Improved method for the quantification of methane concentrations in unconsolidated lake sediments

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Abstract

There is conclusive evidence that the methods most commonly used to sample methane (CH_4) dissolved in pore water of lake sediments produce results that are likely to be affected by gas loss or gas exchange with the atmosphere. To determine the in situ amount of CH_4 per unit mass of pore water in sediments, we developed and validated a new method, that combines techniques developed for noble gas analysis in pore waters with a standard headspace technique to quantify the CH_4 present in the pore space in dissolved and gaseous form. The method was tested at two sites: Lake Lungern, where CH_4 concentrations were close to saturation; and Lake Rotsee, where CH_4 concentrations are known to exceed saturation, and where CH_4 bubble formation and gas ebullition are commonly observed. We demonstrate that the new method, in contrast to the available methods, more reliably captures the total amount of CH_4 per unit mass of pore water consisting of both dissolved and free CH_4 (i.e., gas bubbles) in the pore space of the sediment.

Introduction

Methane (CH_4) in the atmosphere acts as a potent greenhouse gas.[1] Inland waters[2] are one of its many sources, particularly microbiological production in eutrophic lakes.[3,4] Anthropogenically - induced eutrophication currently affects inland waters (lakes, reservoirs, ponds and rivers) on a global scale,[5–7] together with increasing CH_4 production[8], which has recently been identified as relevant for the global carbon budget.[9–12] Taking into account that sediments are the main zone of CH_4 production in lakes and rivers,[13] quantifying the real amount present in sediment pore water is vital for an understanding of its impact on aquatic systems and its relevance for climate change.[13,14]

A method that can accurately determine the spatial and temporal distribution of CH_4 amounts in the sediment pore space is required in order to quantify the CH_4 budget in lake sediments. The central experimental challenge, applying commonly used methods for the analysis of CH_4 concentrations in the pore water of (lacustrine) sediments, is that CH_4 occurs in both dissolved and free gaseous form (e.g., as bubbles).[15] In this paper, we refer to the sum of both the in situ dissolved CH_4 concentration plus the amount of CH_4 present in gaseous form as the total amount of CH_4 per unit mass of pore water (i.e., "CH_4-TAMP"). CH_4 bubbles are formed in the lacustrine sediment when methane concentrations exceed the CH_4 in situ saturation concentration (i.e., supersaturation) in the pore water.[16] Causes for this CH_4 supersaturation are CH_4 production by microorganisms within the sediment and hydrostatic pressure decrease during reservoir drawdown.[17]

In aquatic systems characterised by active bubble emission from the sediments, CH_4 amounts are expected to exceed the in situ saturation concentration in the pore water. However, conventional methods for CH_4 analysis are often subject to gas loss and fail to adequately determine CH_4-TAMP expected in such systems.[8,18,19] Using conventional methods attempting to determine CH_4-TAMP in lacustrine sediments (for a review see Adams et al. 1995), samples are collected either (1) from the recovered cores or (2) by in situ devices,[15] as discussed below.

1. In recovered sediment cores, CH_4-TAMP is usually determined by using a tipless syringe to sub-core the sediment core at previously-defined sampling ports along the core liner (syringe standard method "SSM"). The extracted bulk sediment is transferred by the tipless syringe into a glass vial, which is closed with a septum for subsequent headspace analysis.[8,15,20–24] During this transfer, the sediment is normally exposed to air for about two seconds, resulting in secondary gas exchange, i.e., CH_4 loss from the sample.[20] Such CH_4 loss is estimated to range from 2 to 31% during transfer of the sediment from the core to a sample vial by a syringe, when applying the SSM method to bulk sediment containing numerous bubbles.[15] Although being known to be subject to gas loss, the SSM method is commonly used to quantify CH_4 concentrations in the sediment pore water of lakes and oceans.[8,15,20–24] As a result, the concentrations reported in such studies are conceived to be biased. For example, sediment samples from a study using the SSM method at Lake Wohlen, where an active CH_4 bubble emission to the atmosphere was demonstrated[18], showed CH_4 concentrations that were significantly lower than respective in situ saturation concentration.[8] Another example is the application of the SSM method at Lake Geneva at locations where bubbles were abundant and visible in the sediment core:[19] "Ebullition was observed at several (. . .) coring locations but supersaturation of CH_4, which is needed for bubble formation,[16] was not reached in most of the cores (. . .)".[21] While the authors suggest that this undersaturation is explained by the heterogeneity of the sediment, we hypothesize that it might be the result of gas loss during the sampling procedure. The amounts of CH_4 in the pore water of Lake Rotsee have been investigated in studies applying different methods, one study applied the dialyzer method (see below), whereas the others applied the SSM method.[24–27] The results determined by the SSM method (0.7 - 5.9 mM CH_4) always showed concentrations lower than in situ saturation concentration and were an order of magnitude lower than the CH_4-TAMP determined by the dialyzer method (20 - 40 mM CH_4).[27] To conclude, in productive sediments with obvious

[69] CH_4 supersaturation, the concentrations determined by the SSM method are severely [70] biased toward lower concentrations. This is mainly explained by secondary gas ex- [71] change during SSM sampling, resulting in gas loss. Therefore, the SSM method is not [72] an appropriate method to quantify the true CH_4-TAMP in unconsolidated sediments [73] of lakes (and oceans). Nevertheless the SSM method is frequently applied.[8,15,20–24]

[74] 2. Another method commonly applied for in situ sampling is the peeper or dialyzer [75] method.[15,28,29] According to this method, a plexiglas plate with water-filled cham- [76] bers covered by a dialysis membrane[15] is inserted into the sediment. The plate is left [77] in the sediment for $1 - 3$ weeks until the equilibrium between the pore water and the [78] water in the chambers is attained. After the plate has been retrieved, the water in [79] the chambers is sampled by piercing the membrane with a syringe. Diffusion of gases [80] through the membrane during retrieval of the dialyzer plate and gas exchange with the [81] atmosphere when piercing the membrane of the dialyzer compartments can result in [82] gas loss.[15] In addition, the method is time consuming and the degree of equilibration is [83] often uncertain, as it depends on the sediment porosity, which may not be known. And [84] again, the determined CH_4-TAMPs tend to be biased toward lower values.[15] Peeper [85] methods appear to be inappropriate for quantitatively capturing poorly soluble species, [86] as indicated by the comparison of CH_4-TAMPs obtained from peepers and squeezing [87] technique for the determination of total methane in the sediment.[30] Further disad- [88] vantages are the high expenses and high amounts of work associated with setting and [89] collecting of the dialyzer plates. If dialyzer plates are used to sample gas-rich sediments [90] at great depths, the membranes can break as a result of degassing during retrieval.[28]

[91] In order to reliably quantify the real, in-situ CH_4-TAMP in lacustrine sediments, we [92] propose an adaptation of a method that has been developed to sample and analyse noble [93] gases in the pore water of unconsolidated sediments.[31,32] Noble-gas concentrations in the [94] sediment pore water provide information on transport and gas exchange processes within [95] the sediment and were used to reconstruct past climatic conditions and to quantify CH_4

ebullition.[33–35] The method for noble gas analysis in lacustrine sediments has been shown to prevent degassing and atmospheric contamination artefacts during sampling[31,32,36] and thus might allow the unbiased assessment of the CH_4-TAMP of unconsolidated sediments in rivers, lakes and oceans. We tested the new method in a laboratory experiment and at two Swiss lakes: (1) Lake Lungern, where CH_4-TAMPs throughout the sediment core are expected to agree with the in situ saturation concentration; and (2) Lake Rotsee, where the pore water of the sediment is significantly supersaturated with CH_4 and where bubbles are visible in sediment cores.

Experimental methods and procedures

Methods

To determine CH_4 concentrations in the pore water of sediments, the sampling method commonly used for the measurement of noble gases in the pore water of unconsolidated sediments[31,32] was combined with a standard headspace technique.[37] Important features of this combined method, the copper tube centrifugation ("CTC") method include the separation of pore fluids from the sediment by centrifugation and storage of the pore water in a copper tube, prior to analysis.

Copper tube centrifugation method

Pore water samples for CH_4 analysis were acquired according to the sampling protocol developed and optimised for noble gas analysis in lacustrine sediments[31,32]. The sediment cores were collected using a gravity corer and a plastic liner, where holes (or sampling ports) were drilled along the liner. Threads were carved in these sampling ports allowing the later connection to modified Swagelock-fittings (SS-600-1-6BT). Prior to coring the sampling ports were sealed by adhesive tape. Immediately after core retrieval (within a few to 30 min after core retrieval), each sediment core was placed in a horizontal position to prevent the vertical

migration and loss of bubbles formed in the core during sampling. Copper tubes (30 cm length, ≈1 cm diameter) with modified Swagelock-fittings were then attached to the pre-drilled sample ports of the liner by piercing the adhesive tape. For more details regarding sediment core retrieval and sampling refer to Brennwald et al. 2003. Subsequently, the sediment in the liner was pressurised by two pistons inserted into each end of the core. Such pressurising minimises and counteracts the bubble formation that arises from degassing as a result of increased temperatures and the equilibration of the core with ambient pressure. The pistons were pushed into the liner to increase the pressure acting on the sediment within the liner. Pressure is augmented until pushing the bulk sediment through the ports into the attached sample containers, i.e., copper tubes. This squeezing results in a displacement of the sediment in the liner, which reduces the spatial resolution of the sampling depth. After adequate flushing and optical observation that sediments was pushed through the copper tube, the copper tubes were made airtight using two stainless steel pinch-off clamps (see Figure 1, panel A), the same as those used for sampling noble gases dissolved in lake and groundwater.[38,39] We note that sandy or other coarse sediments where grain size is similar with the diameter of the copper tube, severely constrains sampling. Subsequently the closed copper tubes were split into two aliquots by adding and closing additional pinch-off clamps. The two aliquots of each sample were centrifuged. The first aliquot was used to determine the geometrical position of the sediment/water interface within the copper tube. According to this position (∼3 cm next to the pinch-off clamp in the up position during centrifugation), an additional pinch-off clamp was placed on the remaining aliquot to separate the pure pore water from the compressed sediment matrix.[32]

While the previously described steps of sample processing are the same as in case of processing sediment samples for noble gas analysis (for details see Tomonaga et al. 2011), in the following the processing of the sediment samples for methane analysis differs to the processing of sediment samples for noble gas analysis.[31,32,38] The aliquot samples were treated twice in an ultrasonic bath for 15 minutes each time (i.e., before centrifugation and after separation

[147] of the pure pore water). Treatment in the ultrasonic bath has two purposes: it loosens the [148] sediment matrix (e.g., improves the compressibility of the sediment) and suppresses bacterial [149] activity[40] in the water phase (refer to Figure 1, Panel B, step 1). The storage of the pore [150] water in the copper tube constrains bacterial growth.[41] To further reduce bacterial activity, [151] the samples were kept at +3°C and were processed immediately after sediment sampling. If [152] analysis could not be carried out within a few days after sampling, the samples were frozen [153] and stored at -20°C to inhibit biological activity.
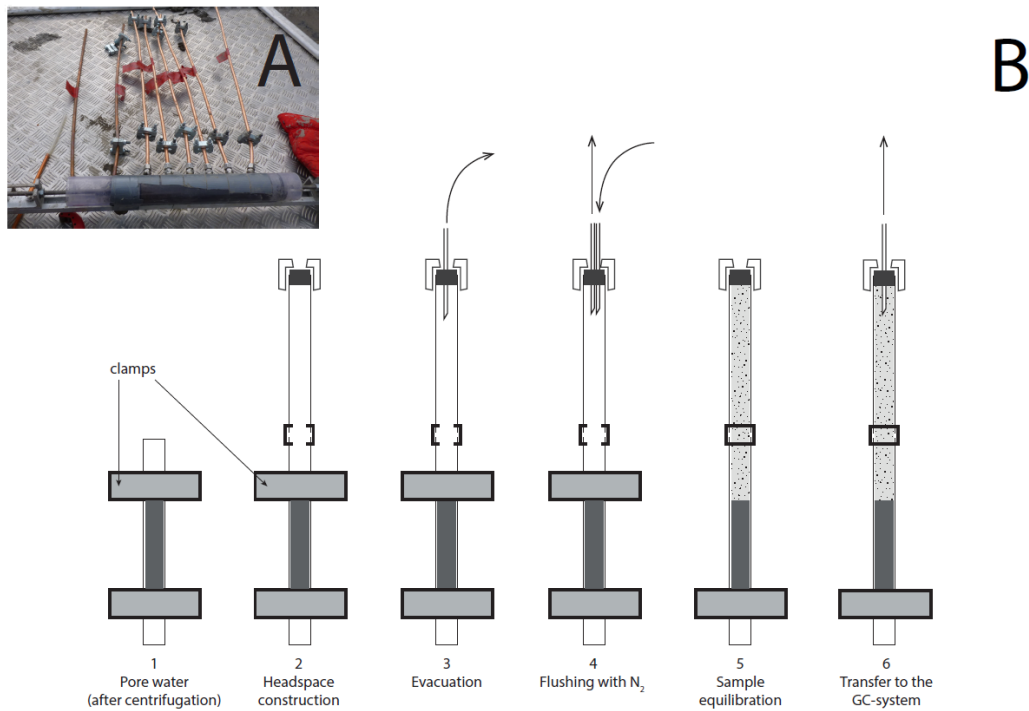
Figure 1: **A.** Experimental set-up: The photo was taken after sampling the sediment and after closing copper tubes airtight with pinch-off clamps. The core liner is mounted in the squeezer and copper tubes with fittings are attached to the sampling ports. **B.** Preparation of the sample's headspace for the subsequent gas/methane analysis by gas chromatography (GC). 1) Pure pore water sample separated from the sediment matrix by centrifugation (Tomonaga et al., 2011). 2) Headspace construction by mounting an additional copper tube segment with Swagelok fittings. 3) Headspace evacuation and 4) flushing the headspace with nitrogen at atmospheric pressure (steps 3 and 4 are repeated three times). 5) Opening and shaking of the water sample 3 times for 60 seconds to reach gas equilibrium with the headspace (the gas mixture from the head space and from the water sample are shown in the graph as grey and dotted area). 6) Gas injection into the GC for final CH_4 quantification.

[154]   For the final gas chromatographic (GC) analysis, the gas content within the sample was

extracted using a common headspace technique. For this purpose, an additional copper tube segment with a septum was attached to build a headspace of about 8 mL. One end of this additional copper tube segment was connected to the pore water sample using a Swagelok SS-600-6 fitting (Figure 1, Panel B, step 2). The other end was sealed airtight with a Swagelok SS-8-VCO-6-600 fitting and a Swagelok SS-8-VCO-4 female nut holding a 3.4-mm-thick PTFE septum (Infochroma G074-SK32FW02) tailored to fit into the connector. The headspace was filled with pure nitrogen (N_2) before opening the sample towards the headspace. To this end, the copper tube segment (headspace) was evacuated and flushed with pure N_2 three times (Figure 1, Panel B, steps 3 and 4) and finally left filled with N_2 at atmospheric pressure. The pinch-off clamp separating the pore water sample from the headspace was then opened. To equilibrate the headspace with the pore water, the sample was shaken for 3 minutes by hand (Figure 1, Panel B, step 5). The sample gas was extracted from the headspace (Figure 1, Panel B, step 6) and injected to a GC for final CH_4 analysis by an gas tight injector, i.e., a needle connected to a metal tube coupled with a 24-port valve (VICI). To control the stability of the analysis a standard with a known methane concentration was measured alternating with the samples. The oven of the GC-FID (flame ionisation detector made up of Agilent HP6890GC, with a 30 m Supelco Carboxen 1010 column x 530 µm inner diameter x 3 µm film thickness, and a carrier gas He) was programmed to run at 100°C for 4 minutes. Subsequently, the temperature was increased by 20°C per minute up to 130°C and kept at that temperature for another 3.5 minutes. The detector signal was converted into CH_4 amounts by calibration against gas standards with known CH_4 concentrations. The used calibration fully covered the range of methane concentrations in the samples. The pore water mass of each sample was determined by the difference in weight between the pore water - sample container (copper tube with N_2-headspace and pore water sample prior to analysis) and the empty sample container (empty copper tube, clean and dry after analysis). In addition, the volume of the headspace was determined for each sample by filling the total volume of the sample container with water

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[182] (copper tube completely filled with water). The headspace volume was then calculated by
[183] the difference in the weight of the total volume of the sample container and the weight of the
[184] pore water - sample container (copper tube with N_2 filled headspace and pore water sample
[185] prior to analysis). The total volume of the sample container was determined for each copper
[186] tube by refilling the empty sample container with water and measuring the quantity. The
[187] CH_4-TAMP in the pore water was calculated using Bunsen solubility[42] for CH_4 at the given
[188] equilibration temperature in the headspace.

Syringe standard method

[190] For the CH_4 analysis by the SSM method[8,15,20–24] sediment cores were collected in the same
[191] manner as for the CTC method (see Brennwald et al. 2003). After core retrieval at each
[192] sampling port, 2.0 ± 0.2 cm^3 of the sediment were extracted with a tipless 5ml-syringe.
[193] Sediments in the syringe were transferred to 25 mL glass vials. At the same time, 5 mL
[194] of 25% sodium hydroxide solution were added to prevent bacterial activity. The headspace
[195] gas contains ambient air ($\approx$1,75 ppm methane). The vials were sealed with a butyl stopper,
[196] crimped with an aluminium cap. The samples were equilibrated overnight in a water bath
[197] at a constant temperature. Subsequently, the headspace gas content was analysed using
[198] the GC-FID described above and the methane concentrations from the whole sediment were
[199] corrected to pore water concentration by accounting the sediment porosity.

Performance of the method

[201] We tested the performance of the CTC method in comparison with the SSM method in
[202] three steps: i. Assessment of the efficiency of the copper-tube headspace gas extraction; ii.
[203] Comparison of the performance of the CTC and SSM methods in the sediment pore water
[204] with CH_4-TAMP in the range of CH_4 in situ saturation concentration (Lake Lungern); and
[205] iii. Comparison of the performance of the CTC and SSM methods for sediments from Lake
[206] Rotsee that were obviously heavily supersaturated in CH_4.

i. *Assessment of the efficiency of the copper-tube headspace gas extraction*

Water with a virtually constant CH_4 concentration was generated by pumping pure CH_4 gas through a diffuser at the bottom of a 10-litre container filled with tap water. Small CH_4 bubbles were generated by the diffuser and, during their rise in the water column, the initially-dissolved gases were replaced by CH_4. The oxygen concentration in the tap water was continuously controlled by an O_2 sensor (WTW Multi 340i-electrode CellOx® 325). When oxygen concentration in the water became zero, the water was assumed to have reached CH_4 saturation and bubbling was stopped. Subsequently, water samples were taken and analysed by means of a standard technique (using 117ml glass vials and N_2 to create a headspace, see Kampbell et al. 1989) for the analysis of dissolved methane[37] and the copper tube headspace extraction (see methods). Samples were taken consecutively through a plastic tube connected to an outlet at the bottom of the water container. Sampling time between consecutive samples was kept short to minimise the effect of gas loss from the tank being covered with a cap.

For the CH_4 analysis by the copper tube headspace technique, a copper tube was flushed with the CH_4-loaded water. A sample of approximately $2 \ cm^3$ was sealed airtight by closing two pinch-off clamps. The volume taken was similar to the amount of pore water extracted by the centrifugation of a typical lacustrine sediment sample. This volume is about 6 times smaller than the sample in the glass vial ($12 \ cm^3$). Results for the copper tube sample were therefore more likely to be affected by weighing errors and errors in determining the headspace volume. As a result, the overall analytical uncertainties are considerably larger than those for the analysis using glass vials. A better analytical precision for the CTC method can be achieved by optimising the sample inlet to the GC, e.g., by extracting the dissolved gases from pore water directly into a pre-evacuated extraction line.[43] Nevertheless, the advantage of using the copper tube headspace for CH_4 extraction is that samples can be readily analysed by most GCs without any modifications.

ii. *Comparison of the performance of the CTC and SSM methods in the sediment pore water where CH_4-TAMP is known to be in the range of CH_4 in situ saturation concentration (Lake Lungern)*

Lake Lungern, a reservoir situated in Canton Obwalden (Switzerland), is used for hydropower production and is therefore subject to high, artificially-induced water level variations. The lake level fluctuates between approximately 650 and 690 m.a.s.l. with low levels in winter and high levels in summer. Most of the littoral sediments originate from cropland that was flooded when the lake was dammed. The organic and mineral load of two inflowing rivers contributes to sediment formation in the littoral zone. High CH_4 concentrations were reported in the water column of Lake Lungern.[44] CH_4 emissions in the form of small bubbles visible at the water surface have also been reported in the littoral area.[45] During field sampling in March 2013, two sediment cores were taken at the same location within a radius of less than 1m, from a site which had shown active CH_4 bubble release in the previous summer when the lake was at its highest level. When sampling the sediment, the water level was at its lowest and had been virtually stable throughout the preceding month. The difference between the lake level at its lowest in the winter and its maximum level in the summer was 20 m. This lowering of the lake level caused a strong pressure release in the sediment and fostered degassing and bubble formation as the overlying water column decreased. Depleted dissolved gas concentrations (i.e., He, Ne, Ar, Kr, Xe) in the pore water of these sediments, with regard to the expected air-saturated water concentrations, were found in an earlier study and were interpreted as resulting from gas stripping by CH_4 bubbles formed in and released from the sediment.[46] Due to low air and water temperatures during sampling (between +4 and -5℃), biological activity in the sediment was most likely very low or even non-existent.[47] In order to avoid the effect of pressure release and degassing during sediment core retrieval, the cores were taken from a site with a water depth of only 5 cm. For these reasons (namely, low hydraulic pressure, limited

biological activity, and stable lake levels over a long period), we assume that CH_4 concentrations in the pore water of the sediments are close or equal to the expected saturation concentration.

iii. *Comparison of the performance of the CTC and SSM methods for sediments supersaturated in methane (Lake Rotsee)*

Lake Rotsee is a small eutrophic pre-Alpine lake, close to the city of Lucerne (Switzerland). Due to its wind shielded location Lake Rotsee only mixes once a year in early spring and has a stable stratified water column and an anoxic hypolimnion for the rest of the year.[24] The sediments of Lake Rotsee are known to emit CH_4.[24–26] The CH_4-TAMP of the sediments had been determined previously by the SSM and dialyzer methods.[24–27] The sediments of Lake Rotsee were sampled towards the end of September 2011, 2013 and 2014. At each campaign, 2 to 4 sediment cores were taken within a radius of circa 15 m from the same location at a water depth of 15–16 m. Because of the stable conditions in Lake Rotsee and because samples were always taken in the same month and at virtually the same location similar methane amounts were expected in the different years. Cores taken in 2011 and 2013 were processed with the CTC method (see Section 2.1). However, the sediment core from 2014 was processed differently. In 2014, the holes for the ports to connect the copper tubes to sample the sediment were drilled after retrieval of the sediment core. This procedure allows the ports to be set in ideal positions with regard to the retrieved sediment core. We note, however, that post-retrieval drilling induces vibration and prolongs sampling time. Both actions foster bubble movement within the sediment core and subsequent bubble loss.

Results and Discussion

Performance of the copper tube headspace gas extraction (lab experiment)

Methane concentrations of CH_4-enriched water determined using a standard technique[37] and copper tube headspace technique agree within experimental errors (see Figure 2), both were in a range of 2 - 3 mM CH_4. Thus, the performance of the copper tube headspace method for CH_4 analysis is at the same level as that of the accepted standard method.
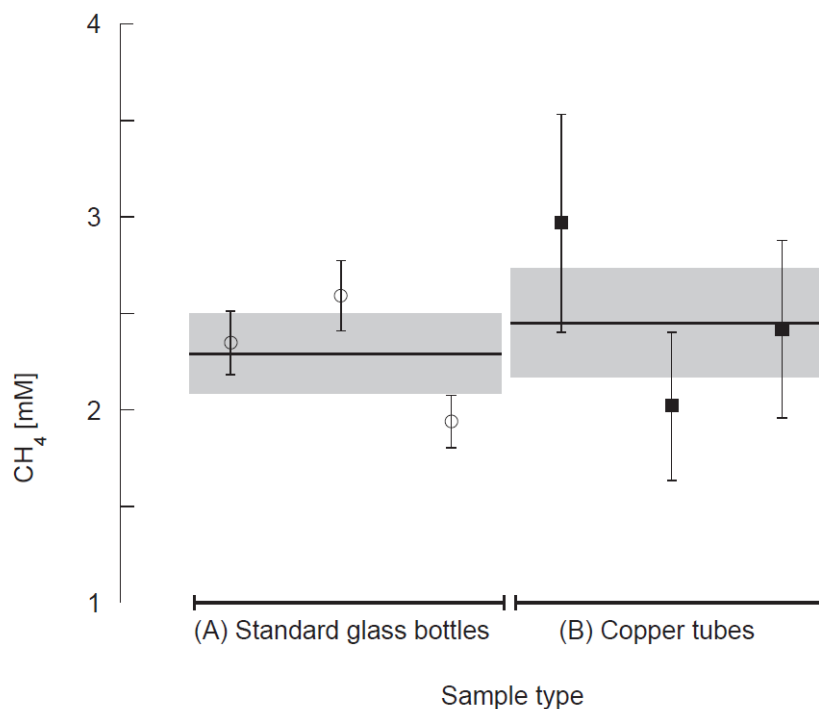

Figure 2: Comparison of the CH_4 concentrations determined in artificially CH_4-supersaturated water samples by (A) standard technique[37] in glass bottles (open circles) and (B) with the new copper tube headspace technique (black squares). The mean CH_4 concentration (continuous black lines) determined with both sampling methods (A) and (B) agrees in terms of experimental errors (grey areas represent the error of the mean). The determined concentrations exceed the expected CH_4 saturation concentration most likely due to microbubbles formation[48], which is often found in aquatic systems that are artificially aerated.[49]

Comparison of the performance of the two methods in sediments that have CH_4 concentrations in the range of the expected methane saturation (Lake Lungern)

SSM method: The CH_4-TAMPs determined with the SSM method in the pore water of Lake Lungern ranged between 0.5 and 1.7 mM (see Figure 3) and were always lower than in situ saturation concentrations for CH_4.

CTC method: The CH_4-TAMPs determined by the CTC method show a gradient in the upper 20 cm of the sediment. Starting at the water/sediment interface, CH_4-TAMP values were continuously increasing and stabilised at about 2.1 mM, at a sediment depth of 20 cm. From a sediment depth of 20 cm and downward, the CH_4-TAMP calculated by the CTC method agrees with the in situ saturation concentration (2.0–2.5 mM CH_4, Figure 3). We note that sampling was performed at a point in time where the sediment had virtually no overlying water column and therefore the retrieval of the sediment core was expected not to foster degassing due to pressure release.

Performance of the two methods when sampling sediments with active bubble formation (Lake Rotsee)

SSM method: In Lake Rotsee, CH_4-TAMPs determined by the SSM method were in the range of 3 to 5 mM CH_4 (see Figure 4). The results are in line with results from previous studies at Lake Rotsee that used the same method.[24] We note that immediately after core recovery, formation of gas bubbles was observed in the sediment during sampling (see Figure 5). The presence of a free gas phase implies that the CH_4-TAMP exceeded the in situ saturation concentration (7°C, approximately 15 to 16 m depth, 5.3–5.6 mM CH_4). Thus, although CH_4 supersaturation was obvious, the CH_4-TAMPs determined by the SSM method were commonly found to be even lower than in situ saturation concentration of CH_4. Only in some samples of the 2014 core CH_4-TAMPs were found to slightly exceed the in situ satur-
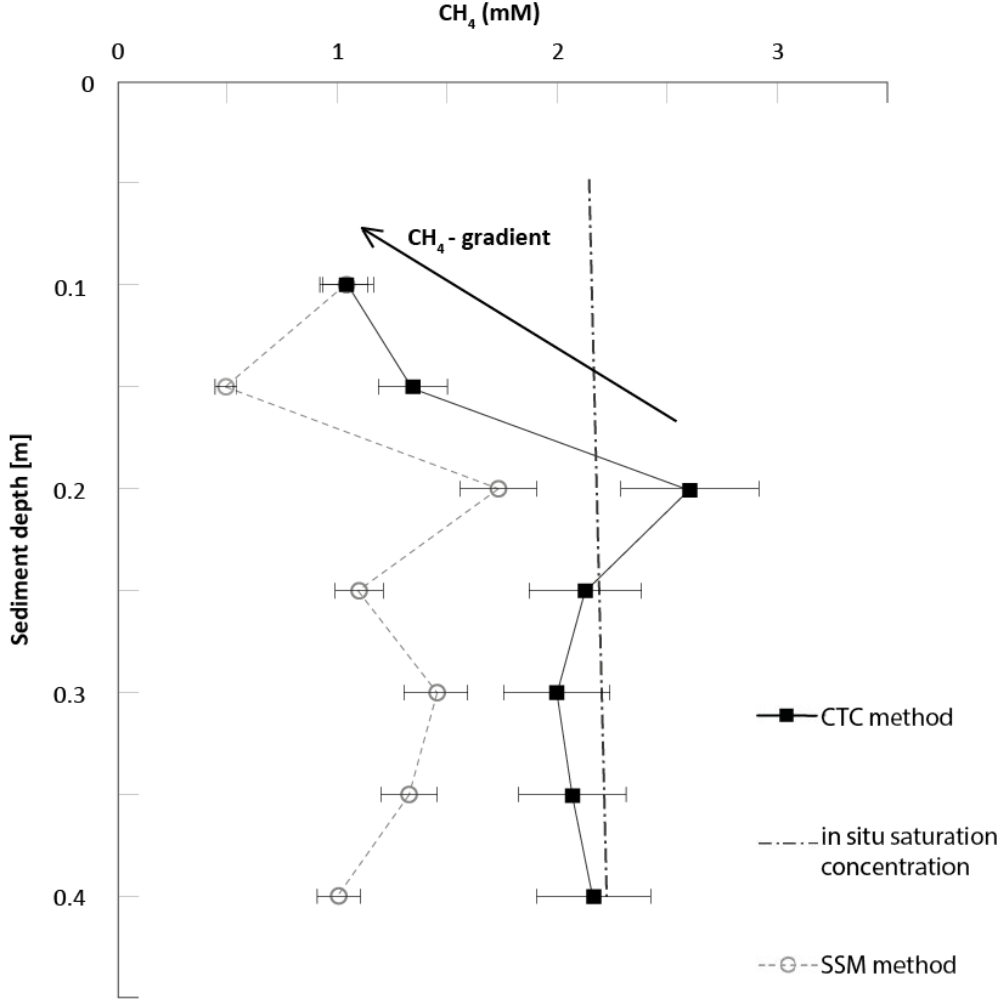
Figure 3: Comparison of the CH$_4$ concentration profiles determined with SSM and CTC method in the pore water in Lake Lungern in the winter of 2012 at low water level and hence with a very low overlying water column (5 cm). We note that CH$_4$ in situ saturation concentration was calculated with Henry's law,[50] assuming a pure CH$_4$ gas phase. Spatial error on the sediment depth varies between 1 cm for the SSM method and 2.5 cm for the CTC method. Due to displacement of the sediment during squeezing the error on the vertical localisation of samples taken with CTC method is higher. In the upper 20 cm of the sediment, CH$_4$ concentrations are characterised by a strong gradient decreasing towards the sediment/water interface.
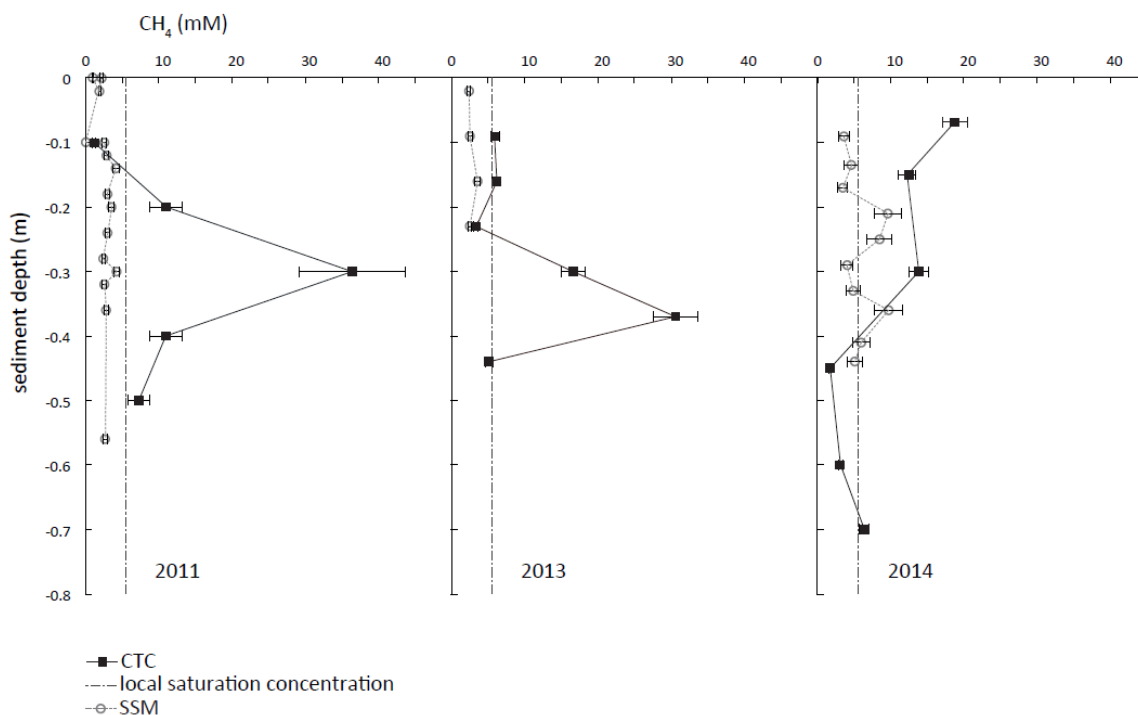
Figure 4: Comparison of the CH_4 concentration profiles measured in the pore water of Lake Rotsee in 2011, 2013 and 2014 at a water depth of about 16 m: SSM; CTC method; and in situ saturation concentration of CH_4 calculated with Henry's law[50] assuming a pure CH_4 gas phase. Due to a different design of the sample inlet to the gas chromatograph (GC), the errors of all samples analysed in 2011 are larger. The spatial error of sediment displacement is: SSM method +/- 2.5 cm; CTC method +/- 1.0 cm.

ation concentration of CH_4. We also note that the CH_4-TAMP values determined using the SSM method show a "scatter" with regard to depth and do not show a clear concentration maximum.

CTC method: CH_4-TAMPs determined by the CTC method were larger than values determined with SSM method. In Lake Rotsee, down to a sediment depth of 30 cm, CH_4-TAMPs in the pore water were higher than the CH_4 in situ saturation (up to 40 mM CH_4, see Figure 4). CH_4-TAMPs in samples taken at a depth below 40 cm were found to be close to the in situ saturation concentration. The CH_4-TAMPs being higher than the CH_4 in situ saturation concentration make a clear argument for the presence of CH_4 bubbles in the sediment and hence are in line with the observation of gas bubbles in the sediment core (see Figure 5). CH_4-TAMPs determined using the CTC method were approximately an order of magnitude higher than those determined by the SSM method. Our maximum CTC CH_4-TAMP results (20 - 35 mM CH_4) agree with the range of results from dialyzer analysis at Lake Rotsee (20 - 40 mM CH_4).[27] Although the dialyzer results at Lake Rotsee[27] agree with the CTC results overall, we note that the dialyzer method did not yield any CH_4-TAMP maximum within the sediments and that concentrations were subject to considerable scatter with regard to depth. As mentioned above, such erratic CH_4-TAMP data may well be result from sampling artefacts, e.g. due to gas exchange with the atmosphere during sampling.[15,29]

CTC samples from 2011 and 2013 repeatedly show a marked CH_4-TAMP maximum at a depth of 30 to 40 cm. Their CH_4-TAMP exceeds the in situ CH_4 saturation concentration by at least an order of magnitude. A slight offset of the peak CH_4-TAMPs in cores between 2011 and 2013 is likely to be related to the uneven sediment displacement in the liner due to squeezing and to the spatial heterogeneity of microbiological CH_4 production. Given a sedimentation rate of between 0.38 and 0.40 cm/y (sedimentation rate was determined by identifying the ^{137}Cs peak of the Chernobyl accident and assuming a constant sedimentation rate[51]), the CH_4-TAMP peak is found in sediments deposited between 1920 and 1950. In the 2014 core, where sampling ports were set after core retrieval, no clear concentration peak

Figure 5: Visible bubbles (within white circle) within the retrieved sediment core from Lake Rotsee 2013. Such bubbles occur spontaneously and immediately after core retrieval indicating that CH_4 concentrations in the pore water is supersaturated.

was observed. Nevertheless, down to a level of 40 cm, CH_4-TAMP was significantly higher than the in situ CH_4 saturation concentration. The total CH_4 excess, defined by saturation concentration and the measured CH_4-TAMP integrated over the sediment depth, is roughly the same for all three cores (2011, 2013 and 2014). Thus, all cores contain a similar amount of CH_4-TAMP; however, spatial distribution varies. We conclude that different vertical CH_4-TAMPs indicate that CH_4 was redistributed within the core due to agitation during drilling in 2014, but was not allowed to escape from the bulk sediment mass.

Implications

Although the sediments investigated in this study are known to actively emit CH_4, the CH_4-TAMPs measured using the SSM method were either lower than the expected CH_4 in situ saturation concentration (Lake Lungern) or were not able to detect the expected CH_4

supersaturation (Lake Rotsee) in the sediment pore - water. The difference between CH_4-TAMPs determined using the SSM and CTC methods increased with higher real CH_4-TAMP and, particularly, with the presence of bubbles in the sediment. CH_4-TAMP determined using the SSM method were severely biased toward lower concentrations. A CH_4 loss of up to 90% was inferred. Our study confirmed that the SSM method fails to quantitatively and reliably determine the in situ CH_4-TAMP of unconsolidated lacustrine sediments. In contrast CH_4-TAMPs determined by the CTC method were always found to be higher than values measured using the SSM method. The concentrations determined by CTC method fell well within the expected CH_4 concentration range.

It is crucial to determine CH_4 in the pore water of lacustrine sediments in a truly quantitative manner in order to set a robust experimental anchor for studying CH_4 dynamics in lakes and their sediments.[24] Our study makes the case that the CTC method may allow the accurate quantification of the real in situ CH_4-TAMP of sediments, even where CH_4 concentrations exceed the in situ saturation concentration, e.g., in productive sediments known to actively emit CH_4 bubbles. The CTC method is applicable in all sediments that can be sampled with a gravity corer and gives good results as long as methane bubbles stay in the local sediment matrix during core recovery. In addition, the CTC method allows us to depict the real spatial distribution of CH_4-TAMPs within the lacustrine sediments, e.g. concentration gradients can be reconstructed accurately (Lake Lungern) and zones of enhanced CH_4 production can be identified (Lake Rotsee). Although rather demanding from an experimental point of view, the CTC method represents a significant improvement in the analysis of the CH_4-TAMP of unconsolidated sediments in lakes and oceans. The sampling technique using gas-tight copper tubes avoids gas loss during sample acquisition, and thus eliminates the most critical sampling artefact when quantifying gas amounts in sediments. Use of the CTC method for noble gas analysis[31,32] showed that CTC method could be applied to the quantification of the gas concentrations in highly compacted sediments, e.g., in ocean sediments or sediments being retrieved by deep drilling.[52,53] Furthermore, in prin-

ciple, the CTC method also makes it possible to determine the real, in situ concentrations of other dissolved gases (e.g., H_2S, NH_3, CO_2, N_2 by using a different head space gas) as well as their isotopic composition in the pore space of unconsolidated sediments. This enables the characterisation of the gas/solute budget in the sediment and the gas exchange at the sediment/water interface.

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References

(1) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R. In *Climate Change 2007: The Physical Science Basis.*; Solomon, S.,

Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press, 2007; pp 131–217.

(2) Kirschke, S. et al. Three decades of global methane sources and sinks. *Nat. Geosci.* **2013**, *6*, 813–823.

(3) Lovley, D. R.; Klug, M. J. Intermediary metabolism of organic matter in the sediments of a eutrophic lake. *Appl. Environ. Microb.* **1982**, *43*, 552–560.

(4) Sobek, S.; E. Durisch-Kaiser, R.; Zurbrügg, N.; Wongfun, M.; Wessels, N.; N., P.; B., W. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnol. Oceanogr.* **2009**, *54*, 2243–2254.

(5) Smith, V. H. Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environ. Sci. Pollut R.* **2003**, *10*, 126–139.

(6) Søndergaard, M.; Jeppesen, E.; Lauridsen, T. L.; Skov, C.; Van Nes, E. H.; Roijackers, R.; Lammens, E.; Portielje, R. Lake restoration: Successes, failures and long-term effects. *J. Appl. Ecol.* **2007**, *44*, 1095–1105.

(7) Downing, J. A.; Cole, J. J.; Middelburg, J. J.; Striegl, R. G.; Duarte, C. M.; Kortelainen, P.; Prairie, Y. T.; Laube, K. Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century. *Global Biogeochem. Cy.* **2008**, *22*.

(8) Sobek, S.; DelSontro, T.; Wongfun, N.; Wehrli, B. Extreme organic carbon burial fuels intense methane bubbling in a temperate reservoir. *Geophys. Res. Lett.* **2012**, *39*.

(9) Battin, T. J.; Luyssaert, S.; Kaplan, L. A.; Aufdenkampe, A. K.; Richter, A.; Tranvik, L. J. The boundless carbon cycle. *Nat. Geosci.* **2009**, *2*, 598–600.

(10) Cole, J.; Prairie, Y.; Caraco, N.; McDowell, W.; Tranvik, L.; Striegl, R.; Duarte, C.; Kortelainen, P.; Downing, J.; Middelburg, J.; Melack, J. Plumbing the global carbon

cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* **2007**, *10*, 172–185.

(11) Downing, J. A. Emerging global role of small lakes and ponds: little things mean a lot. **2010**, *29*, 0009–24.

(12) Ortiz-Llorente, M.; Alvarez-Cobelas, M. Comparison of biogenic methane emissions from unmanaged estuaries, lakes, oceans, rivers and wetlands. *Atmos. Environ.* **2012**, *59*, 328–337.

(13) Bastviken, D.; Cole, J. J.; Pace, M. L.; Van de Bogert, M. C. Fates of methane from different lake habitats: Connecting whole-lake budgets and CH4 emissions. *J. Geophys. Res.)* **2008**, *113*.

(14) Bastviken, D.; Cole, J.; Pace, M.; Tranvik, L. Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochem. Cycles* **2004**, *18*.

(15) Adams, D. D. In *Sediment pore water sampling*; Murdoch, A., MacKnight, S., Eds.; Lewis Publishers: Boca Raton, FL, 1995; pp 171–202.

(16) Boudreau, B. P.; Algar, C.; Johnson, B. D.; Croudace, I.; Reed, A.; Furukawa, Y.; Dorgan, K. M.; Jumars, P. A.; Grader, A. S.; Gardiner, B. S. Bubble growth and rise in soft sediments. *Geology* **2005**, *33*, 517–520.

(17) Joyce, J.; Jewell, P. W. Physical controls on methane ebullition from reservoirs and lakes. *Environ. Eng. Geoscience* **2003**, *9*, 167–178.

(18) DelSontro, T.; McGinnis, D. F.; Sobek, S.; Ostrovsky, I.; Wehrli, B. Extreme methane emissions from a Swiss hydropower reservoir: contribution from bubbling sediments. *Environ. Sci. Technol* **2010**, *44*, 2419–2425.

(19) Corella, J. P.; Arantegui, A.; Loizeau, J.-L.; DelSontro, T.; Le Dantec, N.; Stark, N.; Anselmetti, F.; Girardclos, S. Sediment dynamics in the subaquatic channel of the Rhone delta (Lake Geneva, France/Switzerland). *Aquat. Sci.* **2014**, *76*, 73–87.

(20) Hoehler, T. M.; Alperin, M. J.; Albert, D. B.; Martens, C. S. Field and laboratory studies of methane oxidation in an anoxic marine sediment: Evidence for a methanogen-sulfate reducer consortium. *Global Biogeochem. Cycles* **1994**, *8*, 451–463.

(21) Sollberger, S.; Corella, J. P.; Girardclos, S.; Randlett, M.-E.; Schubert, C.; Senn, D.; Wehrli, B.; DelSontro, T. Spatial heterogeneity of benthic methane dynamics in the subaquatic canyons of the Rhone River Delta (Lake Geneva). *Aquat. Sci.* **2014**, *76*, 89–101.

(22) Jørgensen, B. B.; Weber, A.; Zopfi, J. Sulfate reduction and anaerobic methane oxidation in Black Sea sediments. *Oceanogr. Res. Pap.* **2001**, *48*, 2097–2120.

(23) Popp, B. N.; Sansone, F. J.; Rust, T. M.; Merritt, D. A. Determination of concentration and carbon isotopic composition of dissolved methane in sediments and nearshore waters. *Anal. Chem.* **1995**, *67*, 405–411.

(24) Schubert, C. J.; Lucas, F.; Durisch-Kaiser, E.; Stierli, R.; Diem, T.; Scheidegger, O.; Vazquez, F.; Müller, B. Oxidation and emission of methane in a monomictic lake (Rotsee, Switzerland). *Aquat. Sci.* **2010**, *72*, 455–466.

(25) Naeher, S.; Smittenberg, R. H.; Gilli, A.; Kirilova, E. P.; Lotter, A. F.; Schubert, C. J. Impact of recent lake eutrophication on microbial community changes as revealed by high resolution lipid biomarkers in Rotsee (Switzerland). *Org. Geochem.* **2012**, *49*, 86–95.

(26) Naeher, S.; Niemann, H.; Peterse, F.; Smittenberg, R. H.; Zigah, P. K.; Schubert, C. J. Tracing the methane cycle with lipid biomarkers in Lake Rotsee (Switzerland). *Org. Geochem.* **2014**, *66*, 174–181.

(27) Falz, K. Z.; Holliger, C.; Grosskopf, R.; Liesack, W.; Nozhevnikova, A.; Müller, B.; Wehrli, B.; Hahn, D. Vertical distribution of methanogens in the anoxic sediment of Rotsee (Switzerland). *Appl. Environ. Microb.* **1999**, *65*, 2402–2408.

(28) Stephenson, M.; Schwartz, W. J.; Melnyk, T. W.; Motycka, M. F. Measurement of advective water velocity in lake sediment using natural helium gradients. *J. Hydrol.* **1994**, *154*, 63–84.

(29) Dyck, W.; Da Silva, F. The use of ping-pong balls and latex tubing for sampling the helium content of lake sediments. *J. Geochem. Explor.* **1981**, *14*, 41–48.

(30) Adams, D. D.; Van Eck, G. T. M. Biogeochemical cycling of organic carbon in the sediments of the Grote Rug reservoir. *Archiv für Hydrobiologie Ergebnisse Limnologie* **1988**, *31*.

(31) Brennwald, M. S.; Hofer, M.; Peeters, F.; Aeschbach-Hertig, W.; Strassmann, K.; Kipfer, R.; Imboden, D. M. Analysis of dissolved noble gases in the porewater of lacustrine sediments. *Limmnol. Oceanogr.: Methods* **2003**, *1*, 51–62.

(32) Tomonaga, Y.; Brennwald, M. S.; Kipfer, R. An improved method for the analysis of dissolved noble gases in the porewater of unconsolidated sediments. *Limmnol. Oceanogr.: Methods* **2011**, *9*, 42–49.

(33) Kipfer, R.; Aeschbach-Hertig, W.; Peeters, F.; Stute, M. In *Noble gases in geochemistry and cosmochemistry*; Porcelli, D., Ballentine, C., Wieler, R., Eds.; Mineralogical Society of America, Geochemical Society, 2002; Vol. 47; Chapter Noble gases in lakes and ground waters, pp 615–700.

(34) Brennwald, M.; Vogel, N.; Scheidegger, Y.; Tomonaga, Y.; Livingstone, D.; Kipfer, R. In *The Noble Gases as Geochemical Tracers*; Burnard, P., Hoefs, J., Eds.; Advances in Isotope Geochemistry; Springer: Berlin, Heidelberg, 2013; Chapter Noble gases as

environmental tracers in sediment porewaters and in stalagmite fluid inclusions, pp 123–153.

(35) Brennwald, M. S.; Imboden, D. M.; Kipfer, R. Release of gas bubbles from lake sediment traced by noble gas isotopes in the sediment pore water. *Earth Planet. Sci. Lett.* **2005**, *235*, 31–44.

(36) Brennwald, M.; Vogel, N.; Scheidegger, Y.; Tomonaga, Y.; Livingstone, D.; Kipfer, R. *The Noble Gases as Geochemical Tracers*; Springer, 2013; pp 123–153.

(37) Kampbell, D.; Wilson, J. T.; Vandegrift, S. Dissolved oxygen and methane in water by a GC headspace equilibration technique. *Int. J. Environ. An. Ch.* **1989**, *36*, 249–257.

(38) Beyerle, U.; Aeschbach-Hertig, W.; Imboden, D. M.; Baur, H.; Graf, T.; Kipfer, R. A mass spectrometric system for the analysis of noble gases and tritium from water samples. *Env. Sci. Technol.* **2000**, *34*, 2042–2050.

(39) Kipfer, R. Primordiale Edelgase als Tracer für Fluide aus dem Erdmantel. Ph.D. thesis, ETH Zürich, 1991.

(40) Ince, N. H.; Belen, R. Aqueous phase disinfection with power ultrasound: process kinetics and effect of solid catalysts. *Environ. Sci. Technol.* **2001**, *35*, 1885–1888.

(41) Sarsan, S. Effect of storage of water in different metal vessels on coliforms. *Int. J. Curr. Microbiol. App. Sci* **2013**, *2*, 24–29.

(42) Colt, J. *Dissolved Gas Concentration in Water: Computation as Functions of Temperature, Salinity and Pressure*; Elsevier, 2012.

(43) Brennwald, M. S.; Hofer, M.; Kipfer, R. Simultaneous Analysis of Noble Gases, Sulfur Hexafluoride, and Other Dissolved Gases in Water. *Environ. Sci. Technol.* **2013**, *47*, 8599–8608.

(44) Diem, T.; Koch, S.; Schwarzenbach, S.; Wehrli, B.; Schubert, C. Greenhouse gas emissions (CO2, CH4, and N2O) from several perialpine and alpine hydropower reservoirs by diffusion and loss in turbines. *Aquat. Sci.* **2012**, *74*, 619–635.

(45) Ostrovsky, I. Fish and methane bubbles in aquatic ecosystems: hydroacoustic separation and quantification. *Verhandlungen: Proceedings. Travaux* **2009**, *30*, 870.

(46) Tyroller, L.; Brennwald, M. S.; Ndayisaba, C.; Tomonaga, Y.; Kipfer, R. Linking noble gas and CH4 concentrations in the sediment porewater of Lake Lungern, Switzerland. *Limnol. Oceanogr.: Methods* **2013**, *9*, 42–49.

(47) Duc, N. T.; Crill, P.; Bastviken, D. Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments. *Biogeochemistry* **2010**, *100*, 185–196.

(48) McGinnis, D. F.; Kirillin, G.; Tang, K. W.; Flury, S.; Bodmer, P.; Engelhardt, C.; Casper, P.; Grossart, H.-P. Enhancing Surface Methane Fluxes from an Oligotrophic Lake: Exploring the Microbubble Hypothesis. *Environ. Sci. Technol.* **2015**, *49*, 873–880.

(49) Holzner, C.; Tomonaga, Y.; Stöckli, A.; Denecke, N.; Kipfer, R. Using noble gases to analyze the efficiency of artificial aeration in Lake Hallwil, Switzerland. *Water Resour. Res.* **2012**, *48*.

(50) Sander, R. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. 1999.

(51) Pennington, W.; Cambray, R.; Eakins, J.; Harkness, D. Radionuclide dating of the recent sediments of Blelham Tarn. *Freshwater Biology* **1976**, *6*, 317–331.

(52) Tomonaga, Y.; Brennwald, M. S.; Meydan, A. F.; Kipfer, R. Noble gases in the sed-

545 iments of Lake Van–solute transport and palaeoenvironmental reconstruction. *Quat.*
546 *Sci. Rev.* **2014**, *104*, 117–126.

547 (53) Tomonaga, Y.; Brennwald, M. S.; Kipfer, R. Attenuation of diffusive noble-gas transport
548 in laminated sediments of the Stockholm Archipelago. *Limmnol. Oceanogr.* **2015**, *60*,
549 497–511.