Introduction

Eutrophic freshwater lakes are characterized by a high settling flux of particulate organic carbon (POC) and intensive biogeochemical cycling of carbon at the sediment water interface. The fate of deposited POC is closely coupled to the availability of electron acceptors in the overlying

water column (e.g. Santschi et al. 1990; Gruber et al. 2000). In stratified lakes developing an anoxic hypolimnion, methanogenesis and sulfate reduction are key terminal processes in anaerobic carbon mineralization (Capone and Kiene 1988). One of the factors controlling the end products of microbial decomposition is the competition between methanogenic microorganisms (MM) and sulfate reducing bacteria (SRB) for common substrates such as hydrogen and acetate (Ward and Winfrey 1985). It is well known that in the presence of sulfate, SRB can out-compete MM, restricting methanogenesis to the deeper sediment layers (e.g. Lovley and Klug 1983). Nevertheless methanogenesis was repeatedly shown to be the primary mode of anaerobic respiration when competing with sulfate reduction (Ingvorsen and Brock 1982). In Lake Mendota, for instance, about 54 % of the POC settling flux returned as methane (Fallon et al. 1980), in Lake Loosdrecht (The Netherlands) MM mineralized 75% of the POC input (Sinke et al. 1992), and in Lake Washington, where methanogenesis was observed only in a sediment zone below 16 cm, CH_4 production accounted for 63% of anaerobic respiration (Kuivila et al. 1989). However, these figures, refer to one accumulation period and may vary considerably from year to year as suggested by biannual studies from Lake 227 (Rudd and Hamilton 1978), Shingobee Lake and Williams Lake (Striegl and Michmerhuizen 1998).

Assuming that 10% of the POC generated during the spring algal bloom reaches the sediments, Hadas and Pinkas (1995) estimated that in Lake Kinneret (LK) SRB may decompose ca. 40% of the primary production. The objective of the present study was to quantify the relative amounts of POC mineralization via SRB and MM in LK, and whether the relative roles of each vary from year to year. By monitoring the settling flux of POC together with the hypolimnetic accumulation of sulfide and methane the present study was designed to elucidate the differential impact of both microbial groups on carbon cycling in LK during three consecutive lake cycles. Our work represents one of the first biogeochemical analyses of anaerobic carbon mineralization in a subtropical lake.

Methodological

Study Site

Lake Kinneret (12×22 km, 168 km^2) is located 209 m below mean sea level (M.S.L.) in the northern part of the Afro-Syrian rift valley, at 32:50 N latitude and 35:35 E longitude. Maximum and average depths are 42 m and 24 m, respectively (Serruya 1978). The hydrochemical conditions of the lake are dominated by the Jordan River as the main tributary and submersed saline springs. In the aftermath of the winter flood, typical concentrations of major ions in the water column are 5 mmol l^{-1} chloride, 35–50 μmol l^{-1} nitrate, 600μmol l^{-1} sulfate, and 3.5 mmol l^{-1} carbonate.

Following a mixed period of two month duration in winter, the thermal stratification process starts in March with continuously increasing surface water temperatures reaching 30°C in August. The thermocline depth varies from 14 m in spring to 16–17 m in summer before moving downwards in fall. The spring bloom of the dinoflagelate *Peridinium gatunense* is a prominent biological event during the annual lake cycle (Berman and Pollingher 1974). The decline of the bloom in May leads to an enhanced flux of particulate organic carbon (POC) into the hypolimnion and the sediments. The abundance of organic matter strongly accelerates anaerobiosis, and with the depletion of dissolved oxygen and nitrate, sulfide becomes detectable in the hypolimnion, first in the benthic boundary layer (May) and by the end of June throughout the hypolimnion (Eckert et al. 2002a, b). At the sediment water interface (SWI) of the hypolimnion anaerobic conditions prevail throughout summer and fall until the overturn in December or January.

Sampling and Analytical Methods

Our monitoring and sampling program was carried out at the lake's center (station A, 40 m water depth). The vertical distribution of dissolved methane ($CH_4(d)$) in the water column was followed biweekly in triplicate water samples taken at five-meter depth intervals and—when applicable—in three chemocline samples at

one-meter depth intervals. The samples were filled free of air bubbles into 100-ml pre-weighed crimp bottles, which were then sealed. Bottles were kept on ice and processed immediately upon return to the lab (1–2 h after sampling). $CH_4(d)$ was determined by headspace analysis (modified after Schmidt and Conrad 1993). After weighing the full bottles a headspace was applied by replacing ca. 20 ml of sample with N_2. $CH_4(d)$ was than extracted into the headspace by intensive shaking (30 s). Using a gas-tight syringe, a 1 ml gas sample from the headspace was analyzed for $CH_4(g)$ on a GC with FID detector (SHIMADZU, column: PORAPAK Q). The concentration of $CH_4(d)$ was calculated based on the GC result and the gas/liquid ratio in the sampling bottle as determined by reweighing. $CH_4(d)$ profiles were integrated using linear interpolation. In order to convert the accumulated $CH_4(d)$ into equivalents of POC mineralized by MM we applied a factor of two (Mah et al. 1977).

On each sampling date profiles of temperature (T), dissolved oxygen (DO), redox intensity (pe), pH and hydrogen sulfide (pH_2S) were measured with a custom made multiprobe (modified after Eckert et al. 1990). This probe allows for continuous profiling in the water column with on-line data acquisition at a minimum depth resolution of 1 cm. The measured pH_2S, pH and T data rendered the calculation of total sulfide concentrations (S(-II)) by means of the first dissociation constant of hydrogen sulfide (Eckert 1998). As in the case of $CH_4(d)$ profiles were integrated over the hypolimnion and converted to carbon equivalents by applying a factor of two (Postgate 1984).

The flux of particulate matter (PM) to the lake bottom and the ebullition rate of gaseous methane ($CH_4(g)$) from the sediment were followed by combined gas-seston traps deployed one meter above the lake bottom at station A (A40) with an additional trap in 20 m depth below the metalimnion (A20). The traps consisted of four 50 cm long PVC tubes (diam. 6 cm) each equipped with a 250 ml collecting vessel and two reversed funnels (diam. 42 cm) ending into a 300 ml gas sampling bottle. Traps were sampled biweekly. The gas content in the gas sampling bottles was determined by weighing and the fraction of $CH_4(g)$ in the gas phase via GC-analysis. The PM content in the collecting vessels was quantified by centrifugation followed by drying (24 h, 105°C) and weighing of the residue. The thus measured PM content was than extrapolated to gross sedimentation rate expressed in $gDWm^{-2}d^{-1}$. The organic matter content in the PM was determined by the weight loss of a dried subsample during ignition at 550°C for 2 h (APHA 2001). POC was than calculated according to Hakanson and Jansson (1983):

$$POC[mmol C gDW^{-1}] = \frac{weightloss[mg \cdot g^{-1}] \cdot 0.5}{12}$$

The empirical factor 0.5 was recently verified for suspended matter in LK when POC concentrations determined as described were compared with those measured on a CHN analyzer (PERKIN ELMER, 2400 II, USA) with $r^2 > 0.98$ (Eckert and Parparov, unpublished data).

The time change in the POC concentration at the SWI was followed in monthly sediment cores from Station A. Intact cores were taken using a gravity corer and the uppermost 0.5 cm layer was analyzed for POC as described.

Results

During the three years of our investigations the chemical differentiation in the water column of LK followed closely the thermal stratification pattern as exemplified by the 1999 profile series (Fig. 1). In February (Fig. 1a) the whole water column was mixed at a uniform temperature of 17°C and a dissolved oxygen concentration of 8.2 mg l^{-1} (=ppm). With the beginning of surface water heating in March, indicated by the small deflection in the T profile at a depth of 15 m (arrow in Fig. 1b), the system responded immediately with an enhanced oxygen consumption within the newly formed hypolimnion. By mid-April (Fig. 1c), heterotrophic biological activity eventually led to the depletion of oxygen below a depth of 30 m. In this near-bottom zone previously identified as the benthic boundary layer (BBL, Eckert et al. 2002a) both, sulfide and dissolved methane began to accumulate. At the upper boundary of the BBL a well-defined
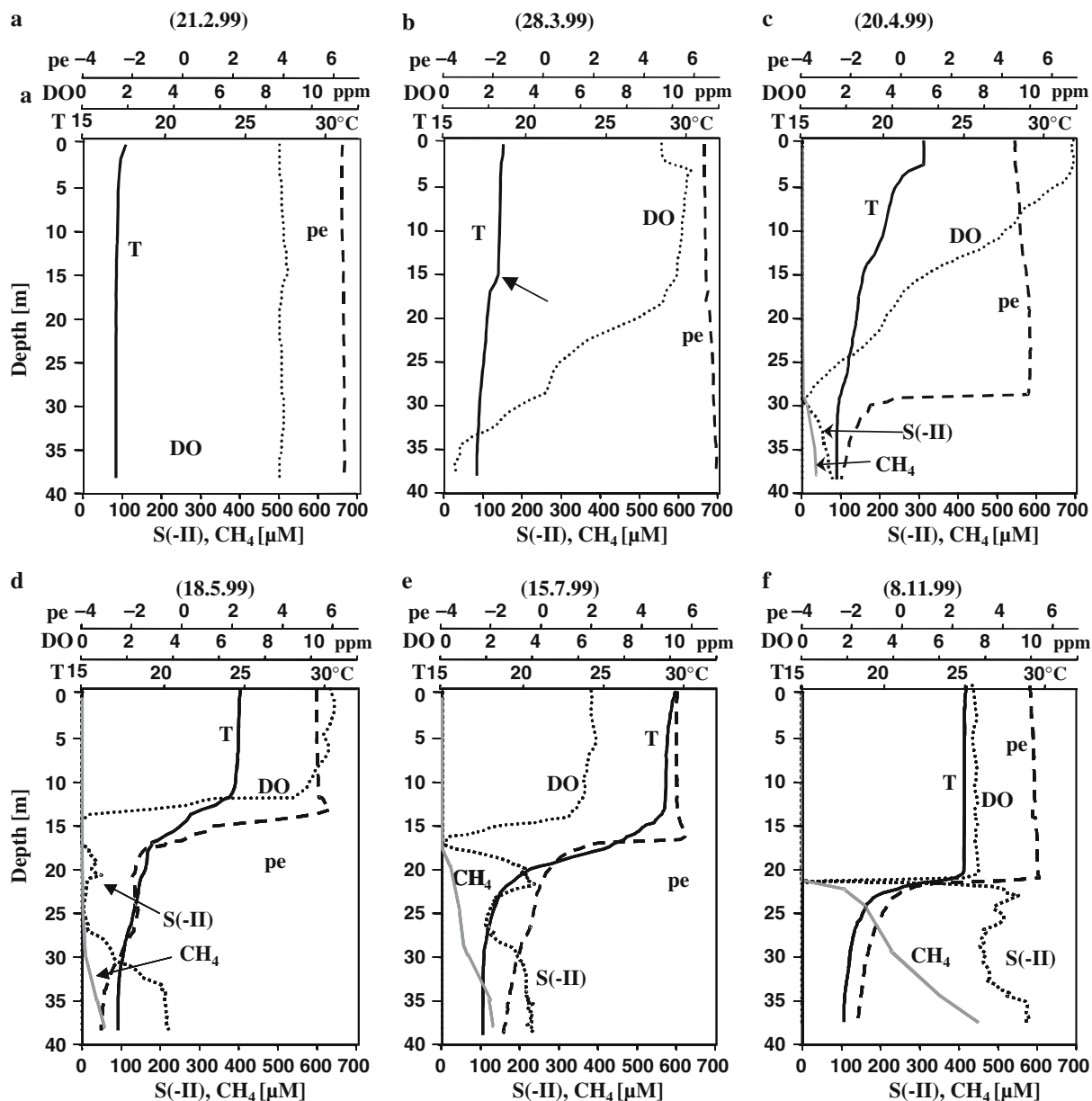
Fig. 1 Profiles of temperature (T), dissolved oxygen (DO), redox intensity (pe), total sulfide (S(-II)) and methane (CH$_4$) measured in the water column of Lake Kinneret at the central station during 1999. (**a**) February 21; (**b**) March 28; (**c**) Aril 20; (**d**) May 18; (**e**) July 15; (**f**) November 8

chemocline separated oxic from anoxic layers with redox intensities dropping from pe 4 to –2. Subsequently, this chemocline rose gradually upwards until mid-May when it reached the depth of the thermocline at about 15 m (Fig. 1d).

With the depletion of hypolimnetic oxygen, S(-II) and CH$_4$(d) increased steadily as shown by the time-change of their concentration profiles (Fig. 1d–f). In the case of CH$_4$(d) near bottom concentrations measured at the central station

increased continuously from April (Fig. 1c) until November 1999 (Fig. 1f) from below 20–450 μ M. In most of the profiles hypolimnetic CH$_4$(d) concentrations decreased linearly from bottom towards the chemocline as further exemplified by our measurements from 1998 (Fig. 2). During the same time interval S(-II) concentrations increased to 580μ M while forming a secondary peak in the metalimnion (Fig. 1 d and e). Towards the end of the stratified season (Fig. 1f) hypolimnetic sulfide concentrations showed a rather uniform distribution (500–600μM).

Regarding both, sulfide and CH$_4$(d), the above-described development was very similar during 1998 and 2000. What varied annually was the timing of the accumulation period, the rate of increase and the established concentration maxima. During the stratified periods of 1998 and 1999, the near bottom concentrations of sulfide and methane showed a nearly identical accumulation pattern with concentration maxima of 390μM sulfide and 410 μM CH$_4$(d) and 600 and 700μM, respectively (Fig. 3). In 2000, methane concentrations remained much lower (max. 280 μM) than those of sulfide (max. 580μM). Hypolimnetic concentrations of both, CH$_4$(d) and sulfide decreased rapidly

Fig. 2 Hypolimnetic profiles of dissolved methane measured during 1998 at the central lake station

upon onset of overturn in November to December and stayed low until March to May.

Another parameter that underwent major changes during the time period of our investigations was the lake level of LK (Fig. 4), which during summers 1999 and 2000 dropped by 1.4 m and 1.9 m, respectively, as a consequence of consecutive drought years in combination with excessive pumping of drinking water. Our data set on the rate of CH$_4$(g) ebullition under the changing hydrostatic pressure conditions (Fig. 4) indicate a prominent increase in July 2000 leading to two ebullition maxima in August (9.5 mmol m^{-2} d^{-1}) and October (8.2 mmol m^{-2} d^{-1}), respectively, before dropping sharply in November. We have to admit however that due to technical problems with our custom-made gas traps the 1999 season is represented by five data points only, which in addition may underestimate gas ebullition rates before November when we changed the trap design.

Gross sedimentation rates derived from the processing of our seston trap material showed a profound seasonal effect (Fig. 5A). Rates measured in the near bottom trap (A40) ranged from 1 to 13 g m^{-2} d^{-1} with values peaking during the time of the winterfloods. In May, sedimentation rates dropped abruptly to ca 1 g m^{-2} d^{-1} in 1998 and 1999 and to ca. 7 g m^{-2} d^{-1} in 2000 when values decreased gradually until November. Analysis of the organic content of settling PM led to an opposite trend with elevated POC concentrations during summer (25 – 40 mmol C gDW^{-1}) and lower concentrations during winter (5–15 mmol C gDW^{-1}, Fig. 5A). Over the three lake cycles average POC concentrations were indistinguishable (16.7 $\pm$ 8.7 in 1998, 20.5 $\pm$ 6.2 in 1999 and 17.3 $\pm$ 8.2 mmol C gDW^{-1} in 2000). Gross sedimentation data measured at A20 (not shown) followed the seasonality of A40. POC concentrations were slightly higher as indicated by the annual averages of 19.4 $\pm$ 7.13 in 1998 and 24.1 $\pm$ 7.1 mmol C gDW^{-1} in 1999. Unfortunately, frequent loss of our sampling equipment forced us to interrupt our sampling scheme at the A20 site in February 2000.
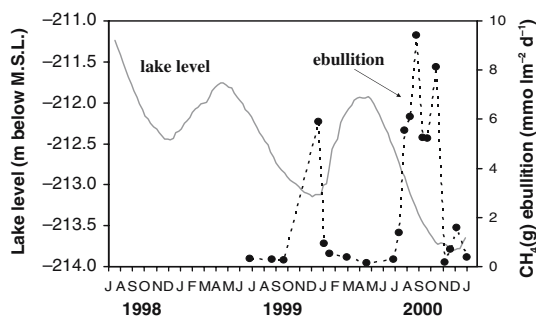
The settling flux of POC (Fig. 5B) at A40 was high during winter and spring (70 – 160 mmol C m^{-2} d^1) and decreased during summer
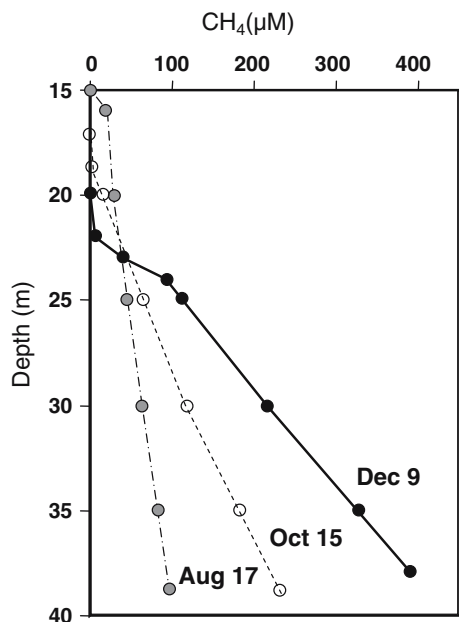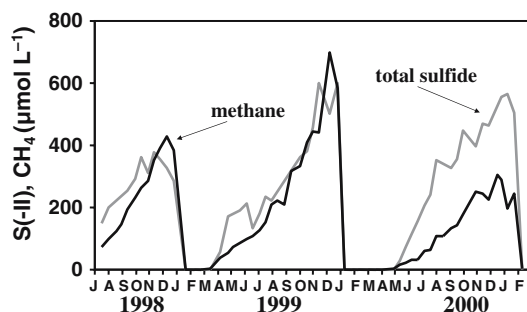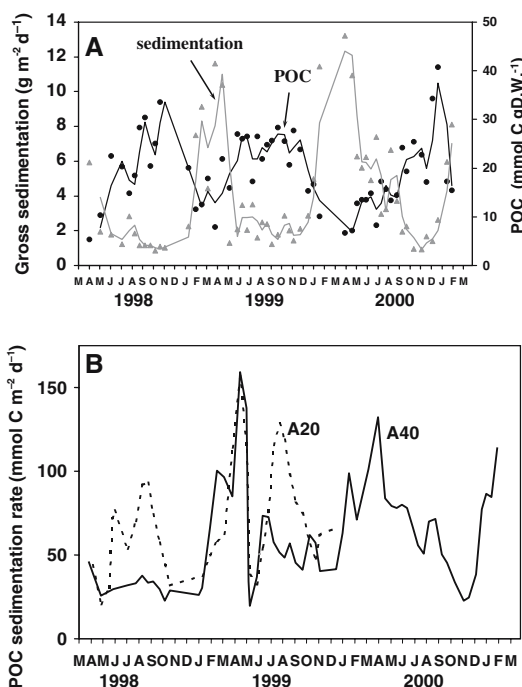
Fig. 3 Time change in near-bottom concentrations of dissolved methane and total sulfide at the central lake station between July 1998 and February 2001. M.S,L. = mean sea level

Fig. 4 Time change of the water level of Lake Kinneret between June 1998 and January 2001 and rates of methane gas ebullition measured 1 m above the bottom at the central lake station between June 1999 and January 2001

Fig. 5 (A) Time change in gross sedimentation rates (Station A40) and the POC concentration in seston material between March 1998 and February 2001. (B) Time change in the sedimentation rates of POC at A20 and A40 between May 1998 and February 2001

Discussion

Our results show that hypolimnetic methane and sulfide accumulation in LK starts in the spring (March until May) following the depletion of dissolved oxygen and lasts until the turnover (December–January, Fig. 3). The upper boundary of the accumulation zone is at all times clearly defined by the chemocline, delineated by the sudden drop in the redox profile (Fig. 1c-f) caused by the presence of sulfide (Eckert and Trüper 1993). The presence of nitrate in LK (< 0.5 mg N l^{-1}) was previously shown to be insignificant for the anaerobiosis in the benthic boundary layer (Fig. 1c) while in the biologically less-active upper hypolimnion it can delay the upward migration of the chemocline by up to one month (Eckert et al. 2002a). As such the sulfide minima in the upper hypolimnion (Fig. 1d–e) are most likely the result of a delay caused by a residual nitrate peak. The sulfide peaks below the oxycline are the result of an enhanced SRB

and fall. Note the relatively low POC flux (25–30 mmol C m^{-2} d^1) during summer 1998 when compared to 1999 and 2000 (50 mmol C m^{-2} d^{-1}). Comparison between the two trap locations indicated higher POC sedimentation rates (≤ 50 mmol C m^{-2} d^1) at A20 during summer (Fig. 5B).

Monthly analysis of subsamples from the uppermost 0.5 cm of bottom sediments from station A reveal POC concentrations between 5 and 10 mmol C gDW^{-1} (Fig. 6) and as such were about four times lower than those measured in the near bottom trap (redrawn in Fig. 6 from Fig. 5A). During the three years of our investigations, POC concentrations in surface sediments followed a distinct seasonality that in 1998 and 1999 corresponded closely to the trend described by the seston POC at A40.
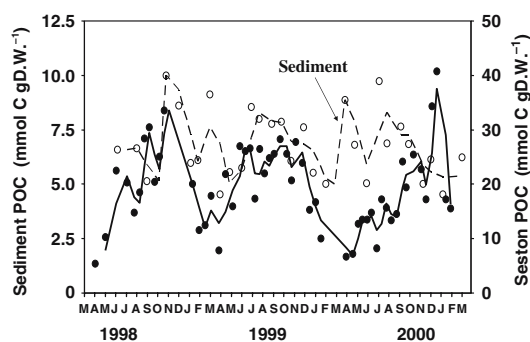
Fig. 6 Time change in the POC concentration in the uppermost sediment layer at the the central lake station in comparison with seston POC concentrations. Note the difference in scales, seston POC = 4 × sediment POC

activity stimulated by the elevated suspended matter concentrations in this zone (Eckert et al. 2002b). This hypolimnetic distribution pattern together with previous findings of enhanced sulfate reduction rates in the uppermost 2.5 (spring)—1.5 (fall) cm of sediments at Station A (Hadas and Pinkas 1992) suggests that the hypo-limnetic distribution pattern of sulfide is the result of sedimentary release in combination with sulfate reduction in the water column.

Due to the lasting presence of sulfate (Hadas and Pinkas 1995) methanogenic activity in the water column of LK is unlikely. Similarly, meth-ane consumption in the anoxic hypolimnion can be excluded because of the absence of suitable electron acceptors for methanotrophic bacteria. Consequently, the observed linear hypolimnetic $CH_4(d)$ distribution (Fig. 1c–f, Fig. 2) can be ex-plained by sedimentary release and turbulent diffusion (Rimmer et al. 2006). Similar observa-tions from other lakes, such as Lake Baldegg (Imboden et al. 1983), Lake George (Bédard and Knowles 1997) and Lake Plußsee (Nüsslein and Conrad 2000) confirm this conclusion. Small local deviations from the linearity can be attributed to horizontal advection as the predominating physi-cal process in the hypolimnion of LK (Eckert et al. 2002a).

Near-bottom concentrations of both sulfide and $CH_4(d)$ increased throughout the stratified period (Figure 3), indicating a continuous sedi-mentary release. For the case of sulfide it was shown previously that the multi-annual variability

in concentration maxima can be related to the length of the stratification period (Hadas and Pinkas1995; Eckert and Hambright 1996). The same seems to hold for $CH_4(d)$ when in 1999 the accumulation period began already in March lasting two months longer than in 1998 and 2000. Near bottom concentrations peaks of $CH_4(d)$ and S(-II) were the highest in that year with 700 and 600μ M, respectively. While in 1998 and 1999 the concentration increase was nearly identical for both solutes, in 2000 $CH_4(d)$ concentrations apparently lagged behind throughout summer and fall reaching only half of those for sulfide. On the other hand our data set on gas ebullition (Fig. 4) indicate for 2000 an increased flux of outgasing $CH_4(g)$. This observation, that to some extent may explain for a reduced $CH_4(d)$ release, is possibly related to a critical decrease in hydraulic pressure during the drop of the water level of LK in 2000 by nearly two meter. The sharp concentration drop observed in winter each year denotes the time point of mixis when oxygen became available and both methane and sulfide were readily oxidized. While sulfide was never detectable above the chemocline, epilimnetic $CH_4(d)$ concentrations (not shown) varied between 0.1 and 0.5 μ M with a distinct peak of ca. 1μM in the aftermath of the turnover.

In order to elucidate the differential impact of MM and SRB on anaerobic carbon mineraliza-tion during the stratified period we have com-pared the cumulative POC flux to the sediment with the depth-integrated hypolimnetic methane and sulfide concentrations, both expressed as carbon equivalents mineralized (Fig. 7). From April to October the dissolved methane inven-tory increased from near zero to values corresponding to 7.3 ± 0.4 mol C m^{-2} in 1998, 8.1 ± 0.1 mol C m^{-2} in 1999 and 5.4 ± 0.8 mol C m^{-2} in 2000. These figures include the amount of $CH_4(d)$ oxidized at the chemocline as estimated from the theoretical extension of the hypolim-netic concentration profile into the eplimnion. Accumulation rates similar to those in LK were observed by Bédard and Knowles (1991) in Lake St. George. The accumulating $CH_4(d)$ accounted for a large part of the carbon supplied by the sedimentation of POC (Fig. 7). However, the accumulation rates of sulfide generally accounted
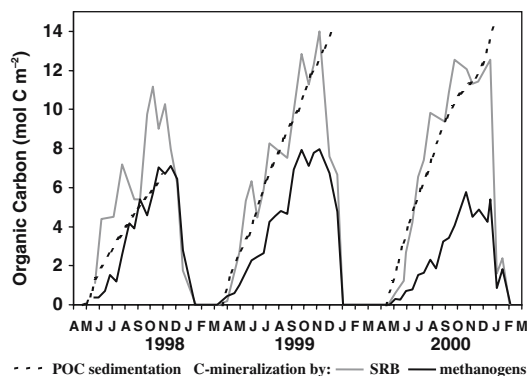
Fig. 7 Comparison of the seasonal accumulation patterns of dissolved methane and total sulfide (expressed in C-equivalents) at the central lake station with the settling particulate organic carbon between 1999 and 2000

for an even larger part, i.e. 11.2 ± 1.0, 12.9 ± 1.2 and 12.6 ± 1.1 mol C m^{-2} a^{-1} for 1998, 1999 and 2000, respectively (Fig. 7). Hence, overall methanogenesis seems to play only a secondary role in the final carbon mineralization process when compared to sulfate reduction. In fact, SRB-driven carbon mineralization corresponded closely to the sedimentary settling flux of POC during the stratified period (Fig. 7).

Further evidence for the dominant role of sulfate reduction in LK can be derived from the observed POC concentration difference between sediment trap material collected at A40 (20 ± 7.3 mmol C gDW^{-1}) and the uppermost sediment layer (6.92 ± 1.64 mmol C gDW^{-1}, Fig. 6) that allows for the conclusion that settling POC is mineralized to a great extent at the SWI. Furthermore, analysis of sedimentary POC concentrations down to a depth of 25 cm (Eckert, unpublished data) revealed a prominent decrease of POC in the upper 3 cm to 4.5 mmol C gDW^{-1} coinciding with the depth of the sulfate boundary (Hadas and Pinkas 1992). In-between 3 and 15 cm sediment depth, POC concentrations decreased gradually before stabilizing at 3 mmol C gDW^{-1}.

In order to evaluate the role of anaerobic carbon mineralization by methanogenesis and sulfate reduction for the annual carbon budget more precisely, we have compared annual POC sedimentation fluxes, measured at stations A20 and A40, with the accumulated sum of dissolved and gaseous methane and SRB-C$_{org}$-equivalents

(Fig. 8). Analysis of our 1998 and 1999 trap data indicates that from the POC that crossed the thermocline, ca. 4 mol were mineralized in the hypolimnion corresponding to 17–23% of the total POC sedimentation flux. Hypolimnetic sulfide accumulation by SRB accounted for 61–67% of the total POC input measured at station A20, i.e. at the top of the hypolimnion. Sedimentary sulfate reduction corresponded to approximately 7 mol, a figure that fits well into the range (6.2 ± 2.0 mol C m^{-2} a^{-1}) measured in the years 1988 and 1989 by Hadas and Pinkas (1995). Together with the accumulation of methane the total amount of organic carbon mineralized anaerobically in the hypolimnion and the sediment was fairly balanced with the total POC input in 1998 and 1999 (Fig. 8). In 2000 by contrast the POC input to the sediment (A40) exceeded the total anaerobic carbon mineralization in the sediment and the hypolimnion. Possibly, not all of the freshly sedimented POC was mineralized in 2000 and instead would possibly increase anaerobic mineralization rates in the following year. Such behavior would also explain the slight imbalances between POC sedimentation and total carbon mineralization observed between 1998 and 1999 (Fig. 8). Despite these small imbalances, our investigation nevertheless justifies the general conclusion that sulfate reduction is the dominant mode of terminal carbon mineralization in Lake Kinneret most likely as a result of its—for a freshwater lake—elevated sulfate concentrations
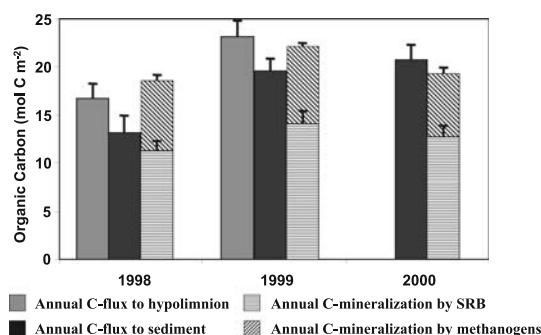
Fig. 8 Annual fluxes of particulate organic carbon to the hypolimnion (20 m) and to the sediment (40 m), accumulated total sulfide (in C-equivalents) and dissolved methane at the central station of Lake Kinneret during 1998–2000

in combination with high microbial activity at the SWI where temperatures never drop below 14°C.

In conclusion, our study has demonstrated that even in a freshwater lake sulfate reduction can account for most of the anaerobic mineralization of POC. Sulfate reduction operated in the sediment as well as the hypolimnetic water column, whereas methane production was restricted to the sediment. The accumulation of methane and sulfide was directly related to the thermal structure of the lake and the development of the chemocline. Collapse of the thermal stratification by the winter overturn resulted in rapid oxidation of both CH_4 and sulfide.

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