

## Wave-induced release of methane: Littoral zones as a source of methane in lakes

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### *Abstract*

This study investigates the role of surface waves and the associated disturbance of littoral sediments for the release and later distribution of dissolved methane in lakes. Surface wave field, wave-induced currents, acoustic backscatter strength, and the concentration and distribution of dissolved methane were measured simultaneously in Lake Constance, Germany. The data indicate that surface waves enhance the release of dissolved methane in the shallow littoral zone via burst-like releases of methane during the passage of wave groups. The amount of released methane depends on the surface wave field and the water temperature that controls the methane production in the sediments. The dissolved methane concentrations in the shallow littoral zone were always higher than concentrations in the deep water and open water, while methane concentrations in the epilimnion were typically higher than methane concentrations in the metalimnion and upper hypolimnion. The relatively high epilimnetic methane concentrations in the pelagial can be explained by lateral transport of methane from the littoral zone to the pelagic zone. Littoral zones can thus be an important source of methane in lakes. Methane released by surface waves from littoral sediments may cause elevated near-surface methane concentrations in large areas that enhance the flux of methane at the air–water interface and, thus, the overall methane emissions from lakes to the atmosphere.

Methane (CH<sub>4</sub>) is a climate-relevant trace gas that accounts for ~ 20% of the Greenhouse Effect (Wuebbles and Hayhoe 2002; IPCC 2007). Lakes, reservoirs, and wetlands provide 6–16% of the total natural methane emissions (more than oceanic emission), indicating that lakes are a significant source in global methane budgets (St. Louis et al. 2000; Bastviken et al. 2004).

Methane is a major product of carbon metabolism in lakes. Anaerobic carbon mineralization, in terms of methanogenesis in anaerobic sediments, can account for up to 50% of the overall carbon mineralized in freshwater lakes (Bastviken et al. 2008). A large proportion of the produced methane is oxidized by methanotrophic bacteria at oxic water and sediment interfaces (Frenzel et al. 1990; Bastviken et al. 2002; Liikanen et al. 2002). The main emission pathways from the waterbody to the atmosphere are summarized by Bastviken et al. (2004), as follows: ebullition from anaerobic sediments (Mattson and Likens 1990; Fendinger et al. 1992; Ramos et al. 2006), diffusive flux across the air–water interface (Stumm and Morgen 1996), plant-mediated flux from the littoral sediments (Segers 1998), and the flux of methane stored in the anoxic waterbody during the stratification period that is rapidly released during overturning and mixing (Michmerhuizen et al. 1996; Riera et al. 1999). The proportion of each individual pathway to the overall lake emission is highly dependent on lake characteristics (e.g., lake size, stratification pattern, nutrient load, and plant cover; Bastviken et al. 2004).

In the past, many investigations were focused on profundal sediments as source of methane (Casper 1992), internal cycling (Rudd and Taylor 1980; Bastviken et al. 2003; Kankaala et al. 2006), and later oxidation in the water column (Utsumi et al. 1998; Bastviken et al. 2002).

Methane produced in epilimnetic sediments is considered an important source for ebullition (Walter et al. 2006, 2008) and the plant-mediated flux (Bastviken et al. 2004; Wang et al. 2006) that causes direct fluxes to the atmosphere. On the other hand, diffusive fluxes from shallow littoral zones were considered to be less important than fluxes from the anoxic profundal sediments (Frenzel et al. 1990; Liikanen et al. 2002). However, other studies (Michmerhuizen et al. 1996; Murase et al. 2005; Bastviken et al. 2008) indicated that especially during summer the methane fluxes from littoral sediments can be higher than those from profundal sediments, because high sediment temperatures at shallow depths support high methane production rates. In addition, it has been observed (Schmidt and Conrad 1993; Schulz et al. 2001; Murase et al. 2005) that dissolved methane concentrations in the epilimnion can be higher than those in the hypolimnion, which indicates that methane release from profundal sediments cannot be the sole source of epilimnetic methane degassing to the atmosphere.

The main differences between littoral and profundal sediments are not only the warmer sediment temperatures in the littoral during summer (which favor higher methane production rates; Thebrath et al. 1993; Casper 1996) but also the exposure to surface waves (Hofmann et al. 2008), which may enhance the release of methane from the sediments. In the absence of waves, the exchange of dissolved methane above the sediment–water interface is dominated by molecular diffusion that limits the flux of methane to the water column and that is accompanied by high methane oxidation rates at the sediment–water interface (Huttunen et al. 2006). Waves cause intense oscillating currents (Hofmann et al. 2008) that may enhance the flux of methane above the sediment–water interface by advective sediment pore-water exchange (wave pumping) (Precht and Huettel 2003) and by resuspension (Nielson 1994; Hofmann 2007) that breaks up the upper

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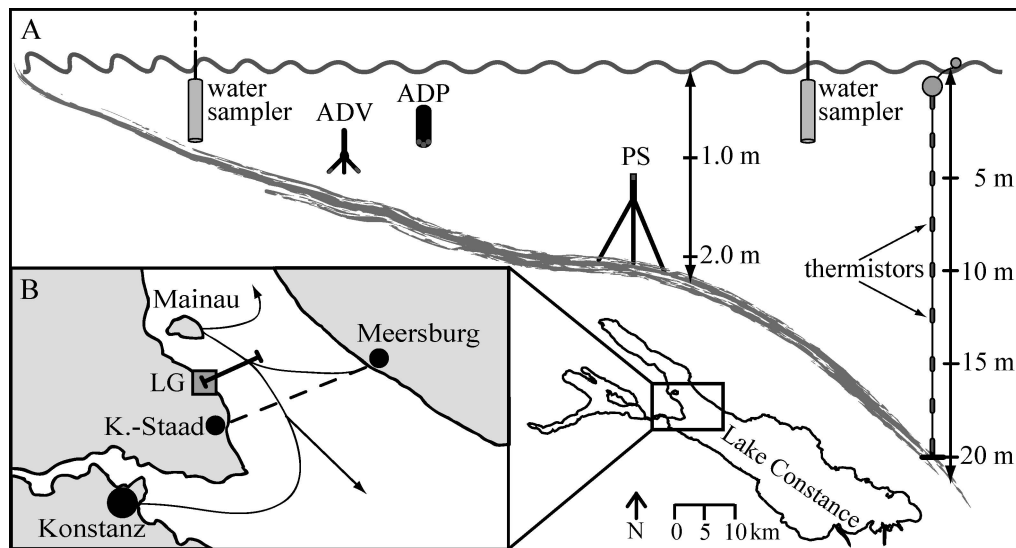


Fig. 1. Experimental set-up and study site. (A) Vertical section with the position of all used devices: ADV, acoustic Doppler velocity meter; ADP, high-resolution acoustic Doppler current profiler; PS, pressure sensor, thermistor chain, and water sampler. (B) Map of Lake Constance. The square shows the section of the study site Littoral Garden (LG), which is situated at Upper Lake Constance, next to the island of Mainau. Site LG is close to the ferry crossing from Meersburg to Konstanz–Staad (dashed line) and experiences the additional traffic associated with large passenger ships (thin, solid lines). The bold, solid line shows the extension of the transect on 05 August 2008.

sediment layer. Laboratory experiments with sediment cores have indicated that resuspension can increase dissolved methane concentrations in the overlying water column (Bussmann 2005) and, thus, could enhance the flux of methane from the sediments to the atmosphere.

Here we investigate the role of surface waves for the release of methane from littoral sediments in the field as well as the resultant spatial and temporal distribution patterns between the littoral and the pelagic zone.

## Methods

**Study site**—The oligotrophic and monomictic Lake Constance is located in southwest Germany and borders Switzerland and Austria. It is the second-largest (by surface area) pre-alpine lake in Europe, with a surface area of 536 km<sup>2</sup> and a maximum depth of 254 m (Braun and Schärpf 1990). Measurements were carried out in the western part of Upper Lake Constance at a site called Littoral Garden (LG; 47°41′29″N, 09°12′11″E), next to the island of Mainau (Fig. 1). The shore is not only exposed to wind waves generated by northeasterly winds but it is also exposed to ship waves. The latter are generated by the ferry crossing from Meersburg to Konstanz–Staad, with regular trips throughout the year, and by large passenger ships that travel parallel to the shoreline during the tourist season (middle of March to middle of October) (Fig. 1B; Hofmann et al. 2008).

The littoral zone has a shelf-like structure and slopes gently over a length of ~60 m before dropping rapidly. The littoral sediments of the cross-section (Fig. 1A) show a gradient between the shallow part (0–1 m) and the deeper part (1–2 m). The shallow part is characterized by gravel–

cobble-like stones, sand, and silt, and the latter part is characterized by sand, silt, and clay.

The whole waterbody of Lake Constance is characterized by high oxygen concentrations, even during the stratification period (IGKB 2002), which reduces possible methane production to the lake sediments.

**Wave, current, and acoustic backscatter measurements**—The surface wave field, the wave-generated near-bottom current velocities, and the acoustic backscatter strength were measured using a pressure sensor (PS), an acoustic Doppler velocity meter (ADV; Vector), and a high-resolution acoustic Doppler current profiler (ADP; Aquadopp HR Profiler). On 02 and 09 July 2008, the instruments were deployed along a cross-shore transect at water depths of ~1.5 m (ADV, ADP) and 2 m (PS) (Fig. 1A).

The custom-made PS has a full range of 7 m and an accuracy of 10 Pa. The sensor was positioned 1 m above the bottom and ~1 m below the surface. Pressure measurements were made at a sampling frequency of 16 Hz. The measured time series of subsurface pressure was converted to a time series of surface elevation following the procedure described by Hofmann et al. (2008). Wave field properties, such as the maximum and significant wave heights ( $H_{\max}$  and  $H_s$ , respectively) and the significant period ( $T_s$ ), were estimated for segments of 1024 (~1.1 min) samples using the zero-upcrossing method (IAHR 1989; Hofmann et al. 2008).

The ADV and the data acquisition system were attached to a bottom-resting tripod. The sensor head was looking downward, with its sampling volume located 0.05 m above the bottom. The near-bottom current velocities were

measured within a range of  $\pm 0.3 \text{ m s}^{-1}$ , with an accuracy of  $10^{-3} \text{ m s}^{-1}$  and a sampling frequency of 8 Hz. The maximum near-bottom current velocity ( $u_{\text{max}}$ ) was calculated from the magnitude of the two horizontal velocity components for time segments of 30 s. Within each interval,  $u_{\text{max}}$  was defined as the mean of the 1% largest current velocities. The suspended sediment concentration (SSC) was determined after calibration of the acoustic backscatter strength of the ADV against in situ water samples (Hofmann 2007). The SSC was calculated as the mean of all samples within time segments of 30 s.

The near-bottom vertical distribution of suspended particles was measured with the ADP mounted on a tripod. The sensor head was looking downward 0.3 m and 0.6 m above the sediment on 02 and 09 July 2008, respectively. Current and backscatter data were measured with a high vertical resolution of 0.03 m and a sampling frequency of 1 Hz.

*Methane measurements and analysis*—Characteristics of the release and the distribution of dissolved methane were measured along a profiling transect positioned perpendicular to the shore of the study site by taking water samples with a 2-liter sampler (Limnos) at depths of 1, 2.5, 5, 7.5, 10, 12.5, 15, 20, 25, and 30 m.

On 02 and 09 July 2008, the transect comprised six stations that covered the littoral zone with distances of 5, 45, 60, 70, 85, and 120 m (P1–P6) and total depths of 1, 2.5, 5, 10, 20, and 30 m, respectively. On both days, these transects were sampled in the morning (07:00–08:00 h), at midday (12:00–13:00 h), and in the evening (19:00–20:00 h). Additionally, water samples were taken at the nearshore station (5 m from the shore, with a total water depth of 1.5 m next to the ADV and the ADP) every half hour and during various ship-wave events every 30 or 60 s to cover the background and the immediate dissolved methane concentration in the water column before, during, and after potential wave-induced release events. In total, 13 ship-wave events were monitored with 6–18 water samples each. On 05 August 2008, the previous transect was extended by four stations that covered not only the nearshore littoral zone but also the offshore pelagic zone, with distances of 5, 45, 60, 70, 85, 120, 490, 880, 1265, and 1590 m (P1–P10; Fig. 1B). Water samples were taken in the surface water layer at depths of 1, 2.5, and 5 m in the morning (07:00–08:00 h), at midday (13:00–14:00 h), and in the evening (18:00–19:00 h).

The dissolved methane concentration of the upper water samples was measured using the headspace method, as described in detail by Casper et al. (2003). Serum bottles were filled with an oversaturated solution of sodium chloride and evacuated. In the field, subsamples of 60 mL were taken from the sampler using a syringe. The aliquot in the syringe was injected in the field into the previously evacuated and pre-capped serum bottle with a total volume of 122 mL. The oversaturated solution of sodium chloride in the serum bottle caused saturation of the added aliquot. Under these conditions methane is degassed quantitatively (nearly 100%) into the remaining headspace ( $\sim 22 \text{ mL}$ ) from the water phase, and methane oxidation was avoided

by killing the freshwater-adapted bacteria (Heyer and Suckow 1985; Casper 1992). Methane concentration in the headspace was measured by gas chromatography using a flame ionization detector (GC-FID, Carlo Erba Instruments—GC 6000) after equilibration (with nitrogen) between the water and headspace. Gas standards of 10, 50, and  $100 \mu\text{L L}^{-1}$  (Air Liquide) were used for the calibration of the GC data. The calibration was repeated every five to 10 water samples and was used for the subsequent samples (respectively). On average, concentration measurements of replicate samples varied by  $\sim 5\%$  (methodical error).

*Time-series analysis and statistics*—The time shift between the observation of elevated dissolved methane concentrations and the occurrence of high  $u_{\text{max}}$  and SSC due to waves was estimated using a cross-correlation technique. First, the mean was removed from the time series of dissolved methane measured on 02 and 09 July 2008. Then, the data on  $u_{\text{max}}$  and SSC were linearly interpolated to provide  $u_{\text{max}}$  and SSC at the times at which dissolved methane was measured. Finally, the linearly interpolated time series of  $u_{\text{max}}$  and SSC, respectively, were correlated with the methane time series, providing the linear correlation coefficient ( $R$ ) and the probability ( $p$ ) within a 95% confidence interval. The procedure was repeated for different time shifts between the methane and the  $u_{\text{max}}$  and SSC time series by interpolating the latter to a time vector shifted relative to the times at which the dissolved methane concentrations were measured.

Daily mean methane profiles at each station and the corresponding standard deviations were calculated by averaging all samples at the respective station collected during three transects measured on 02 and 09 July 2008, respectively. On 05 August 2008, contour plots of the methane distribution were calculated by linear interpolation within the upper water column (1-, 2.5-, and 5-m sampling depths).

On 05 August 2008, the gradient of the dissolved methane concentration in 1-m water depth with increasing distance to shore was analyzed using separate linear regression models (LRM) for the time periods of morning, midday, and evening. Additionally, the effect of the distance to shore (onshore, offshore) and of the time of day (morning, midday, evening) was tested via a two-factorial ANOVA. The data from the first three littoral sampling stations (P1–P3) were considered to represent onshore conditions, whereas the data from the last three pelagic sampling stations (P8–P10) were considered to represent offshore conditions. Post hoc comparisons were done with a Tukey test.

*Temperature measurements*—Between 02 and 09 July 2008, water temperature was measured continuously along a vertical chain of eight thermistors (RBR, TR-1060) at depths of 1, 2.5, 5, 10, 12.5, 15, 17.5, and 20 m, with a sampling frequency of 0.1 Hz. The thermistor chain was positioned 85 m offshore (Fig. 1A). Water temperature was also measured by the attached thermistor of the manual water sampler (Limnos) at each station and water depth

during the methane sampling. Temperature profiles were calculated as daily averages, with their standard deviation from the data of the thermistor chain and the thermistor of the water sampler.

## Results

*Wave-induced release of methane*—On all sampling days, wind-generated waves (wind waves) were of minor importance. At our sampling site, wind waves were characterized by short wave periods (0.5–1.5 s) and respectively short wave lengths ( $\sim 1$ –3 m) and had only small wave heights (below 0.05 m). In contrast, the regularly observed ship waves had wave heights measuring between 0.1 and 0.3 m, indicating that the surface wave field (sum of all measured surface waves with their characteristics) was dominated by ship waves (Fig. 2A,B; Hofmann et al. 2008). These waves were generated by nearby crossing ferries and passenger ships that travel parallel to the shore. Both ship types operate mainly during daytime hours (06:00–21:00 h) and thus create a diurnal pattern of the wave field, with high and regular-occurring waves during daytime and nearly none at night (Hofmann et al. 2008). The ship waves typically have periods of between 3 and 4 s and wave lengths between 12 and 17 m (calculated for deep-water waves) and thus can easily be distinguished from the wind waves.

At the nearshore methane sampling station (water depth, 1.5 m), these ship waves induced maximum near-bottom current velocities ( $u_{\max}$ ) of  $\sim 0.1$ – $0.3$  m s $^{-1}$  that periodically reoccur over several minutes, a time period corresponding to the passage of a single ship-generated wave group (Fig. 2). During these single ship-generated wave events, particle resuspension occurred regularly, leading to SSC values of  $\sim 20$ – $200$  mg L $^{-1}$  (Fig. 2), extending up to 0.3–0.4 m into the water column above the sediment bottom (Fig. 2C,D). The rapid increase and later decrease of  $u_{\max}$  and the SSC were accompanied by a short-lasting (10–20 min) increase in the dissolved methane concentration (Fig. 2C,D). The increase in methane concentration was delayed by  $\sim 2$ – $4$  min, compared to the increase in the SSC and  $u_{\max}$ . Peak values of the methane concentration measured up to 50% above background concentrations and remained for several minutes (3–15 min). On 02 and 09 July, in total 13 single ship-generated wave events were monitored. Eleven of these events were accompanied by a pronounced increase in the dissolved methane concentration, following the same pattern described above. Methane concentration did not increase (09 July, 13:50–14:00 h) or was characterized by an ambiguous pattern (09 July, 12:00–12:20 h) during only two events. Analysis of both days' time series (02 and 09 July) using a cross-correlation technique affirmed the previously observed time shift between the time series of the dissolved methane concentration and  $u_{\max}$  and SSC, respectively. Within a realistic 10 min time range, correlation coefficients were highest at 3.5 min, on average (02 July:  $R = 0.31$ ,  $p < 0.002$ ; 09 July:  $R = 0.22$ ,  $p < 0.04$ ).

In general, the methane concentration was highly variable in the shallow littoral zone during the day; it is

likely that this finding was caused by the regularly occurring ship wave-induced methane-release events (Fig. 2). The methane background concentrations at midday and in the evening tended to be higher than in the morning (Fig. 2A,B). On 02 July, the methane concentrations in the shallow littoral were about two times higher than those observed on 09 July (Figs. 2A,B, 3A–F). On both days the surface wave field was similar (evident based on the similar course of  $u_{\max}$  and SSC), but the near-surface temperatures in the shallow water differed by 6°C (i.e., the water temperatures were  $\sim 23.5^\circ\text{C}$  on 02 July and  $\sim 17.5^\circ\text{C}$  on 09 July, respectively; Fig. 3G). Despite the difference in the absolute concentration in dissolved methane, the patterns of evolution of the methane concentration during the day and during single ship-wave events were similar on both days (Fig. 2).

*Spatial and temporal distribution of methane*—The distribution of dissolved methane measured along profiling transects was characterized by strong and pronounced spatial and temporal gradients on all sampling days (02 and 09 July and 05 August) (Figs. 3A–F, 4), which corresponded to the enhanced release of methane in the shallow littoral zone and the temperature distribution.

*Nearshore*—On 02 and 09 July, dissolved methane concentrations were highest near the water surface (1.24 and 0.67  $\mu\text{mol L}^{-1}$ , average of all profiles at 1 m water depth). Within the profiles methane generally decreased with depth (Fig. 3A–F). On 02 July, methane concentrations in the upper 15 m of the water column were typically about two times higher than on 09 July, when water temperatures in the upper 15 m were  $\sim 6^\circ\text{C}$  lower than on 02 July (Fig. 3). On 02 and 09 July, average methane concentrations in the upper 5 m of the water column decreased between Sta. P1 and Sta. P3 by  $\sim 0.43$   $\mu\text{mol L}^{-1}$  and 0.14  $\mu\text{mol L}^{-1}$ , respectively, and decreased between Sta. P3 and Sta. P6 by  $\sim 0.20$   $\mu\text{mol L}^{-1}$  and 0.14  $\mu\text{mol L}^{-1}$ , respectively. These lateral differences in methane concentration indicate that on both days a methane gradient in the offshore direction existed, with high concentrations in the nearshore littoral zone and low concentrations further offshore. The methane gradient was higher on the warm day (02 July) than on the cold day (09 July). Below 15 m the absolute methane concentrations were only  $\sim 0.08$   $\mu\text{mol L}^{-1}$  (average of the profiles P5 and P6 below 15-m water depth), which are very low compared to the concentration in the overlaying water column and the differences observed between both sampling days (Fig. 3A–F).

*Between the nearshore littoral and the pelagial*—On 05 August, the nearshore transects, taken in the morning (07:00–08:00 h), at midday (13:00–14:00 h), and in the evening (18:00–19:00 h), were complemented by additional measurements in the upper water column further offshore in order to measure the spatio-temporal distribution of dissolved methane between the shallow littoral zone and the pelagic zone. During the course of the day, methane concentrations in the nearshore, shallow littoral zone increased from  $\sim 0.41$   $\mu\text{mol L}^{-1}$  in the morning to

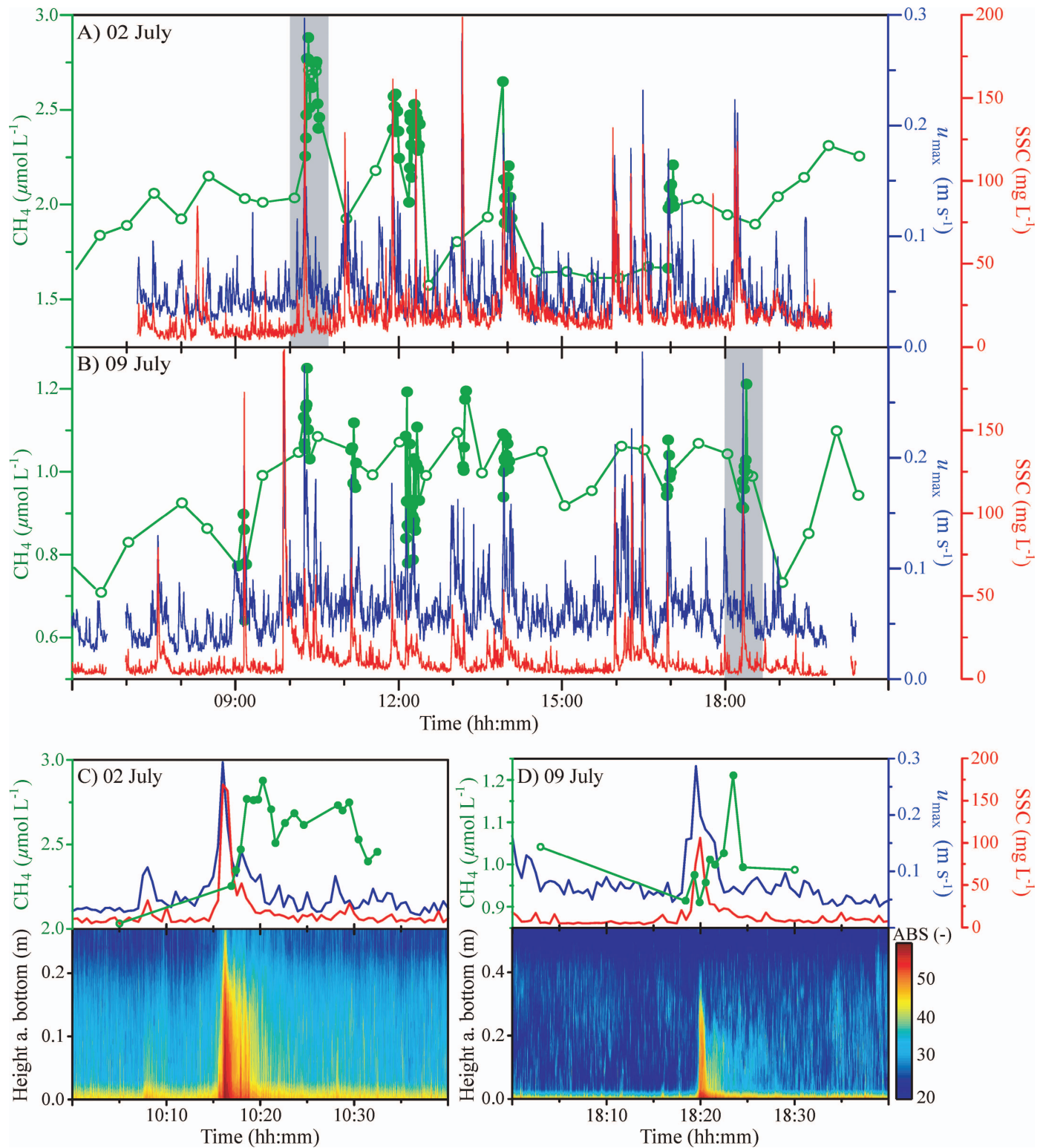


Fig. 2. Variation of the wave-induced, maximum near-bottom current velocity  $u_{\max}$ , the suspended sediment concentration (SSC), and the dissolved methane concentration in the shallow littoral. (A, B) Diurnal variation and (C, D) single ship-wave-induced methane release event, with contour plot of the acoustic backscatter strength, on 02 and 09 July 2008, respectively. The green, open circles indicate the continuous sampling of methane and the filled circles indicate the event-like sampling of methane. The gray bars in panels A and B indicate the specific wave events shown in panel C and D. Note the different scaling of the dissolved methane concentration and the height above bottom on 02 and 09 July 2008.

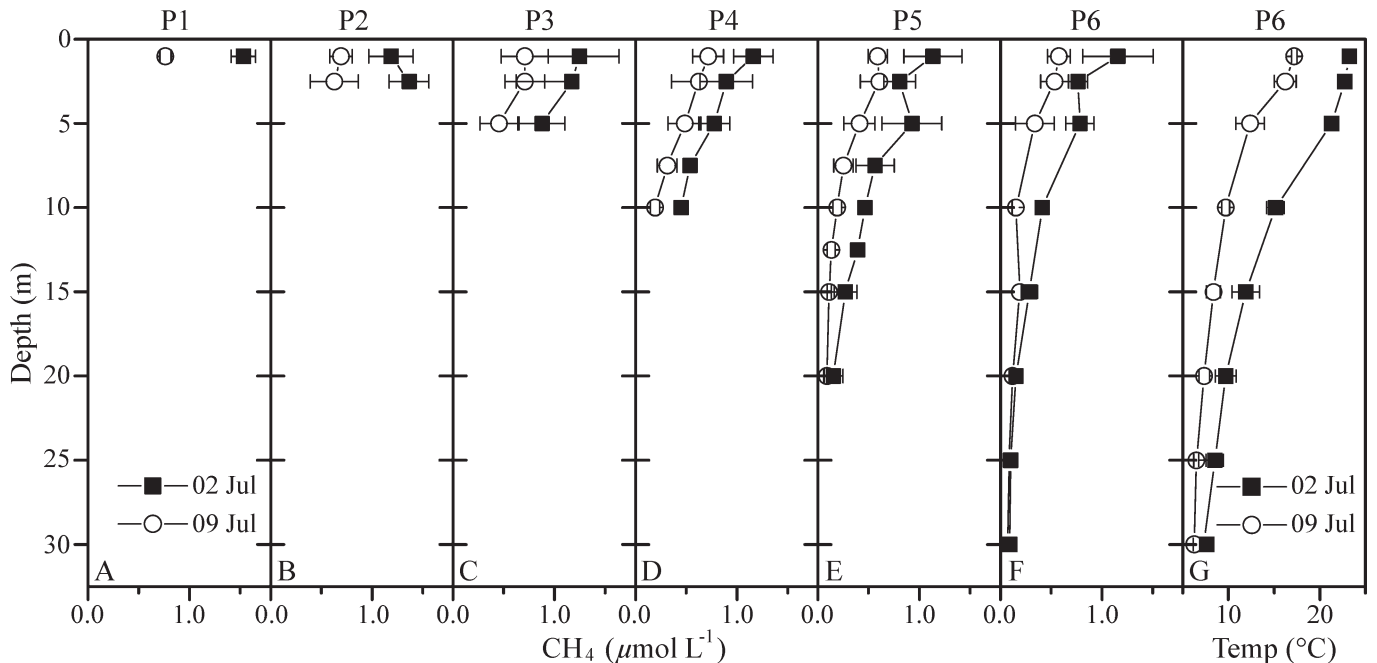


Fig. 3. (A–F) Methane and (G) temperature profiles (mean  $\pm$  SD) on 02 and 09 July 2008.

$0.52 \mu\text{mol L}^{-1}$  at midday and  $0.66 \mu\text{mol L}^{-1}$  in the evening (average of the two first sampling stations nearshore at depths of 1-m and 2.5-m; Fig. 4A–C). Changing high methane concentrations were also observed around 500 m offshore in terms of an enclosed near-surface cloud (Fig. 4A–C). Further offshore, between 1100 and 1590 m, methane concentrations were the lowest, measuring  $\sim 0.3 \mu\text{mol L}^{-1}$ , on average, throughout the day. In general, the increase in methane concentrations at the nearshore stations over the course of the day (Fig. 4) resulted in an increased gradient (LRM; morning: slope  $[S] = -6.02 \times 10^{-5} \mu\text{mol m}^{-1}$ ,  $R^2 = 0.20$ ; midday:  $S = -1.95 \times 10^{-4} \mu\text{mol m}^{-1}$ ,  $R^2 = 0.71$ ; evening:  $S = -1.43 \times 10^{-4} \mu\text{mol m}^{-1}$ ,  $R^2 = 0.44$ ) between the high methane concentrations in the shallow littoral zone and the low concentrations in the epilimnetic waters of the pelagic zone. These results are confirmed by the ANOVA: the dissolved methane concentrations of the first three littoral sampling stations (P1–P3) differed significantly from the concentrations of the last three pelagic sampling stations (P8–P10) (ANOVA:  $F_{1,12} = 18.75$ ,  $p < 0.001$ ), regardless of the time of the day (ANOVA:  $F_{2,12} = 3.61$ ,  $p > 0.05$ ). Additionally, the overall dissolved methane concentration increased during the course of the day (ANOVA:  $F_{2,12} = 6.29$ ,  $p = 0.014$ ), resulting in a significant difference between the morning and midday concentrations (Tukey test:  $p = 0.012$ ).

## Discussion

*The role and importance of surface waves for the release of methane in lake littoral zones*—In lake sediments, methane is produced in the lower anoxic sediment layer and diffuses from there toward the sediment–water interface. At the sediment–water interface  $\sim 90\%$  of the produced methane

is again oxidized in a very thin oxic sediment layer (Frenzel et al. 1990; Rolletschek 1997). The remaining low methane concentration in the upper sediment layer leads to a vertical methane gradient between sediment and water column that is responsible for the methane flux (driven by molecular diffusion) from the sediment to the water column (Huttunen et al. 2006).

During summer, the littoral sediments as well as the profundal sediments of Lake Constance are rich in fresh organic material (J. Deutzmann pers. comm.). The main differences between littoral and profundal sediments are the warmer water and sediment temperatures in the littoral during summer and the exposure of littoral sediments to forcing by surface waves. Higher temperatures support higher methane production rates (methane production rates in littoral sediments of Lake Constance were measured by Thebrath et al. [1993], as follows: in winter:  $\sim 5 \text{ mmol m}^{-2} \text{ d}^{-1}$ , in summer:  $30\text{--}95 \text{ mmol m}^{-2} \text{ d}^{-1}$ ), whereas surface waves acting on the sediment surface may substantially enhance the methane flux from the sediments.

Hydrodynamically, surface waves represent the most important process in the littoral zone, causing intense pressure oscillations and large oscillating currents (Hofmann et al. 2008). The pressure fluctuations can enhance interfacial sediment pore-water exchange by causing wave pumping (Precht et al. 2004). The large currents generate turbulence that reduces the thickness of the diffusive boundary layer, which results in an increase in the diffusive flux from the sediments (Lorke and Peeters 2006). Furthermore, the current shear can cause a breaking up of the sediment surface via particle resuspension (Nielson 1994; Hofmann 2007) and thereby can directly release pore water to the water column. Our investigations have shown that burst-like releases of methane into the water column are connected to wave-induced sediment resuspension

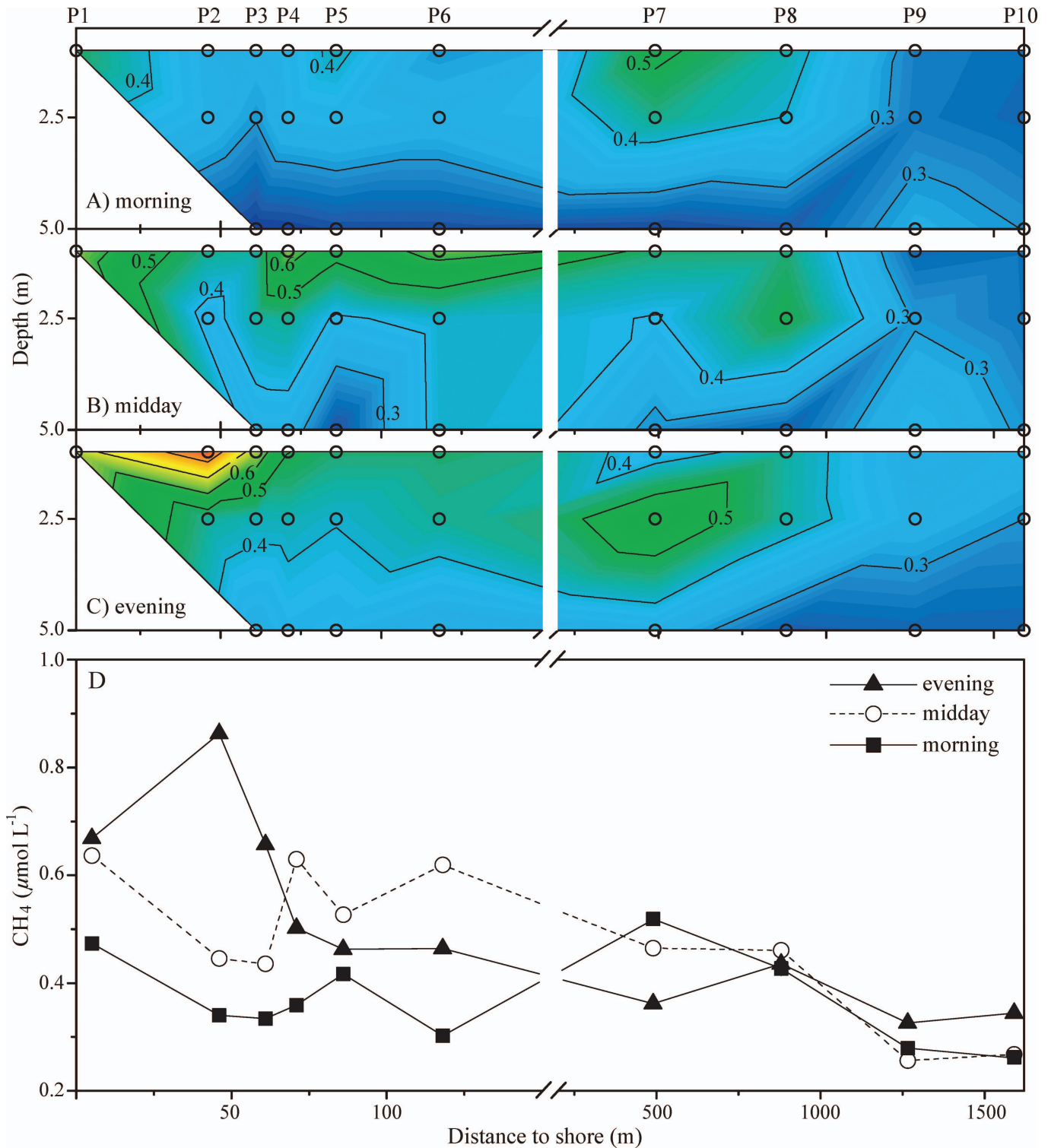


Fig. 4. Diurnal and cross-shore variation of dissolved methane on 05 August 2008. (A–C) Contour plots of the dissolved methane concentration ( $\mu\text{mol L}^{-1}$ ) in the upper water column (1–5 m) in the morning, at midday, and in the evening. The black circles represent the sampling grid. (D) Line plots of the dissolved methane concentration at a depth of 1 m in the morning, at midday, and in the evening.

(Fig. 2), indicating that resuspension reaches down to the methane-rich anoxic sediment layer. The resultant dissolved methane concentrations were far above the background concentrations and, thus, above those associated

with the non- or pre-wave situations, in which the release of methane from the undisturbed and consolidated sediments was dominated by diffusion. Hence, surface waves are an important trigger that temporally enhances the release of

methane from the littoral sediments to the water column and thus causes an increase in the dissolved methane concentration in lake littoral zones.

The pattern and the amount of released methane from littoral sediments are correlated with the characteristics of the surface wave field. On all sampling days, the wave field was dominated by ship waves, since wind waves had very low wave heights (below 0.05 m). The wave field generated by the ship traffic on Lake Constance is characterized by a pronounced diurnal pattern, with wave groups occurring regularly and periodically during the day and with nearly no wave action during the night (Hofmann et al. 2008). This wave-field pattern implies reduced disturbances of the sediment and, thus, reduced release of methane during the night. Hence, the methane produced in the sediments can accumulate during the night. In the morning, before the first ship-wave groups have propagated into the littoral zone, dissolved methane concentrations in the water column are low, but the littoral sediments below the very thin oxic sediment layer can be considered to be saturated or even oversaturated with methane (Thebrath et al. 1993; Casper 1996). Thus, the first wave groups, and especially the ones that induce resuspension, have the greatest potential to cause a substantial release of the methane that accumulated overnight in the upper sediment layer, near the sediment–water interface (Fig. 2). The subsequent wave-induced events of methane release are less effective at enhancing the dissolved methane concentration in the water column (Fig. 2A), because the methane concentrations in the upper, suspendable sediment layer are already depleted by the previous release events. Over the course of the day, the frequent occurrence of ship waves hinders sediment consolidation (Schoellhamer 1996; Hofmann 2007) and, hence, the accumulation of significant amounts of methane in the pore water of the upper, suspendable sediment layers. In general, the amount of released methane depends on the time between two successive wave groups and the methane production rate. On 02 July, the dissolved methane concentrations and the amplitudes of the methane burst events were about two times higher than on 09 July. These findings not only support the hypothesis that higher sediment temperatures lead to higher methane production in the sediments, but they also indicate that the wave-induced release events are capable of efficiently mobilizing this additionally produced methane from the top sediment layer.

Typically, dissolved methane concentrations in the shallow littoral zone were low in the morning and increased over the course of the day (Fig. 2A,B). However, the methane concentration had a high temporal variability, with significant peaks that usually occurred shortly after the passage of surface waves (Fig. 2). The variability in the methane concentrations can be explained by a number of processes: (1) Methane released at the sediment–water interface is diluted with the methane-poor water of the overlying water column, where vertical and horizontal mixing are able to reduce the peak concentration to near background concentrations within several minutes after the release event (Fig. 2C,D). (2) The heterogeneity of the littoral sediments may result in small-scale and large-scale

heterogeneity in the amount of released methane. Thus, cross-shore and along-shore currents can transport methane-rich water, but also methane-poor water, in both directions, which alters the methane background concentrations, apart from the wave-induced release events (Fig. 2A,B). (3) During a release event, not only does methane-rich pore water enter the overlying water column, but the methane-oxidizing bacteria previously situated at the sediment–water interface enter the overlying water column as well. These methane-oxidizing bacteria may enhance the rate of methane oxidation in the water column after the releasing event (Bastviken et al. 2002). The last process seems to be more pronounced when water temperatures are high (Thebrath et al. 1993; Casper 1996). Nevertheless, in our observations the methane peak concentrations remained high for a longer period of time at higher water temperatures (02 July) than at lower water temperatures (09 July) (Fig. 2C,D). This indicates that methane oxidation within the water column alone cannot be the reason for the fast decline in methane concentration after the release events.

The importance of ebullition, which may also contribute to an increase in dissolved methane, was not investigated but seems to be limited, since the exchange of methane from rising bubbles with ambient water is very small along short trajectories (McGinnis et al. 2006). However, the regular and periodic ship-wave-dominated wave field may reduce the amount of methane released by ebullition from the sediments and later the direct emissions to the atmosphere, because these ship waves enhance the transport of dissolved methane from the sediment pore water to the water column on a regular basis. This reduces the probability of methane oversaturation in the upper sediment layers required for the formation of gas bubbles. Thus, ship waves and waves in general can be expected to reduce the formation of gas bubbles but to increase the proportion and concentration of methane that is dissolved in the water column.

How wind waves affect the release of methane from the littoral sediments is still an open question and was not investigated in this study. The release pattern of methane in a wind-wave-dominated littoral is expected to be different from that in a ship-wave-dominated littoral, because wind waves typically occur sporadically and can last for hours (Hofmann et al. 2008), rather than for minutes, as is the case for ship-wave groups. Because wave heights associated with wind waves are typically higher than those connected to ship waves, one may expect a stronger effect on methane release by wind waves compared to ship waves. This is especially the case in the shallow littoral zone during storm events, during which wind waves are able to remobilize deep sediment layers with methane. However, depending on the fetch, wind waves typically have shorter wave lengths than ship waves, at which current velocities attenuate faster with depth and, thus, the potential for resuspension (Hofmann et al. 2008) and methane release. Furthermore, the long duration of wind-wave events may result in an exhaustion of the methane stored in the sediments such that toward the end of the wind event only little methane is available for mobilization by the wind



waves. Lakes that are characterized by periodic day–night winds (e.g., Lake Kinneret [Marti and Imberger 2008] or Lake Erie [Bolsenga and Herdendorf 1999]), and thus by a periodically occurring wave field, may have a similar pattern of methane emissions from the sediments, compared with shore regions with a ship-wave–dominated wave field. However, lake shorelines that are exposed to surface waves can be expected to be hot spots for high dissolved methane concentrations, especially if these sites are characterized by sediments that are fine grained and rich in organic material (e.g., river estuaries, embayments, or bays).

*Spatial and temporal distribution of methane: Littoral zones as a source of methane*—During the summer, littoral sediments are expected to have higher methane production rates compared to the sediments in the profundal (Thebrath et al. 1993; Casper 1996), because littoral sediments have higher temperatures than profundal sediments. Additionally, surface waves were found to trigger and enhance the release of dissolved methane in the shallow littoral zone of lakes. Hence, the combination of high water temperatures and the action of surface waves in the littoral zone creates and intensifies spatial and temporal methane gradients between the shallow littoral and the open water and deep water (pelagial).

In lakes with an anoxic hypolimnion methane usually increases from the surface to the deep water (Bastviken et al. 2008; Fahrner et al. 2008). Since the sources of methane are the sediments one would also expect to find in lakes with an oxic hypolimnion, such as Lake Constance, open-water methane decreases from the sediments to the lake surface where methane, being very poorly soluble, degasses to the atmosphere. However, in our profiles the methane concentrations near the lake surface are higher than below the surface (Fig. 3A–F), confirming earlier measurements from Lake Constance (Schulz et al. 2001) as well as data from other lakes with an oxic hypolimnion (Smith and Lewis 1992; Murase et al. 2003). Because the methane concentrations in the hypolimnion are lower than in the epilimnion under stratified conditions, the hypolimnion cannot be the source of the high methane concentrations in the epilimnion.

During daytime, the dissolved methane concentrations decreased along the cross-shore transect, with high concentrations in the littoral zone (onshore) and low concentrations further offshore (Fig. 4). The high methane concentrations measured around 500 m offshore may originate from methane that was transported as a plume from surrounding littoral zones to the investigated cross-section and that rendered the measured methane gradient weaker. However, the decrease in methane from the shallow littoral to the pelagic zone implies that water exchange by advection and diffusion leads to a horizontal transport of methane from the shallow littoral zone to the open water. The production and release of methane in the littoral sediments keep methane concentrations in the littoral zone at a high level, especially during the day (Fig. 4). This indicates that the flux of methane from littoral sediments is sufficient to compensate the methane

fluxes from the littoral zone to the open water, the oxidation in the water column, the flux due to vertical mixing with underlying methane-poor waters, and the gas exchange with the atmosphere. Hence, the high methane concentrations in the nearshore littoral zone (Figs. 3A–F, 4) may act as source of methane for the pelagic zone via lateral transport. Because of the small vertical mixing across the thermocline under stratified conditions, the methane flux from the littoral zone may explain the higher concentrations of methane in the epilimnion, compared to those in the upper hypolimnion. In conclusion, the data on methane distribution indicate that methane released from littoral sediments and transported laterally from the littoral to the pelagic zone is the origin of the elevated methane concentrations observed in the epilimnion of the pelagial (Figs. 3A–F, 4). The sequence of elevated methane production in the littoral sediments, compared to the profundal sediments; surface wave–induced pore-water release of methane to the littoral water column; and subsequent distribution of this methane within the surface layer of lakes enhance the near-surface methane concentrations in a large area, which leads to an increased flux of methane at the air–water interface and thus enhances the overall emissions of methane from lakes to the atmosphere.

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