Sources and sinks of methane in Lake Baikal: A synthesis of measurements and modeling

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Abstract

We studied the methane (CH$_4$) budget of Lake Baikal, the most voluminous lake in the world and the only freshwater body with known occurrences of methane hydrates in the sediments. CH$_4$ concentrations were measured in water samples taken during six expeditions between October 2002 and June 2004; these expeditions covered the entire lake volume. A one-dimensional model was applied to (1) estimate the large-scale vertical CH$_4$ fluxes within the South Basin of Lake Baikal, (2) determine the exchange with the atmosphere, and (3) constrain the CH$_4$ inputs from seeps and mud volcanoes to the deep water. Fluxes were generally several orders of magnitude below previous estimates. The annual internal source of CH$_4$ to the pelagic surface mixed layer was roughly estimated to be 40 Mg CH$_4$. A large part of this input diffuses downwards and is consumed in the water column, with a CH$_4$ residence time of about 4 yr. The input of CH$_4$ from deep gas seeps and mud volcanoes is less than a few 10 Mg CH$_4$ yr$^{-1}$, most of which is oxidized before reaching the surface. The net CH$_4$ flux between the atmosphere and the main waterbody distant from shallow areas is negligible and not significantly different from zero. However, occasional high CH$_4$ concentrations, both in the surface water and in the atmosphere, indicate that the region near the Selenga delta is a local CH$_4$ source to the atmosphere. CH$_4$ fluxes in the Central Basin are very similar to those in the South Basin, whereas in the North Basin, the shallow CH$_4$ sources are weaker.

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Lake Baikal methane balance

By volume, Lake Baikal is the largest freshwater body on earth (23,615 km$^3$), and it covers a surface area of 31,722 km$^2$ (all volumes and areas provided by the INTAS Project 99-1669 Team 2002). The lake consists of three basins, the deepest of which is the Central Basin, with a maximum depth of 1,642 m. Most of the following analysis focuses on the South Basin, which covers an area of 7,432 km$^2$ and contains a volume of 6,343 km$^3$. The lake’s two main tributaries (the Selenga River, which forms a large delta between the Central and the South Basins, and the Upper Angara River, which enters the lake at its northern end) are the major external sources of organic material (Granina 1997). The total inflow of all tributaries was estimated to be 61 km$^3$ yr$^{-1}$ (Callender and Granina 1997), leading to an average water residence time within the lake of about 400 yr.

Despite the enormous depth, the water column is oxic down to the sediment surface (Votintsev 1961) as a result of intense turbulent vertical mixing (Ravens et al. 2000) and seasonally occurring advective intrusions from the near-surface to the deep water (Weiss et al. 1991; Hohmann et al. 1997; Wüst et al. 2005). Oxygen even penetrates several millimeters to centimeters into the sediment (Martin et al. 1998; Maerki et al. 2006). Consequently, both biological methane (CH$_4$) production and oxidation occur in the sediment. Observations by Dagurova et al. (2004) indicate that oxidation rates generally exceed production in the sediment. Therefore, the sediment surface is a sink rather than a source for CH$_4$. Nevertheless, gas seeps have been acoustically observed in several shallow areas of the lake (Fig. 1).

Besides the Black Sea (Vassilev and Dimitrov 2002), Lake Baikal is the only inland water mass in which large amounts of methane hydrates have been observed in the sediment (Hutchinson et al. 1991; Golmshotk et al. 1997; Kuzmin et al. 2000) (Fig. 1). These methane hydrates occur (at depths of >580 m) almost symmetrically on both sides of the Selenga delta in the South and Central Basins. Vanneste et al. (2001) roughly estimated from seismic surveys that the total amount of CH$_4$ stored as hydrates in the sediments could be as high as 6 Pg. Based on its carbon isotopic composition, it has been suggested that the CH$_4$ in hydrates from the South Basin may be of biogenic origin (Kuzmin et al. 2000), whereas recent observations indicate also a thermogenic component in hydrates collected in the Central Basin (Kida et al. 2006). CH$_4$ is locally released by gas seeps and mud volcanoes (Fig. 1) into the open water at locations near fault lines, where hydrates are destabilized by increased heat flows due to hydrothermal activity (Van Rensbergen et al. 2002). The destabilization of hydrates is a potentially large source of CH$_4$ to the water column of the lake and, finally, to the atmosphere.

The recent global emissions of the greenhouse gas CH$_4$ to the atmosphere have been estimated to be 500–600 Tg yr$^{-1}$; approximately one third of these emissions stem from natural sources, while two thirds are of anthropogenic origin (Khalil and Shearer 2000; IPCC 2001). The total atmospheric balance is well constrained, but there are considerable uncertainties in the contributions of the different sources. Emissions of CH$_4$ from lakes and artificial reservoirs are one of the important CH$_4$ sources of yet-unknown quantities. St. Louis et al. (2000) estimated the global emissions from reservoirs to measure 70 Tg yr$^{-1}$, stemming mainly from tropical reservoirs. Based on an extensive database of observed CH$_4$ fluxes, Bastviken et al. (2004) developed simple regression models relating the CH$_4$ emissions from lakes to their surface area. Using this approach they estimated the global CH$_4$ emissions from lakes to be 6 Tg yr$^{-1}$, with an uncertainty range of 2–25 Tg yr$^{-1}$, and in addition, they estimated approximately the same amount to stem from plant-mediated emissions in shallow water zones. Even though the emissions per lake area generally decline with the size of the lake, applying the regression equations of Bastviken et al. (2004) to the huge surface area of Lake Baikal yields annual emissions of about 20 Gg yr$^{-1}$. While this approach was not designed to estimate emissions for a specific lake, particularly not for such an exceptional case as Lake Baikal, it does indicate that Lake Baikal could be expected to be a significant CH$_4$ source to the atmosphere. Based on the $\delta^{13}$C isotopic composition of the dissolved inorganic carbon and the phytoplankton, Prokopenko and Williams (2005) proposed a winter accumulation of CH$_4$ in the water column of Lake Baikal (below the ice) in the range of several 100 $\mu$mol L$^{-1}$, and they proposed the emission of at least a part of this CH$_4$ after the spring ice break-up. Given a mixing depth of 200–300 m, this could produce an enormous emission pulse of several teragrams for the whole lake area. However, their estimates were not based on direct measurements of CH$_4$ in the water column of the lake. Furthermore, such high fluxes would have to be of geogenic origin, as they exceed the vertical biogenic carbon (C) fluxes determined by Müller et al. (2005) and could not be maintained by biological methanogenesis.

In the present article, we use a systems-analysis approach to estimate the CH$_4$ budget of Lake Baikal. The estimations are based on measured CH$_4$ concentrations in the water column and in the atmosphere close to the lake surface as well as on the current knowledge of mixing and transport processes within the water column and between the surface waters and the atmosphere. We first analyze the observed CH$_4$ concentrations in the water column to determine the spatial and temporal heterogeneity. Potential direct emissions from seeps to the atmosphere are assessed using a bubble-plume model. Based on these analyses, we estimate possible ranges for the major CH$_4$ fluxes in the South Basin of the lake using a one-dimensional model. Finally, we discuss how far these results can be extrapolated to the whole lake and their significance for other water bodies and the global CH$_4$ budget.

Measurements and methods

Methane concentrations in water samples—CH$_4$ concentrations were measured in 1,283 water samples, which were obtained during six campaigns: from four cruises with the research vessels RV Vereshchagin and RV Titov in October 2002, June 2003, November 2003, and June 2004, and directly from the ice in February/March 2003 and March 2004 (Table 1; Fig. 1). The sampling covered the whole
Lake volume, but most of the measurements were performed in the South Basin. The Central (both years) and North Basins (2003) were only sampled in June.

Water samples were retrieved with 5-liter Niskin sampling bottles, from which 0.5 liters was transferred into glass bottles, avoiding contact with the atmosphere. Gas was extracted from these bottles (Obzhirov 1993) by connecting a previously evacuated 0.6-liter bottle to the sample. Using a vacuum pump, the extracted gas was transferred into a vacuum line filled with salt-saturated water. The vacuum line was disconnected from the sampling bottle, and the gas was then pushed into a burette contained in the vacuum line. The gas volume was measured and corrected for pressure, and the gas was collected in a glass syringe. This procedure was repeated until no more gas could be extracted from the sample. The CH\textsubscript{4} concentration in the gas sample was determined at a temperature of 25°C by an SRI 8610C gas chromatograph with a flame ionization detector, using N\textsubscript{2} as the carrier gas (accuracy, ±5%; CH\textsubscript{4} threshold concentration, 0.1 ppm). The analysis was performed on board the research vessel during summer expeditions and in the laboratory of the Limnological Institute in Bolshie Koty during winter expeditions. Gas standards (Scotty II; Alltech Associates) with concentrations of 10, 100, and 1,000 ppm CH\textsubscript{4} were used for calibration.

Fig. 1. Map of Lake Baikal with locations of known CH\textsubscript{4} seeps, mud volcanoes (including mud-volcano–like deep seeps, partially from Klerkx et al. [2006] and partially from our own observations), and historically observed “ice stream-throughs” (Granin and Granina 2002). Gas hydrate accumulations in the sediment are shown in yellow (Golmshtok et al. 1997). The contour lines show depth intervals of 250 m. The dark green squares indicate sites at which CH\textsubscript{4} concentration profiles covering the full depth were taken, while at the sites marked with light green squares, only single surface or deep samples were obtained. The green line represents the transect used for drawing Fig. 3.
Table 1. Overview of measurements used in this study.

<table>
<thead>
<tr>
<th>CH₄ concentrations in water samples</th>
<th>No. of samples</th>
<th>Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>20–23 Oct 2002</td>
<td>1,283 (19 profiles plus 2 surface samples and 2 deep samples*)</td>
<td>South Basin</td>
</tr>
<tr>
<td>26 Feb–31 Mar 2003</td>
<td>249 (22 profiles plus 28 surface samples and 3 deep samples*)</td>
<td>South Basin</td>
</tr>
<tr>
<td>11–20 Jun 2003</td>
<td>387 (43 profiles plus 24 surface samples)</td>
<td>South, Central, and North Basins</td>
</tr>
<tr>
<td>01–05 Nov 2003</td>
<td>149 (16 profiles plus 2 surface samples and 12 deep samples*)</td>
<td>South Basin</td>
</tr>
<tr>
<td>23–31 Mar 2004</td>
<td>105 (5 profiles plus 34 surface samples)</td>
<td>South Basin</td>
</tr>
<tr>
<td>16–24 Jun 2004</td>
<td>251 (19 profiles plus 55 surface samples and 26 deep samples*)</td>
<td>South Basin</td>
</tr>
<tr>
<td>CH₄ concentrations in near-surface air</td>
<td>Semicontinuous sampling with temporal resolution of 12 s</td>
<td>South and Central Basins</td>
</tr>
<tr>
<td>16–24 Jun 2004</td>
<td>Lake surface temperature</td>
<td>Semicontinuous with hourly resolution</td>
</tr>
<tr>
<td>01 Jan–31 Dec 2002</td>
<td></td>
<td>(51°42'N, 105°01'E)</td>
</tr>
</tbody>
</table>

* Deep samples were taken near the local bottom at sites near known CH₄ seeps or mud volcanoes.

Methane concentrations in near-surface air—CH₄ concentrations in near-surface air were measured during the June 2004 expedition along key transects across Lake Baikal using a diode laser CH₄ gas analyzer (Kapitanov et al. 2007a,b). The tunable GaInPAs diode laser was scanned over the wave number range from 6,000 to 6,080 cm⁻¹ (1.645–1.666 μm), which contains several strong CH₄ absorption lines. The laser beam was transmitted through the measuring cell (volume, 0.012 m³) on a multipass track with a length of 157.5 m followed by a photodetector. A second beam from the same source was passed through a reference cell with a known mixture of nitrogen and CH₄ before reaching another photodetector. The CH₄ concentration in the measuring cell was then determined from the comparison of the absorption spectra of the two beams. Near-surface air (2 m above water surface) was continuously pumped at a rate of 1.25 × 10⁻⁴ m³ s⁻¹ through the measuring cell, and the CH₄ concentration was determined every 12 s. The system had a response time (renewal time of the air in the measuring cell) of 96 s, yielding a spatial resolution of 453 m at the maximum vessel speed of 17 km h⁻¹. The threshold sensitivity of the gas analyzer is about 10 ppb under laboratory conditions. The accuracy of the measurements is tested with gas standards with concentrations of 2,000 and 5,000 ppb CH₄ before every measurement campaign, resulting in an estimated standard deviation of 3%. On board the research vessel, an average baseline drift of 50 ppb h⁻¹ was observed. To compensate for the drift, the baseline was determined every hour using pure nitrogen. The average CH₄ concentration (temporal and spatial) during the cruise amounted to 1,910 ppb, with a standard deviation of 70 ppb, while background measurements at Bolshie Koty from 08 to 16 June 2004 yielded an average concentration of 1,887 ppb, with a standard deviation of 19 ppb. In the following, we consistently use 1,900 ppb as an estimate for the average CH₄ concentration in the near-surface atmosphere above Lake Baikal.

Calculation of exchange between lake water and the atmosphere—The CH₄ flux, $F_{CH₄}$ (mol m⁻² d⁻¹), between the lake surface and the atmosphere was estimated based on wind speed and air and water surface temperature, measured concurrently at each sampling location, and the observed CH₄ concentrations in the water, using the following equation (Lyakhin 1978; Cai and Wang 1998; Mizandrontsev and Mizandrontseva 1999):

$$F_{CH₄} = f(W) K_{ex} H_{CH₄} (P_W - P_A)$$  \( (1) \)

$K_{ex}$ (m s⁻¹) = $D/Z$ is the gas exchange coefficient, $D$ (m² s⁻¹) is the molecular diffusion coefficient of CH₄ in water at the lake surface temperature (Kafarov 1962), $H_{CH₄}$ (mol L⁻¹ Pa⁻¹) is the solubility of CH₄ as a function of temperature (Wiesenburg and Guinasso 1979), $f(W)$ is a coefficient determining the influence of wind speed, $W$ (Lyakhin 1978; Mishukova and Mishukov 2002), equal to $(1 + 0.058 \times W^2)$ for $W \leq 5$ m s⁻¹ and $(1 + 0.047 \times W^2)$ for $W > 5$ m s⁻¹, $P_A$ and $P_W$ (Pa) are the partial pressures of CH₄ in the atmosphere (corresponding to a concentration of 1.900 ppb) and the surface water, respectively, and $Z$ is the thickness of the surface diffusion layer, which depends on the surface currents (Levich 1962). For the pelagic zone of Lake Baikal, $Z$ has been estimated, depending on the wind speed, $W$, to be $1.96 \times 10^{-4}$ m for $W < 5$ m s⁻¹ and $1.74 \times 10^{-4}$ m for $W > 5$ m s⁻¹, based on the data of Mishukova and Mishukov (2002). While there are many parameterizations for estimating gas exchange available in the literature, the one presented above was specifically tested for Lake Baikal by Mishukova and Mishukov (2002) and yields values in the upper range of the variability. However, as will be clear from the results presented below, selecting another formulation would not alter the conclusions of this study.

Simulation of rising methane bubbles and plumes—To estimate whether rising bubbles could lead to significant CH₄ emissions, we applied the bubble transport model,
described by McGinnis et al. (2006), to Lake Baikal, using the background profiles of temperature, salinity, and concentrations of oxygen and methane observed in the South Basin of Lake Baikal in June 2004 as boundary conditions. The model calculates the rising velocity of a bubble as a function of the bubble size; the exchange of CH₄, oxygen, nitrogen, and argon between the bubble and the water; as well as the impeding effect on these gas exchange fluxes caused by a solid hydrate rim at the bubble surface within the hydrate stability zone below 580 m in depth. The following cases were simulated: (1) single CH₄ bubbles released from shallow sources at depths between 5 and 200 m, with diameters ranging from 1 to 20 mm; (2) single bubbles released at 1,350 m in depth with varying diameters; and (3) a two-phase bubble plume released from 1,400 m in depth with a source strength of 1 kg CH₄ s⁻¹, and a source area of 12 m², simulated using a combination of the bubble-plume model developed by Wüst et al. (1992) and the CH₄ bubble model of McGinnis et al. (2006), analogous to the calculations made for the Black Sea by Kourtidis et al. (2006).

**One-dimensional model**—The background CH₄ concentrations in the South Basin were simulated with a basic one-dimensional reaction–advection–diffusion model. Of course, the large size of the lake leads to horizontal inhomogeneities that are not compatible with a one-dimensional approach. However, as the results below show, the one-dimensional model yields an excellent overview of the relevant processes involved. The limitations of this approach will be further assessed in the Results and discussion section.

Two different software packages were used for the simulations. In a first step, vertical turbulent diffusivities for the top 400 m were calculated with the k-ε model of Goudsmit et al. (2002). The basic idea behind the k-ε approach is the combination of the budget of turbulent kinetic energy (k), representing the source of turbulent mixing, with the budget of the dissipation rate (ε). Apart from the classical k sources, shear and buoyancy, Goudsmit et al. (2002) introduced an additional term to account for boundary mixing by internal currents. The vertical diffusivities are then calculated from k, ε, and the density stratification. The model was extended to include the effects of pressure on the thermal expansivity of water (Chen and Millero 1986) in the calculation of the stability of the water column, which plays an important role in the density stratification of Lake Baikal. Inputs for the k-ε model include average monthly wind speeds (Shimaraev et al. 1994), average monthly solar radiation from the NCEP-NCAR reanalysis (Kalnay et al. 1996), and water temperatures observed at 15-m depth in the year 2002 (Müller et al. 2005), which showed a trend very similar to the long-term average monthly surface temperatures (Shimaraev et al. 1994). The wind drag coefficient was set to 0.0045 instead of the usual values of 0.001–0.002, because average monthly wind speeds were used instead of much more variable data with hourly or daily resolution. Since the energy input from wind approximately depends on the third power of wind speed, it would otherwise have been substantially underestimated using the average monthly values. Two model parameters were fitted to achieve a qualitative agreement with observed mixing regimes and to approach an average diffusivity of 1.25 × 10⁻³ m² s⁻¹ at 400-m depth (Wüst et al. 2000): the fraction z of wind energy entering the lake internal currents was set to 0.003; the parameter q, which defines the vertical distribution of the dissipation of internal kinetic energy as a function of stratification, was set to 0.35. For a detailed description of the model and these parameters, see Goudsmit et al. (2002). Since the k-ε model is less reliable for the very weakly stratified deep water and far away from the energy input at the lake surface, we used a homogeneous diffusivity below 400-m depth. Possible effects of this simplification are discussed below.

The calculated diffusivities were then used as input for the one-dimensional advection–diffusion–reaction model. These simulations were performed with the lake module of the software AQUASIM 2.1 (Reichert 1994), which is designed to simulate physical mixing and biogeochemical processes in natural and artificial aquatic systems. The software has been successfully applied to simulate biogeochemical and transport processes in many different lake systems, (e.g., Schmid et al. 2006; Matzinger et al. 2007). A vertical grid of 2 m was used, while the time step was adjusted by the software depending on stability criteria for the solution of the differential equation system.

Generally speaking, the model numerically solves the equation:

\[
\frac{\partial [CH_4]}{\partial t} = \frac{1}{A} \frac{\partial}{\partial z} \left( AK_z \frac{\partial [CH_4]}{\partial z} - Q[CH_4] \right) - k_{Ox}[CH_4] + r_{CH_4}
\]

where \([CH_4]\) (µmol m⁻³) is the CH₄ concentration, \(A\) (m²) is the lake area, \(K_z\) (m² s⁻¹) is the vertical diffusivity, \(Q\) (m³ s⁻¹) is the vertical water flow due to the deep-water intrusions, \(k_{Ox}\) (s⁻¹) is the first-order oxidation rate coefficient of CH₄, \(r_{CH_4}\) (µmol m⁻³ s⁻¹) is the source term, and \(z\) (m) is the vertical dimension positive upwards.

In previous modeling studies, CH₄ consumption was usually simulated either as a first-order reaction (e.g., Nihous and Masutani 2006) or using Michaelis–Menten kinetics (see, for example, Hanson and Hanson 1996), which, at the low concentrations in Lake Baikal, also reduces to a first-order reaction. Even though lab experiments indicated a lower threshold for CH₄ oxidation of several nmol L⁻¹ (e.g., King 1990), it seems that in natural systems where the community is adapted to low concentrations, CH₄ is generally consumed down to much lower levels (Hanson and Hanson 1996). This was also confirmed by our observations in Lake Baikal (see below). We therefore simulated CH₄ consumption using a first-order reaction without a lower threshold.

The CH₄ source term was set to 0 for the whole depth, except for the top 20 m, where a gas input was assumed. This assumption is based on the observed gas accumulation in the surface layer below the ice during winter, while the concentrations were usually already near or below equilibrium with the atmosphere at 50-m depth. Additional
simulations were performed, with a similar source term between 1,000 and 1,100 m in depth, to test the sensitivity of the water column methane concentrations to deep gas sources. The known deep gas seeps and mud volcanoes are located between 800 m and 1,400 m in depth. The lake was assumed to be ice-covered from 10 January to 04 May (Todd and Mackay 2003), and both wind forcing for mixing (in the k-e model described above) and gas exchange with the atmosphere were suspended during this time.

The boundary conditions for the AQUASIM model were monthly average wind speeds (Shimaraev et al. 1994), smoothed surface temperatures measured in 2002, and the diffusivities previously calculated with the k-e model. The gas flux between the lake surface and the atmosphere was calculated using Eq. 1 with wind speed, surface temperature, an average atmospheric pressure of 956 mbar, and an average CH$_4$ concentration in the air of 1,900 ppb. The CH$_4$ input to the top 20 m of the water column and the first-order CH$_4$ consumption rate coefficient $k_{Ox}$ were adjusted to approach the observed background vertical profiles in March (under the ice), June, and October after 100 years of simulation when the model approached steady state. The vertical CH$_4$ profiles observed in the South Basin at deep sites away from the vicinity of known CH$_4$ seeps were used to define the background concentrations.

Results and discussion

*Methane concentrations in the lake water*—The CH$_4$ concentrations observed in the lake water can be divided into a background concentration with some scatter observed at most locations that were not directly influenced by local CH$_4$ sources, and elevated concentrations observed near CH$_4$ sources, either in shallow regions or near deep gas seep locations (Fig. 2). The background concentrations at the surface (~4 nmol L$^{-1}$) are approximately in equilibrium with the atmosphere (~1,900 ppb). CH$_4$ concentrations generally decrease with depth, indicating a downward transport and CH$_4$ oxidation within the deep water. Toward the bottom, concentrations increase slightly in several of the profiles, which is consistent with observations of deep cold-water intrusions (Wüst et al. 2005). Except near known gas seeps, deep-water concentrations do not exceed equilibrium concentrations. Both the seasonal variations as well as the variations between the three basins were small. Surface concentrations tended to be elevated in winter under the ice cover, indicating an accumulation of CH$_4$ because of the restricted gas exchange with the atmosphere. This accumulation is not so obvious from Fig. 2, where the numerous surface samples taken in June near seep locations raise the median value, but it is much more easily discernible in the comparison of observed and simulated concentrations in the Simulations section below, where only those measurements at sites far from seep areas were considered.

The main difference observed between the three basins in June 2003 was that CH$_4$ concentrations were higher in the surface layer of the South and Central Basins compared to the North Basin, especially in the vicinity of the Selenga delta (Fig. 3). Elevated surface concentrations in this region were observed during all cruises, indicating a local shallow CH$_4$ source near the Selenga delta. The Selenga is the largest external source of organic carbon to Lake Baikal (Granina 1997), and increased CH$_4$ production was observed in the sediments near the delta (Dagurova et al. 2004). Furthermore, several shallow CH$_4$ seeps have been observed in this region (Isaev 2001), and numerous historical records exist of so-called “ice stream-throughs” in the vicinity of the delta (Fig. 1). The latter are holes in the ice that were regularly observed in the first half of the 20th century and that can be attributed to active gas seeps...
Finally, a few measurements made in Selenga River water indicate that CH$_4$ concentrations in the river can reach up to 1 $\mu$mol L$^{-1}$ (Zemskaya et al. 2005). Considering the discharge of about 30 $km^3$ yr$^{-1}$, an average concentration of 1 $\mu$mol L$^{-1}$ would correspond to a CH$_4$ input of 500 Mg yr$^{-1}$, which could explain the observed increased surface concentrations. Increased surface concentrations observed in the western part of the South Basin in June 2003 seemed to originate from the coastal region near Baikal'sk (Murinskaya bank), as indicated by the higher concentrations observed in a profile nearer to the coast. However, this observation was not confirmed during the other cruises.

Deep-water concentrations were slightly elevated in the North Basin compared to the Central and South Basins (Figs. 2, 3), indicating either more efficient deep-water renewal, in agreement with the observations of Hohmann et al. (1998), or a lower oxidation rate. The latter could be explained by the absence of deep gas seeps, which may help to support methanotrophic bacteria in the South and Central Basins.

Methane concentrations in the near-surface air—During the June 2004 cruise, concentrations were simultaneously measured in the near-surface air and the water surface. Atmospheric concentrations generally ranged between 1,800 and 2,100 ppb, with an average concentration of 1,910 ppb. Considering the measurement accuracy of 3%, this is not significantly different from the large-scale background value of 1,850 ppb observed in June 2004 at the two nearest stations of the Global Atmosphere Watch program in Ulaan Uul (Mongolia) and on Mt. Waliguan (China). At six locations (Fig. 4) concentration peaks above 3,000 ppb were observed; three such locations are depicted in Fig. 5. Five of these locations were situated in shallow water at depths between 20 and 60 m near known CH$_4$ seeps, but one (Fig. 5a) was situated above a known deep (≈1,400-m) CH$_4$ seep 7 km from Mishikha (51°41′N, 105°27′E) in the South Basin. These observations indicate that CH$_4$ from seeps, and occasionally even from very deep sources, can be emitted to the atmosphere, as will be further discussed below, based on the simulation of rising methane bubbles and plumes. The peaks generally consisted of a rapid increase caused by local occurrences of high CH$_4$ concentrations and then a decrease that followed the exponential decay caused by flushing the measuring cell with air with a background concentration of 1,800–1,900 ppb. The increased concentrations were restricted to areas with diameters on the order of 10–100 m.

Much more detailed information on the state of the atmospheric boundary layer and additional CH$_4$ measurements would be needed to accurately estimate the local CH$_4$ fluxes to the atmosphere at these sites. As a very rough estimate, we can use a residence time of a few hours within a stable atmospheric boundary layer of a few tens of meters in thickness. A flux on the order of 0.1–1 $\mu$mol m$^{-2}$ s$^{-1}$ within the emission area would then produce an excess signal of a few thousand ppb in the atmosphere, and, if running continuously over an area of 1,000 m$^2$, would yield annual emissions of 50–500 kg. This is equal to the typical flux rates of CH$_4$ seeps in the Black Sea (Dimitrov 2002a).

A comparison between the concentrations at the water surface and in the atmospheric boundary layer, measured at the same positions in June 2004, shows some correlation (Fig. 6a), indicating that elevated atmospheric concentrations were indeed caused by emissions from the lake. Elevated CH$_4$ concentrations at the water surface were usually observed at sites with a depth of less than 200 m that is reached by seasonal mixing (Fig. 6b), similar to the observations of Schmale et al. (2005) and Kourtidis et al. (2006) in the Black Sea. However, occasionally they were also observed at sites with depths between 1,000 and 1,400 m, indicating again that a direct transfer of CH$_4$ from deep seeps to the surface is possible. The correlation between atmospheric and lake surface concentrations implies that the emission signal is visible in the atmosphere and, consequently, that micrometeorological methods (e.g.,
Fig. 4. Tracks of CH$_4$ near-surface air concentration measurements in June 2004. Concentration peaks of >3,000 ppb were observed at six locations (A–F).

Fig. 5. Atmospheric CH$_4$ concentrations and tracks at three of the six sites at which strong CH$_4$ peaks were observed. The sites correspond to the positions marked with A, B, and C in Fig. 4. The color coding is identical for each corresponding pair of panels. The magenta line in panel a shows an exponential decay with the residence time of 96 s of the gas in the measuring cell.
Laurila et al. (2005) might be a promising option to estimate regional emissions in the vicinity of the Selenga delta.

Methane fluxes between the lake and the atmosphere—The CH$_4$ fluxes from the lake to the atmosphere, calculated with Eq. 1 for 62 surface samples from June 2003, are shown in Fig. 7. The area-weighted average flux for the whole lake was $10^{2.5} \mu$mol m$^{-2}$ s$^{-1}$, and it was not significantly different from zero for the areas overlying the deep regions. These results agree with the fluxes estimated with the one-dimensional model below. Considering only the open water, the estimated fluxes were not significantly different from zero. Five positions with exceptionally high surface-water concentrations were excluded. Four of them yielded local emission rates on the order of $10^{-3} \mu$mol m$^{-2}$ s$^{-1}$ (i.e., two orders of magnitude above the average), while one directly above a shallow seep in the Selenga delta resulted in a flux of almost 1 $\mu$mol m$^{-2}$ s$^{-1}$.

Simulation of rising methane bubbles and plumes—As reported by Schmale et al. (2005) and McGinnis et al. (2006), CH$_4$ bubbles released from shallow sites (<100 m) are the only ones that directly emit significant amounts of CH$_4$ to the atmosphere. The fraction of CH$_4$ that reaches the atmosphere from bubble transport was presented for the Black Sea by McGinnis et al. (2006) as a function of the initial bubble size and bubble release depth. Analogous calculations using the background stratification and CH$_4$ concentrations of Lake Baikal yielded very similar results. In most cases, while the bubble may still reach the surface and remain a significant size, most of the CH$_4$ would have been dissolved in the water column and replaced by other gases, particularly oxygen and nitrogen, even for shallow sources at depths of <100 m.

To estimate whether CH$_4$ from deep seeps could be directly transferred to the lake surface and the atmosphere, single rising bubbles with hydrate rims released from 1,350-m depth were simulated. An ~20-mm-diameter bubble, which is in the upper range of the sizes of 1.4–18.2-mm diameter observed in the Black Sea (Egorov et al. 2003), can just reach the surface. However, almost all of the CH$_4$ is dissolved by about 200 m in depth. It can be concluded that the CH$_4$ of such bubbles will not reach the atmosphere directly. Significant direct emissions would only be possible if larger chunks of hydrates broke out from the sediment and rose to the surface (Brewer et al. 2002), a hypothesis that has been put forward based on observations of presumed pieces of gas hydrates on the ice of the lake (Granin and Granina 2002).

The situation is different if we consider a two-phase bubble plume that could be caused by a short-term CH$_4$ outburst. Evidence of such intermittent CH$_4$ plume
outbursts from mud volcanoes in the Black Sea is available (McGinnis unpubl. data). Our simulations indicate that a mud volcano outburst at 1,400-m depth of only about 1 kg gaseous CH$_4$ over a source area of 12 m$^2$ can already reach the surface during the weakly stratified periods in June or November/December (not shown). Such an outburst is very small compared to eruptions on the order of 100 Gg, which are known to occur from mud volcanoes (Dimitrov 2002). However, these calculations should be interpreted with care, since the density differences between the plume and the ambient water are extremely small in the case of Lake Baikal and because friction is not incorporated into the model. The bubble plume transports almost all the CH$_4$ released from the seep to the surface layer, from which location it can be emitted to the atmosphere. However, there is no direct emission by bubbles, as the initial 6-mm–diameter bubbles (a likely initial bubble size reported by McGinnis et al. [2006]) dissolve below 600 m in depth. If we tentatively estimate an outburst duration of a few minutes, a few hundred kg of dissolved CH$_4$ would reach the surface layer. It would take several days to weeks to exchange this CH$_4$ with the atmosphere. If the exchange happens within a diameter of 100 m, this would lead to emissions on the order of 0.1–1 μmol m$^{-2}$ s$^{-1}$, in agreement with the fluxes estimated above to explain the observed high CH$_4$ anomalies in the atmosphere.

The above analysis shows that direct emissions to the atmosphere, both from shallow and deep seep sites, are possible. However, in all cases, a large fraction (if not all) of the CH$_4$ is dissolved before reaching the atmosphere and—due to the slow oxidation (see below)—should be observed in the water column. Therefore, restrictions similar to those derived below for the maximal possible input of CH$_4$ to the water column apply as well to the maximal amount of CH$_4$ emitted by bubbles.

Simulations of methane concentrations and fluxes with the one-dimensional model—The vertical diffusivities calculated with the k-ε model (Fig. 8) show all the features typically observed in the South Basin of Lake Baikal (Shimaraev et al. 1994): the top 200–250 m are convectively mixed twice a year, in early June and early December; mixing is reduced and steadily declines while winter stratification develops under the ice, until a convectively mixed layer is formed toward the end of the ice-covered period as a result of solar heating (depending on the snow cover above the ice); a growing mixed surface layer develops toward the end of summer stratification; and, finally, a mixed zone of approximately 100-m thickness appears near the depth where the temperature profile intersects the vertical profile of the temperature of maximum density between December and May (Wüst et al. 2005).

The observed background CH$_4$ concentrations in the water column could best be reproduced with a CH$_4$ source to the surface layer of $5 \times 10^{-7}$ μmol m$^{-3}$ s$^{-1}$ for the top 20 m, which corresponds to a total annual input of 37 Mg CH$_4$ for the entire South Basin. This amount is assumed to be emitted by shallow sources to the background water column and is required mainly to reproduce the observed accumulation of CH$_4$ under the ice during winter (Fig. 9b). Although the lake cannot be regarded as a completely
closed system during the ice-covered period, gas exchange with the atmosphere is certainly strongly reduced.

The best prediction of the decline of CH$_4$ concentrations with depth was achieved with a first-order CH$_4$ oxidation rate coefficient, $k_{Ox}$, of $8.0 \times 10^{-9}$ s$^{-1}$, corresponding to a CH$_4$ residence time of 4 yr. Dagurova et al. (2004) measured CH$_4$ oxidation rates in water samples taken in a vertical profile from the surface to 825-m depth near Zavorotnyi Cape on the Western shore of the North Basin. Dividing their CH$_4$ concentrations by their oxidation rates yields comparable residence times of 0.4–1.4 yr. In the oxic zone of the Black Sea, oxidation rates corresponding to residence times of 1–2 yr and 5–20 yr were observed in seep regions, and away from seep regions, respectively (Durisch-Kaiser et al. 2005). The same orders of magnitude were also observed in the El River Basin in the Eastern Pacific, with residence times of 1.5 yr near CH$_4$ vents and of several decades far from the sources (Valentine et al. 2001).

The model allows narrowing the possible range of CH$_4$ inputs to the deep water by seeps within the hydrate stability zone. Two simulations with inputs of 10 and 20 Mg CH$_4$ yr$^{-1}$ to the layer between 1,100 and 1,200 m in depth, where elevated concentrations were regularly observed at some sites (Fig. 2), yielded the concentrations shown as dashed and dotted lines in Fig. 9a. Based on the fact that such a signal was not observed, we can exclude an input of significantly more than a few tens of megagrams of CH$_4$ per year from the deep seeps to the deep water of the South Basin, even if we assume that, as is the case in the Black Sea and the Pacific Ocean, oxidation is faster in seep regions as a result of local populations of methanotrophic bacteria.

Figure 10 shows the sensitivity of the model to the main input parameters (i.e., their error contributions, assuming a deviation of the parameter, as given in the legend for Fig. 10). The simulated CH$_4$ concentrations are clearly most sensitive to the following three key parameters, which define the major processes of CH$_4$ input, transport, and consumption within the system: the vertical diffusivity, the CH$_4$ input to the surface layer, and the CH$_4$ consumption rate coefficient. Since model results are very sensitive to the two latter parameters that were determined by fitting, these parameters can be estimated with relatively high confidence. In the deep water, the advective intrusion flow volume also has a significant influence. The assumption of homogeneous diffusivity in the deep water might be the cause of the simulated peak in the deepest layer. In reality,
mixing is increased in the bottom boundary layer (Wüst and Lorke 2003), which would tend to “smear out” such peaks. However, increased oxidation due to the higher sediment area per volume could also be the reason for the absence of a peak near the bottom in most profiles.

The simulated CH$_4$ exchange fluxes between the lake and the atmosphere are negligible (Fig. 11a). During the ice-covered period, there is no gas exchange between the atmosphere and the lake, and CH$_4$ can accumulate under the ice. After the ice break-up, about 2 Mg of this accumulated CH$_4$ is emitted from the South Basin. Another burst of emissions of 3 Mg is simulated during the summer stratification, caused by the reduction of solubility due to increased water temperatures. These emissions are approximately balanced by two periods of CH$_4$ uptake of 1 and 6 Mg CH$_4$ during June and November/December, respectively. During these periods, lake surface water is mixed with CH$_4$-depleted deep water, which leads to an undersaturation at the surface. Altogether this yields a net uptake of 1.8 Mg yr$^{-1}$, but this is well within the error range of ±17 Mg yr$^{-1}$. Consequently, it is not possible to determine whether the background CH$_4$ concentrations in Lake Baikal indicate a net emission or a net uptake of CH$_4$.

The surface fluxes are mainly determined by the input of CH$_4$ to the surface waters from shallow sources and the CH$_4$ consumption rate coefficient (Fig. 11b). According to the simulations, two thirds of additional CH$_4$ inputs to the surface layer would be emitted to the atmosphere, while the rest would be oxidized in the water column. The net effect of an increased gas exchange velocity is negligible, as it mainly enlarges the amplitude of both the negative and the positive fluxes.

The concentrations observed in the Central Basin are very similar to those in the South Basin, as is the mixing regime. Furthermore, both basins are similarly influenced by the local CH$_4$ source of the Selenga delta. Consequently, we do not expect significant differences in the CH$_4$ balance of these two basins. In the North Basin, surface background concentrations are lower, indicating fewer shallow gas seeps and possibly a larger net CH$_4$ uptake, but this is only based on measurements from June 2003. Under-ice concentration measurements would be required to allow more reliable estimates of the net CH$_4$ fluxes. Finally, the one-dimensional model, of course, cannot capture the elevated CH$_4$ concentrations and fluxes observed in the region of the Selenga delta (Figs. 3, 7).

It can be concluded that Lake Baikal is probably a small source of CH$_4$ to the atmosphere as a result of local emissions caused by shallow gas seeps, decomposition of organic matter, or direct riverine inputs near the major inflows, mainly near the Selenga delta but also near the inflows of the Barguzin and the Upper Angara. However, this source is most likely not larger than a few tens of megagrams CH$_4$ per year and is not in the range of several gigagrams, as estimated by applying the regression equation of Bastviken et al. (2004), or even on the order of several teragrams, as speculated by Prokopenko and Williams (2005). Consequently, the contribution of Lake Baikal to the global atmospheric CH$_4$ balance—and even to the total emissions from lakes and reservoirs—is negligible.

Similar conclusions have recently been drawn for the Black Sea, where numerous seeps release CH$_4$ bubbles to the deep water (Kessler et al. 2006a; Naudts et al. 2006). There, most of the CH$_4$ is dissolved during the rise of the bubbles (McGinnis et al. 2006), oxidized in the water column (Durisch-Kaiser et al. 2005; Kessler et al. 2006b), and consequently is not transferred to the atmosphere. However, the situation in the Black Sea is also different, since the CH$_4$ input is several orders of magnitude higher, and since most of it is consumed by anaerobic methane oxidation in the deep water (Kessler et al. 2006a). As was the case with Lake Baikal, investigations in oligotrophic Lake Biwa showed that the inflowing river and the littoral sediments were the major CH$_4$ source for the epilimnion, causing a net CH$_4$ transfer from the epilimnion to both the hypolimnion, where it is slowly consumed by microbial oxidation, and to the atmosphere (Murasu et al. 2005). Since Lake Baikal is a very special lake in several respects (size, depth, occurrence of hydrates), it is not possible to generalize the results of this study to other lakes. However, it can be expected that deep, oxygenated lakes generally are not significant CH$_4$ sources, since any CH$_4$ released from the sediments is likely to be oxidized within the water column.

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Lake Baikal methane balance


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