Methane cycling in the sediments of Lake Washington

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Abstract

Aerobic oxidation is important in the cycling of methane in the sediments of Lake Washington. About half of the methane flux from depth is oxidized to CO_2 in the upper 0.7 cm of the sediments and the remainder escapes into the water column. In terms of the total carbon budget of the lake, the upward flux of methane is insignificant with only about 2% of the carbon fixed by primary production being returned as methane. The upward flux of methane, however, does represent about 20% of the organic carbon decomposed within the sediments. In addition, methane oxidation consumes 7–10% of the total oxygen flux into the sediments. Measured kinetic parameters suggest that methane oxidation is restricted to the top 6–7 mm of sediment where oxygen is present and that the rate of this process is probably controlled by the concentration of methane.

As an end product in the degradation of organic carbon, methane is an important component in the carbon cycle of freshwater environments. Although methane is produced anaerobically, the primary removal mechanism is thought to be aerobic oxidation (Rudd and Taylor 1980). Most previous studies of methane cycling in lakes have been done at locations with permanently or seasonally anoxic hypolimnia. These studies have shown that most of the methane consumption occurs within the water column (Rudd and Taylor 1980). In two African rift lakes with permanently anoxic hypolimnia (Kivu and Tanganyika), methane is transported primarily by diffusion to the anaerobic–aerobic interface in the water column where it is completely oxidized (Degens et al. 1973; Jannasch 1975.

Well-studied lakes with seasonally anoxic hypolimnia include Lake 227 in the Canadian Experimental Lakes Area, Lake Mendota, and three small lakes in Michigan (Frain's, Third Sister, and Wintergreen). Methane consumption is important in both the carbon and oxygen cycles of Lake 227, but oxidation is highly episodic with >95% of the annual methane oxidation occurring during and just after overturn (Rudd et al. 1976). Cycling of methane is less seasonal in Lake Mendota with only 45% of the annual methane consumption taking place during summer stratification (Fallon et al. 1980). In addition to oxidation, ebullition from the sediments and exchange of methane across the air–water interface can account for significant loss to the atmosphere, especially in some shallow lakes (Strayer and Tiedje 1978; Barber and Ensign 1979; Robertson 1979). By comparison, there have been fewer studies of sedimentary organic matter diagenesis or the methane cycle in oligotrophic lakes.

In this study we examine the importance and ultimate fate of methane in the carbon cycle of Lake Washington. Unlike most lakes studied previously, this lake is relatively deep, with oxygen always present in the hypolimnion. Consumption of methane occurs primarily within the sediments (Kuivila and Murray 1984; Lidstrom and Somers

1984) where sedimentary aerobic reactions are restricted to a narrow oxygenated zone. The absence of ebullition tends to close the methane cycle within the sediments of the lake. Here we use concentration profiles and measured fluxes of methane and oxygen to quantify the cycling of methane within the sediments of Lake Washington. The calculated rate of methane oxidation is then incorporated into the carbon balance of the lake and the sedimentary oxygen cycle to determine the relative importance of this process. Finally, the measured kinetic parameters of the aerobic methane oxidation reaction are used to identify the factors controlling the location and rate of methane oxidation.

Methods

Study site—Lake Washington is a monomictic, mesotrophic freshwater lake adjacent to Seattle. Previous studies of the lake include investigations of primary productivity (Edmondson 1972; Devol and Packard 1978), nutrient cycling (Lehman 1978; Devol 1979; Edmondson and Lehman 1981), trace metal cycling (Murray 1987), ecology (Eggers et al. 1978; Edmondson and Litt 1982), sedimentary processes (Thut 1969; Edmondson and Allison 1970; Shapiro et al. 1971; Birch et al. 1980), and the overall carbon cycle (Kuivila and Murray 1984; Quay et al. 1986). Nearly all of these studies, as well as the one presented here, have been conducted at a 62-m-deep station in the central lake basin (*see* Kuivila and Murray 1984).

Flux measurements and box coring— Measurements of the exchange of solutes between the sediments and the bottom waters (benthic fluxes) were made in situ with the tripod described by Devol (1987). The tripod consists of an aluminum frame within which two stainless steel boxes (412 cm^2 each) are mounted on a movable tray. After the tripod is lowered to the bottom, the box cores or flux chambers are partially implanted into the sediments. Lead weights supply the driving force, and the rate of penetration is hydraulically damped.

During this coring operation both the tops and bottoms of the chambers are open. The

lids for the flux chambers, which are mounted on hinged arms attached to the movable tray, are closed 10–20 min after implantations, isolating a volume of overlying water. All in situ operations are accomplished by dissolving-link releases that are fully programmable. Time-series samples of overlying water in the flux chambers are taken with spring-actuated 50-ml syringes. Mounted in line between the syringes and the lids are calibrated loops (~4 ml) used to take samples for dissolved gas analysis. Water withdrawn from the flux chambers during sampling (5–10% of the total volume) is replaced with bottom water. After all the samples are taken, the box-core shovels are closed and the tripod retrieved. Once on deck, the six-port rotary valves containing the gas sample loops are closed to the atmosphere and stored in icewater until analysis.

Benthic fluxes were measured in Lake Washington on two occasions—February and October 1983. Deployment times were about 15 h, and samples were withdrawn at approximately 3-h intervals. Overlying water volumes varied between 0.9 and 1.6 liters. Visual inspection after retrieval revealed no apparent disturbance to the sediment–water interface.

Because the tripod is capable of taking box cores with an extremely well-preserved sediment–water interface and because the aerobic layer within the sediments was known to be on the order of 1 cm thick (Kuivila and Murray 1984), the tripod was also used to obtain samples for oxygen microelectrode profiling, determination of detailed methane concentration gradients, and measurement of the kinetic parameters of aerobic methane oxidation. These samples were taken in March 1984. When the tripod was used for coring, only the implantation and lid and shovel closure functions were programmed. Thus, each box core could be subcored and sectioned or profiled within a few hours of deployment.

Dissolved gas analysis—Dissolved oxygen profiles in the sediment pore water were measured in March 1984 with a double-junction microelectrode similar to that described by Revsbech (1983) except that the outer glass capillary was formed from only

one piece of Na-lime glass, and the upper glass-glass-epoxy junction was wrapped in electrical, heat-shrink tubing (Reimers unpubl. design). The sampling procedure was similar to that described in detail by Reimers et al. (1984). The two profiles reported are from a single tripod subcore that was placed in a temperature-controlled water bath (10°C) and analyzed within 2 h of retrieval. For these determinations, 5 cm of overlying bottom water was retained in the subcore. The electrode was lowered stepwise through the overlying water into the sediment, with the sediment surface taken as the first significant decrease in current (Revsbech et al. 1980). As the microelectrode output is strictly linear, it was calibrated with two points, the anoxic layers of the sediment (output 3–4 pA) and the overlying water (output 575–580 pA). The oxygen concentration in the overlying water was determined by micro-Winkler titration of replicate 5-ml samples (Strickland and Parsons 1968).

Samples for the dissolved pore-water methane analyses (also sampled in March 1984) were obtained by extruding and sectioning a subcore in 0.5-cm intervals in a N_2-purged glove bag within 3 h of sampling. Screwcap centrifuge tubes were filled completely with sediment and centrifuged for 10 min. The pore water was then drawn into 1-ml nylon gas-sample loops and stored submerged in icewater for subsequent analysis by gas chromatography. The greatest potential loss of methane was by gas exchange between when the sediment sample was centrifuged and before the interstitial water was transferred into the sampling loop. Therefore, this step was done as quickly as possible.

The methane was stripped from the sample in a closed system with a helium flow of 100 ml min^{-1} that was routed directly into a Hewlett-Packard gas chromatograph. Methane was separated from other gases on a Molecular Sieve 5A column (100–120 mesh, 6.4 mm × 1.8 m) at 60°C. The flame ionization detector was operated with a H_2 flow of 100 ml min^{-1} and an air flow of 400 ml min^{-1}. The detection limit for methane was 40 nM. The time series of gas samples from the tripod flux chambers was analyzed

with the same system. In this case, however, O_2 plus Ar was first measured with a thermal conductivity detector, then the gas stream flowed directly in series to a flame ionization detector for methane analyses. The thermistor detector was operated at 25°C for maximal sensitivity. Precision of the oxygen analysis was ±5% (2 σ) with a detection limit of 20 μM.

Kinetic parameters—Michaelis-Menten kinetic parameters for methane oxidation were estimated from ^{14}C-labeled methane incubation experiments (March 1984). The $^{14}CH_4$ used for these experiments was synthesized microbiologically (Daniels and Zeikus 1983) and had a specific activity of 5 × 10^5 dpm μmol^{-1}. Samples for measurement of methane consumption rate were taken from two different depths: the interfacial "fluff" layer and the underlying centimeter of sediment.

Sediments were placed in 50-ml Hungate tubes, stoppered, and stored on ice (<2 h) until the incubation experiments began. Bottom water that had passed through a 0.2-μm Millipore filter was then added to the sediment sample to make a 1:1 (vol:vol) slurry, after which different samples were spiked with $^{14}CH_4$, unlabeled CH_4, and O_2 (as air) in varying amounts and incubated at 10°C with continous shaking. At various times, a 1-ml subsample of the slurry was withdrawn by syringe for measurement of the amount of $^{14}CO_2$ and ^{14}C cell material that had been produced. The $^{14}CO_2$ was determined by counting after acidification and adsorption onto phenethylamine-impregnated filters; ^{14}C cell material was measured by counting a portion of the acidified slurry that had been purged with N_2 gas. Rates, calculated as total CO_2 and cell material produced, were determined from the linear portion of the time-course (detection limit of 0.05 μmol liter^{-1} h^{-1}). The details of the recovery and counting procedures are given elsewhere (Lidstrom and Somers 1984).

Results

The oxygen concentration in the water overlying the sediment subcores was 310 μM at the time the microelectrode profiles were measured. Oxygen concentrations in the sediments decreased rapidly with in-
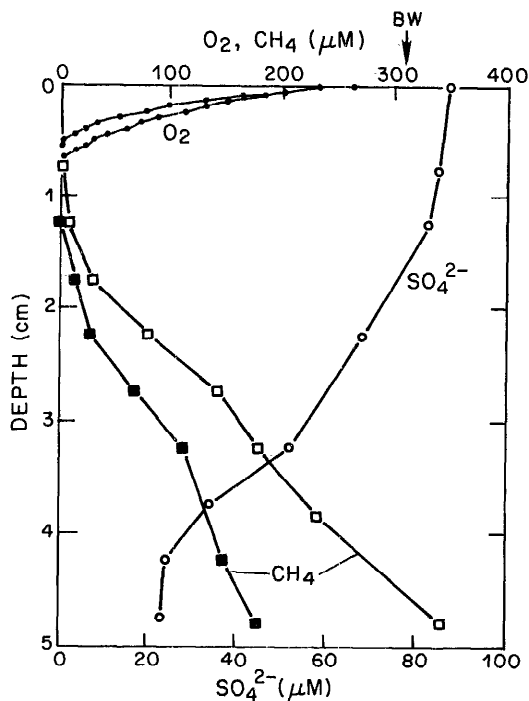
Fig. 1.   Profiles of oxygen, sulfate, and methane in the pore waters of the top 5 cm of the sediments of Lake Washington.

creasing sediment depth and undetectable levels were encountered at depths of 6–7 mm (Fig. 1). The sulfate profile suggests that sulfate reduction began below about 1.5 cm. This suggestion was confirmed by direct rate measurements (Devol unpubl. data) that showed significant sulfate reduction rates below 4.5 cm in the sediments. Methane concentration in the water overlying the core was 600 nM and remained low throughout the oxygenated zone but appeared to increase linearly with depth below the oxygenated zone.

During each of the two benthic flux deployments replicate fluxes were measured. The volume of the overlying water varied, and thus the concentration changes with time cannot be compared directly. The measured concentrations do illustrate (Figs. 2 and 3) the magnitudes of the changes observed within the boxes. The fluxes were calculated by dividing the rate of change of the absolute number of moles by the volume and area of the box. The bottom-water

oxygen values, determined from hydrocasts, were 319 μM in February and 198 μM in October. In all cases, oxygen decreased systematically during the 15-h period. In February (Fig. 2A), the resulting oxygen fluxes (with their 95% C.L.) in the two chambers were equal to 5,380±1,520 and 5,870±2,580 μmol m^{-2} d^{-1}. In October the bottom-water oxygen concentration was lower, but the measured fluxes were not significantly different, 4,430±870 and 4,800±2,540 μmol m^{-2} d^{-1}. Methane, on the other hand, increased within the chambers from bottom-water values of 0.55 μM in February and 0.69 μM in October to porewater values as high as 9 μM. The measured replicate fluxes of methane out of the sediment were also similar at the two different sampling dates: 233±62 and 196±61 μmol m^{-2} d^{-1} in February and 311±152 and 311±112 in October.

The Michaelis-Menten kinetic parameters of the methane oxidation reaction (the half-saturation constant, K_m, and the maximal rate, V_{max}) were determined from Lineweaver-Burk linearization of the experimental data (Fig. 4). In such plots, the slope equals K_m/V_{max} and the intercept equals $1/V_{max}$. The experimentally determined K_m values (with their respective 95% C.L.) for CH$_4$ were 5.1±2.1 μM for the interfacial fluff layer and 10.0±7.0 μM for the underlying 1-cm sediment layer. The 95% C.L. for these values overlap suggesting that they are not statistically different. The corresponding V_{max} values were 29.7±11.3 and 26.4±18 μmol liter^{-1} h^{-1} for the two different depths. Within the 95% C.L., V_{max} is the same in both layers. Similar results were found by Lidstrom and Somers (1984) for the top 1 cm of sediment in May and June 1983 with K_m values for methane between 8.3 and 10.7 μM and V_{max} values between 33 and 43 μmol liter^{-1} h^{-1}. These K_m values for CH$_4$ are in the same range as those reported for pure cultures of methanotrophs (Joergensen and Degn 1983).

Lidstrom and Somers (1984) also determined the kinetic parameters for oxygen in the aerobic methane oxidation reaction. In the top 1 cm of sediment, the K_m value for O$_2$ was between 17 and 25 μM and the V_{max} was between 33 and 57 μmol liter^{-1} h^{-1} (Lid-
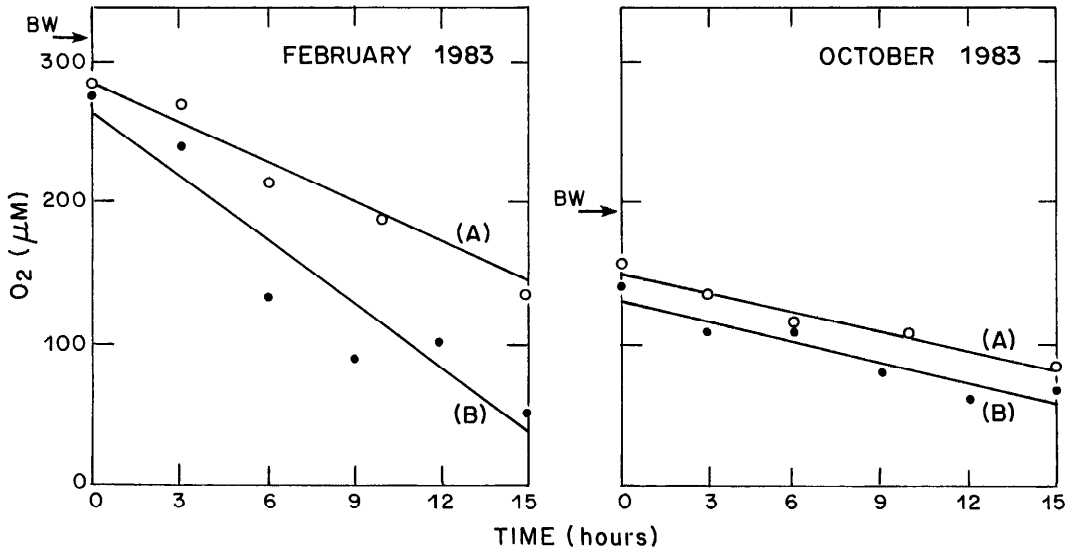
Fig. 2.   Dissolved oxygen vs. time in the two chambers of the benthic flux tripod deployed in Lake Washington in February 1983 and October 1983. The lines represent least-squares fits and the corresponding values of r^2 are: February—A, 0.980; B, 0.940; October—A, 0.990; B, 0.934.

strom and Somers 1984). The ratio of the oxygen to methane utilization was calculated to be 1.5–1.7 (data not shown). This value agrees well with pure culture utilization ratios (Joergensen and Degn 1983).

Discussion

Methane flux balance—In freshwater lakes with anoxic hypolimnia, methane produc-

tion and oxidation are frequently significant parts of the total carbon cycle. For example, in Lake 227, 55% of the total carbon input is regenerated as methane, the oxidation of which occurs almost exclusively during and just after fall overturn when two-thirds of the methane produced during the year is consumed (Rudd and Hamilton 1978, 1979). Similarly, 54% of the carbon reach-
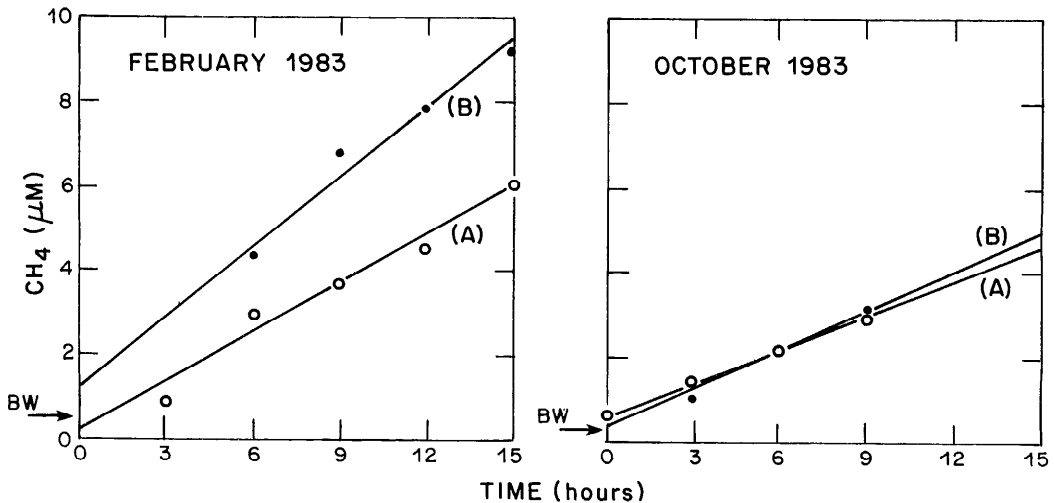

Fig. 3.   As Fig. 2, but of dissolved methane vs. time. The corresponding values of r^2 are: February—A, 0.984; B, 0.983; October—A, 0.979; B, 0.988.
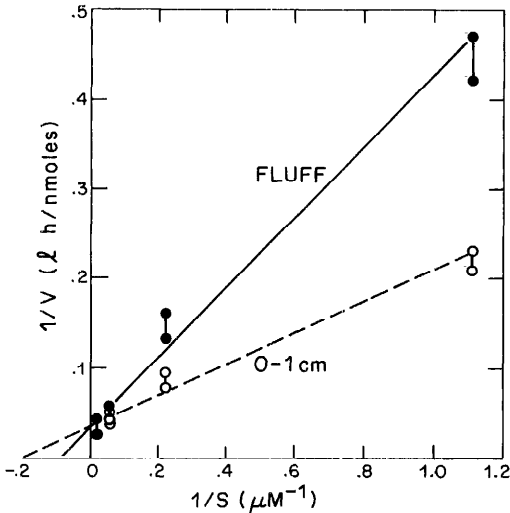
Fig. 4.   Kinetics of methane oxidation in sediment samples from the fluffy surficial layer (●) and the top 1 cm of sediment (○) from Lake Washington. Results are shown as a double reciprocal (Lineweaver-Burk) plot of methane oxidation at different methane concentrations. The lines represent least-squares fits to the data and the r^2 values are 0.992 for the fluff layer and 0.989 for the top 1 cm.

Fig. 5.   Schematic diagram showing the main pathways of CH_4 cycling in the aerobic zone of the sediments of Lake Washington.

ing the sediments in Lake Mendota was converted to methane (Fallon et al. 1980), although it was oxidized throughout the entire year. Evasion rates (as a percentage of methane production) to the atmosphere are only 8% for Lake Mendota and 5% for Lake 227. In both of these environments, methane production and oxidation are significant in comparison to the total carbon input. In contrast, the hypolimnion of Lake Washington is well oxygenated throughout the year, so it might be expected that methane production may not be very large and that methane oxidation within the sediments would be more significant.

The importance of methane oxidation in the carbon and oxygen cycles of Lake Washington was investigated by constructing a methane flux balance for the aerobic zone of the sediments (Fig. 5 and Table 1). The dominant processes affecting the concentration of methane within the aerobic zone are the rates of supply of oxygen and methane, the rate of methane oxidation at or near the interface, and the loss of methane to the overlying water column. The input rate to the sedimentary aerobic zone can be esti-
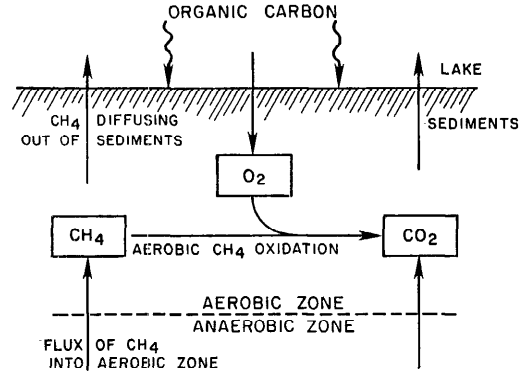
mated from the pore-water methane profile; the escape rate of methane to the overlying water column can be measured directly with the benthic tripod. The difference between the supply of methane to the aerobic layer and the escape rate to the water column is equal to the methane oxidation rate within the aerobic zone of the sediments. The oxygen flux into the sediments can be estimated both from the microelectrode profiles and from the directly measured benthic tripod fluxes. The kinetic parameters of the oxidation reaction can be used to determine which factors control the activity of the methanotrophs and also to provide an independent estimate of the methane oxidation rate.

The flux of CH_4 up to the aerobic layer was calculated with Fick's first law:

$$J_s = -\phi D_s \, \partial C/\partial z \qquad (1)$$

where J_s is the diffusive flux in the sediment, ϕ the porosity, D_s the sediment diffusion coefficient, and $\partial C/\partial z$ the measured methane concentration gradient. The bulk solution diffusion coefficient, corrected for porosity and tortuosity (Lerman 1979), yielded a D_s value of 9.36×10^{-6} cm^2 s^{-1}.

The methane concentration profiles in the sediment have been measured at this site eight different times between 1980 and 1984 with no apparent seasonal variability in the calculated upward methane flux from the anaerobic zone (Kuivila and Murray 1984; unpubl. data). The average measured meth-

Table 1. Quantitative estimates of methane cycling within the sediments of Lake Washington.

Process	Reaction rate (μmol m^{-2} d^{-1})	
Details within the methane cycle		
Avg flux of CH$_4$ into the aerobic zone calculated from CH$_4$ profile, assuming molecular diffusion	560±130	
CH$_4$ diffusing into water column measured with the benthic tripod	210±60	Feb 1983
	310±130	Oct 1983
CH$_4$ oxidation rate—calculated difference between flux into and out of aerobic zone	250–350	50% of CH$_4$ flux
Integrated CH$_4$ oxidation rate calculated from kinetics of oxidation reaction and CH$_4$ and O$_2$ profiles	340 740	
Details within the total carbon cycle		
Avg primary production (annual avg d^{-1})	36,000	
Sediment trap flux to the sediments*	12,500	
Burial rate of organic C calculated from sedimentation rate and % organic C in sediments†	9,400	75% of sediment trap flux
Regeneration of carbon in the sediments—difference between input and burial	3,100	25% of trap flux
Regeneration of carbon in the sediments calculated from the average oxygen flux minus CH$_4$ oxidation	4,106	33% of trap flux
Methane production calculated from CH$_4$ profiles‡	560	5% of trap flux

* Barnes 1976; W. T. Edmondson pers. comm.
† Sedimentation rate, 3.1 mm yr^{-1} (Edmondson and Allison 1970), 5.3% organic C in the sediments (Kuivila and Murray 1984).
‡ Calculated flux (molecular diffusion) from measured profiles.

ane gradient for this set of eight profiles was 76±10 nmol cm^{-4}. The lack of significant temporal variability is not surprising considering that the upward methane flux is the result of relatively slow methane production occurring over an interval of about 15 cm, deep below the sediment–water interface (Kuivila 1986). The measured average methane gradient resulted in a calculated flux of methane into the aerobic zone of 560±130 μmol m^{-2} d^{-1}. In contrast, the fluxes of methane into the hypolimnion, as directly measured with the benthic tripod, were only about half this value or 210±60 and 310±150 μmol m^{-2} d^{-1} (February and October 1983, respectively).

The flux of methane into the aerobic zone minus the flux of methane into the overlying water column yields the amount consumed within the sediments. Thus, the estimated rate of methane oxidation ranged from 250 to 350 μmol m^{-2} d^{-1} (Table 1). So, in terms of a methane flux balance, about half (45–62%) of the upward methane flux is oxidized within the narrow aerobic zone in the sediments.

The methane components of the carbon cycle calculated here can be put into the context of the total carbon budget for Lake

Washington (Table 1). Kuivila and Murray (1984) calculated that about 75% of the sedimenting organic carbon (9,400 μmol m^{-2} d^{-1}) is permanently buried and the remaining 25% (by difference), i.e. 3,100 μmol m^{-2} d^{-1}, must be regenerated, mostly by aerobic respiration. The direct estimate of carbon regeneration from the oxygen flux corrected for methane oxidation is 33% of the sediment trap flux or 4,106 μmol m^{-2} d^{-1}. The average flux of methane from the deeper anaerobic zone (560 μmol m^{-2} d^{-1}) is equal to about 2% of the primary productivity, 5% of the sediment trap flux, or about 20% of the regenerated organic matter. Methane is known to play an important role in the carbon cycle of lakes with anaerobic hypolimnia. Here we show that in a lake with an aerobic hypolimnion, methane is not only unimportant in the total carbon cycle, it also only amounts to about 20% of the decomposing organic matter in the sediments. Furthermore, aerobic methane oxidation within the top 7 mm of the sediments consumes about half of the upward methane flux, leaving only 10% of the decomposing organic carbon to escape the sediments as CH$_4$.

*Importance of methane oxidation in the sediment oxygen cycle—*Methane oxidation

is also important in the O_2 cycle of many lakes. In Lake 227, methane oxidation is thought to be the most important factor in hypolimnetic oxygen consumption, at times producing whole-lake anoxia after formation of ice cover in the winter (Rudd and Hamilton 1978, 1979). Mayer et al. (1982) calculated that methane oxidation in Lake Sebasticook, a hypereutrophic, dimictic lake in Maine, constituted 65% of the hypolimnetic oxygen demand during summer stagnation. In Pluß See this reaction accounted for 70% of the oxygen consumption (Anagnostidis and Overbeck 1966, *cited by* Golterman 1976).

In Lake Washington, oxygen fluxes measured directly by the tripod flux chambers in February 1983 ($5,600\pm2,000$ μmol m^{-2} d^{-1}) did not vary significantly from those measured in October 1983 ($4,600\pm1,200$ μmol m^{-2} d^{-1}) even though the bottom-water oxygen concentration was 319 μM in February compared to only 198 μM in October. The typical yearly range for oxygen concentration in the bottom water of Lake Washington is from $\sim$145 μM during the fall stratification to $\sim$360 μM during the spring bloom (Edmondson 1963). The lack of significant difference between the oxygen fluxes measured in February and October, even though the bottom-water oxygen concentrations were nearly at their yearly maximum and minimum at these two times, suggests that there may be little seasonal variability in the oxygen flux to the sediments. This constancy could be due to rapid resupply of oxygen to the water overlying the sediments and the high consumption rate of oxygen in the surface sediments (which creates the steep oxygen gradient).

The oxygen flux into the sediments can also be calculated from the two microelectrode profiles (March 1984), assuming Fickian diffusion (Eq. 1), and that bioturbation, irrigation, and other nondiffusive exchange processes are negligible. The sediment diffusion coefficient, after correction for porosity and tortuosity (Lerman 1979), was taken as 15.0×10^{-6} cm^2 s^{-1} (at 10°C). Calculated oxygen flux into the sediment equaled 8,800 and 4,300 μmol m^{-2} d^{-1} for the two microelectrode profiles. Benthic organisms, such as chironomids and tubi-

ficids, that could significantly enhance solute exchange between the interstitial and overlying water are commonly observed in Lake Washington sediments (W. T. Edmondson pers. comm.). Good agreement between the average calculated fluxes (6,550 μmol m^{-2} d^{-1}) and the average of those measured directly with the tripod (5,100 μmol m^{-2} d^{-1}) suggest, however, that irrigation is unimportant at our study site, at least within the error limits of these measurements and that molecular diffusion is the primary transport mechanism for oxygen. If we assume that methane oxidation consumes 1.6 mol of oxygen for every mole of methane, the rate of oxygen consumption can be calculated from the previously estimated rate of methane oxidation (250–350 μmol m^{-2} d^{-1} from Table 1) as 400–560 μmol O_2 m^{-2} d^{-1}. It is equal to 7–10% of the total oxygen flux into the sediments.

Factors controlling methane consumption—Various factors appear to control the location and activity of methanotrophs among different environments. Rudd and Hamilton (1978, 1979) concluded that in Lake 227 the combination of fixed nitrogen and oxygen requirements placed restrictions on the methane oxidation reaction. Under low dissolved inorganic nitrogen conditions, the methanotrophs fixed N_2 and were sensitive to high concentrations of oxygen, confining them to a narrow zone within the thermocline. Their activities thus were limited during most of the year when the lake was stratified; methane oxidation was only widespread during fall overturn. In comparison, methanotrophs in Lake Mendota (Harrits and Hanson 1980) were also restricted to a narrow band, but in this case methane oxidation occurred at a rate dependent on the methane concentration in aerobic waters. Laboratory experiments suggested that high oxygen concentrations or addition of inorganic nitrogen did not affect the rates of methane oxidation in Lake Mendota sediments (Harrits and Hanson 1980).

These previous studies have focused on water-column processes. In Lake Washington, however, little if any methane oxidation occurs within the water column (Lidstrom and Somers 1984). Methane oxidation

occurs within the top 6–7 mm of the sedi-
ments, limited to the region where methane
and oxygen co-occur. The concentration of
dissolved nitrogen species in this zone is
high enough that the methanotrophs are
probably not fixing N_2 as in Lake 227 (Rudd
and Hamilton 1978, 1979; Kuivila and
Murray 1984; Lidstrom and Somers 1984).
The measured O_2 concentration was signif-
icantly above the range of estimated K_m (17–
25 μM) (Lidstrom and Somers 1984) for the
methane oxidation reaction throughout
most of the aerobic zone in the sediments
(Fig. 6). If the methane oxidation reaction
was not restricted to the lower boundary,
then oxygen concentration should not be the
major factor limiting the rate of methane
oxidation. Oxygen values are important,
however, for delineating the deepest depth
for occurrence of aerobic methane oxida-
tion in the sediments. In contrast, the mea-
sured methane concentrations within the
aerobic layer were well below the range of
K_m values (5–10 μM) for methane (Fig. 6).
This finding implies that the concentration
of methane probably limits the actual rate
of methane consumption throughout most
of the aerobic layer in the sediments, similar
to the situation in Lake Mendota (Harrits
and Hanson 1980).

An independent estimate of the integrat-
ed oxidation rate of methane in Lake Wash-
ington sediments was also calculated with
the experimentally measured kinetic pa-
rameters, K_m and V_{max}. The methane oxi-
dation reaction was assumed to follow Mi-
chaelis-Menten kinetics (*see* Conrad 1984)
and, based on the above discussion, was
simplified to be methane limited, so that its
rate, R, could be calculated from the expres-
sion

$$R = V_{max}[CH_4]/([CH_4] + K_m). \quad (2)$$

The narrow aerobic zone in Lake Wash-
ington sediments (~7 mm thick) precluded
detailed sampling for the kinetic parameters
and concentrations. Due to the way the
samples were taken, however, each mea-
sured value of K_m and V_{max} actually repre-
sents the integral of the bacterial population
within the surface fluff layer or the under-
lying 1 cm of sediment. Similarly, each mea-
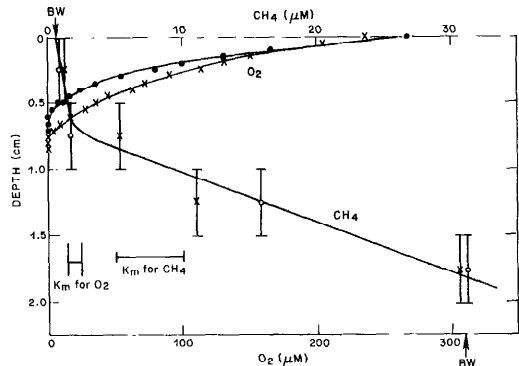sured methane concentration is an average

Fig. 6. Profiles of oxygen and methane in the aero-
bic layer with the corresponding K_m values for the aero-
bic methane oxidation reaction marked for reference.

over the sampling interval (0.5 cm) so we
simply fit a straight line to the methane val-
ues at the two depths for each profile. These
methane concentration equations were then
combined with Eq. 2 to estimate the meth-
ane oxidation rate at any depth. In reality,
the methane profile is assuredly not linear.
Also, there is probably a small zone near
the base of the oxygen profile where oxygen,
rather than methane, is rate limiting. Never-
theless, due to the limited amount of data
and the fine scale of the reaction zone and
concentration gradients, a more complex
model with dual oxygen and methane lim-
itation is not warranted here, and we will
use the simple model to approximate the
methane oxidation rate.

By combining the methane concentration
equations with the rate equation (Eq. 2), and
integrating over the 7-mm aerobic zone, the
integrated methane consumption rate was
calculated to be 340 and 740 μmol m^{-2} d^{-1}
for the two measured methane profiles
(March 1984). These rates are only slightly
higher than those values calculated from the
methane flux balance (250–350 μmol m^{-2}
d^{-1}).

The seasonal stability of the location and
rate of methane oxidation in Lake Wash-
ington is probably due to its occurrence in
the sediments. Lake Washington is a rela-
tively deep lake with a dark and isothermal
hypolimnion. Even more importantly, the
input rates of methane and oxygen to the
reaction zone (i.e. the controlling factors of

aerobic methane oxidation) appear to have little temporal variation.

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