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Technical Note: Disturbance of soil structure can lead to release of entrapped methane in glacier forefield soils

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Abstract. Investigations of sources and sinks of atmospheric CH_4 are needed to understand the global CH_4 cycle and climate-change mitigation options. Glaciated environments might play a critical role due to potential feedbacks with global glacial meltdown. In an emerging glacier forefield, an ecological shift occurs from an anoxic, potentially methanogenic subglacial sediment to an oxic proglacial soil, in which soil-microbial consumption of atmospheric CH_4 is initiated. The development of this change in CH_4 turnover can be quantified by soil-gas profile analysis.

We found evidence for CH_4 entrapped in glacier forefield soils when comparing two methods for the collection of soil-gas samples: a modified steel rod (SR) designed for one-time sampling and rapid screening (samples collected $\sim$1 min after hammering the SR into the soil), and a novel multilevel sampler (MLS) for repetitive sampling through a previously installed access tube (samples collected weeks after access-tube installation). In glacier forefields on siliceous bedrock, sub-atmospheric CH_4 concentrations were observed with both methods. Conversely, elevated soil-CH_4 concentrations were observed in calcareous glacier forefields, but only in samples collected with the SR, while MLS samples all showed sub-atmospheric CH_4 concentrations. Time-series of SR soil-gas sampling (additional samples collected 2, 3, 5, and 7 min after hammering) confirmed the transient nature of the elevated soil-CH_4 concentrations, which were decreasing from $\sim 100\,\mu L\,L^{-1}$ towards background levels within minutes. This hints towards the existence of entrapped CH_4 in calcareous glacier forefield soil that can be released when sampling soil-gas with the SR.

Laboratory experiments with miniature soil cores collected from two glacier forefields confirmed CH_4 entrapment in these soils. Treatment by sonication and acidification resulted in a massive release of CH_4 from calcareous cores (on average 0.3–1.8 µg CH_4 (g d.w.)$^{-1}$) (d.w. – dry weight); release from siliceous cores was 1–2 orders of magnitude lower (0.02–0.03 µg CH_4 (g d.w.)$^{-1}$). Clearly, some form of CH_4 entrapment exists in calcareous glacier forefield soils, and to a much lesser extent in siliceous glacier forefield soils. Its nature and origin remain unclear and will be subject of future investigations.

1 Introduction

Methane in the atmosphere contributes significantly to global climate change (Forster et al., 2007). The total global CH_4 budget is relatively well-constrained, but uncertainties in estimates of individual source and sink contributions remain high (Bousquet et al., 2006; Bridgham et al., 2013). About 70 % of CH_4 is from microbial sources (Conrad, 2009); other sources comprise fossil fuel extraction and mining ($\sim$18 %) and biomass burning ($\sim$7 %). There is still much debate about the contribution of plant-derived CH_4 (Bruhn et al., 2012) and, recently, geologic sources (natural CH_4 emissions related to hydrocarbon reservoirs or geothermal areas) have also been proposed to contribute significantly to the global budget (Etiope and Klusman, 2002, 2010; Milkov et al., 2003). Only three sinks of atmospheric CH_4 have been identified: photochemical oxidation by OH radicals (> 80 %), losses to the stratosphere, and oxidation by methane-oxidizing bacteria in unsaturated soils (Crutzen, 1991; Dutaur and Verchot, 2007).

In the wake of global change, glaciers and ice sheets have been subject to extensive investigations, resulting in the recognition of subglacial microbial life (Sharp et al., 1999;

Skidmore et al., 2000, 2005). In this context, certain observations fueled speculations about widespread methanogenesis under ice, e.g. prevalent anoxic conditions under glaciers (Wadham et al., 2004), elevated CH_4 concentrations in ice cores (Price and Sowers, 2004; Miteva et al., 2009), molecular evidence of the presence of methanogenic archaea (Miteva et al., 2009) and long-term incubation experiments (Boyd et al., 2010; Stibal et al., 2012). Potential climate feedbacks are subject of an ongoing debate, as the produced CH_4 might be released with glacial meltdown (Wadham et al., 2008, 2012; Boyd et al., 2010).

Areas in front of receding glaciers, termed glacier forefields, are ecosystems created by glacial meltdown. With the ice melt causing a dramatic shift from a subglacial (anoxic, constantly cold, dark) to a proglacial habitat (oxic, temperature fluctuations, UV-light), organisms already present either adapt or disappear, while new organisms start to colonize the substrate. As exposure of subglacial sediments to the atmosphere occurs gradually, forming a well-defined soil chronosequence, glacier forefields are ideal environments to investigate soil development and microbial succession (Stevens and Walker, 1970; Sigler and Zeyer, 2002; Duc et al., 2009; Lazzaro et al., 2009, 2012). However, little is known of CH_4 cycling in these environments.

Recently, microbial oxidation of atmospheric CH_4 has been confirmed in glacier forefield soils in Greenland and Switzerland (Bárcena et al., 2010, 2011; Nauer et al., 2012). Methods employed to estimate soil-CH_4 oxidation in the field included flux chambers and soil-CH_4 profiles, respectively. Flux chambers should be inserted at least 5–10 cm into the soil to minimize lateral gas flux (Rochette and Bertrand, 2007; Rochette and Eriksen-Hamel, 2008). In the stony soil of a glacier forefield, finding locations where this is possible can be challenging and time-consuming. Hence, for the first survey on soil-CH_4 oxidation in glacier forefields in the Swiss Alps (Nauer et al., 2012), the soil-CH_4 profile method was employed using a steel rod (SR) designed for rapid soil-gas extraction in stony soils. Yet, repetitive sampling at the same location was not possible with this device. Consequently, a novel multilevel sampler (MLS) was developed for repeated soil-gas sampling at multiple depths (Nauer et al., 2013). Remarkably, elevated CH_4 concentrations previously observed in SR samples from glacier forefields on calcareous bedrock could not be detected in samples from the MLS during initial tests.

Hence, our objectives for this study were (i) to compare the two sampling instruments (MLS and SR) side by side at three locations in a siliceous and a calcareous glacier forefield to confirm the disagreement with respect to elevated CH_4 concentrations, (ii) to examine the possibility of temporary CH_4 release during SR sampling by performing time-series sampling, and (iii) to provide a first quantitative assessment of potentially entrapped CH_4 in glacier forefield soils by disturbing miniature soil cores in the laboratory using sonication and acidification.

2 Materials and methods

2.1 Field sites

Soil-gas samples and miniature soil cores were collected in two glacier forefields that were part of the initial survey on CH_4 oxidation in the Swiss Alps (Nauer et al., 2012): the Damma Glacier forefield (DAM) on siliceous bedrock, and the Griessfirn Glacier forefield (GRF) on calcareous bedrock. Details on their soil-physical and chemical properties can be found in the literature (Lazzaro et al., 2009; Bernasconi et al., 2011; Nauer et al., 2012). In summary, soils in both glacier forefields ranged from barren glacial till to poorly developed Leptosols (IUSS Working Group WRB, 2006) with dominating sand and gravel fractions. Organic carbon and nutrient contents were low, but increasing with soil age. In each glacier forefield we sampled at three locations with increasing distance to the glacier. Location A was ice-free for < 20 yr, location B for ∼ 40–50 yr, and location C for ∼ 50–70 yr. Soils around location A at both sites and location B at GRF were largely devoid of vegetation, with occasional pioneer species such as *Cerastium uniflorum* at DAM, and *Linaria alpina* and *Saxifraga aizoides* at GRF. At location C at GRF we observed patchy ground cover of mainly *Salix retusa* and other creeping *Salix* spp. Location B and C at DAM came to lie in the "intermediate age section" as described in Bernasconi et al. (2011), and therefore exhibited similar vegetation cover and soil properties.

2.2 Soil-gas sampling

Collection of soil-gas samples was accomplished using the SR (Nauer et al., 2012) and the MLS as part of a newly developed sampling system (Nauer et al., 2013). A graphical overview of both instruments is given in the supporting information. The SR is a 2 cm diameter rod with an inner capillary to extract soil gas. It is hammered into the soil in user-defined increments and from each depth one soil-gas sample is collected, typically within ∼ 1 min after hammering ceased. Conversely, the MLS is designed as an insert for perforated access tubes installed at least 2 weeks prior to soil-gas sampling. With the MLS, up to 20 depths down to 1 m can be sampled through the access tubes wall, while an inflatable packer system seals the 5 cm interspace between the sampled depths.

The access tubes for the MLS were installed on 12 July 2012 at the GRF locations, and on 8 and 13 July 2012 at the DAM locations. Actual soil-gas sampling with the MLS took place on 25 July and 17 September 2012 at GRF, and on 31 July and 25 September 2012 at DAM. On the sampling days in September we subsequently sampled soil gas with the SR within ∼ 0.5 m distance from the installed access tubes at all locations (except for DAM C due to a sudden rain event). In addition to the typically collected single sample from each depth, we left the SR in place and collected another four soil-gas samples in sequence at $t_n = 2$, 3, 5 and 7 min, respectively, after hammering ceased. Hence, a time-series of total $n = 5$ samples were collected at each of the 3–4 selected depths (up to 65 cm). The first samples from each depth at t_1 ($\sim$ 1 min after hammering ceased) were used for comparison with the MLS data, as they represented profiles equivalent to typically performed one-time sampling with the SR.

The procedure of soil-gas sampling was identical for both instruments. At the respective valve of the instrument we collected 15 mL soil gas with a plastic syringe (after discarding the respective dead volume) and injected it into previously evacuated 10 mL glass vials. Air from 2 m above ground was sampled in similar fashion. Pressure was measured with a manometer (LEO 1, Keller AG, Winterthur, Switzerland) to account for dilution and altitude-related concentration differences. Methane from all soil-gas samples was measured on a GC-FID as described in Nauer and Schroth (2010), while oxygen in selected samples was measured on a GC-TCD according to Urmann et al. (2007).

2.3 Miniature-soil-core experiments

To test soils from both glacier forefields in the laboratory for potentially entrapped CH_4, we collected miniature soil cores on the day after respective sampling with the SR. At each of the SR sampling locations, a 60–70 cm deep and $\sim$ 50 cm wide soil profile was excavated. Soil cores were collected at 24–30 arbitrary spots along the profile using a small steel tube of 10 mm i.d. (inner diameter) and 80 mm length, which was horizontally driven 2–5 cm into the soil. We checked for compaction by comparing the insertion depth outside and core length inside the tube. Compacted cores were discarded on the spot, while cores with negligible compaction were immediately transferred into a 20 mL autosampler glass vial and sealed by crimped butyl rubber stoppers. To prevent microbial oxidation of potentially released CH_4 we added 0.4 mL of acetylene (C_2H_2) as inhibitor, resulting in a C_2H_2 gas concentration of approximately 2 v/v %. After transfer to the laboratory, 4–5 mL of N_2 was added to each vial to create an overpressure, and the cores were stored at 8 °C until further treatment.

To disturb the soil structure, cores in glass vials were subjected to two different treatments (addition of water with sonication, and acidification). Pressure and CH_4 concentrations were measured before and immediately after each treatment to determine the mass difference of CH_4(Δ CH_4) in the vial's headspace. The initial mass of CH_4 after closure in the field (0-value field) was estimated using ambient pressure, temperature and CH_4 concentrations in air on the day of sampling. The mass of CH_4 in the headspace determined before the first treatment was denoted as 0-value lab. Five milliliters of ultrapure H_2O was then added to each vial, followed by vigorous shaking of the vial for 30 s to suspend the soil core and to dissolve any water-soluble soil structure. Preliminary experiments showed that this had only marginal effects on CH_4 concentrations, therefore, the ΔCH_4 was determined after the following sonication treatment. For this the vials were submerged in an ultrasonic bath (USC500D, VWR International, Radnor, Pennsylvania, USA) and sonicated for 5 min at the highest level (45 kHz, 100 W), to disrupt any loosely bound colloids or organic aggregates. Finally, we added 1 mL of 6 N HCl to each vial to dissolve carbonate minerals and potential carbonate precipitates. The cores from GRF immediately released CO_2; however, the acid was largely buffered within minutes. During the reaction, the headspace was connected to a 60 mL syringe, and the additionally produced gas volume was transferred to two empty and pre-evacuated 20 mL vials. Pressure and CH_4 concentrations were determined together with the original vials to calculate total mass of released CH_4. Five vials each of laboratory air and air with 2 v/v % of C_2H_2 served as control and underwent the same treatments. Temperature was approximately 20 °C during all laboratory experiments. Methane was determined as described above, but with additional runtime to allow for C_2H_2 elution.

3 Results and discussion

3.1 Comparison of MLS and SR profiles

In both glacier forefields, all CH_4 concentrations measured in samples from the MLS were below atmospheric values (Fig. 1). The profiles from July and September generally agreed well and displayed no major discrepancies. Concentrations of CH_4 showed a gradual decrease with depth, typical for soils with a stable soil-CH_4 sink and no inherent CH_4 source. The lowest CH_4 concentrations were around 1 $\mu L\,L^{-1}$ in young soils (A locations), and tended to decrease to 0.5 $\mu L\,L^{-1}$ in older soil (B and C locations). In contrast, SR samples collected $\sim$ 1 min after hammering ceased (t_1; Fig. 1) showed elevated CH_4 concentrations of up to 130 $\mu L\,L^{-1}$ at all GRF locations. These samples depict profiles comparable with one-time sampling with the SR (Nauer et al., 2012). Concentrations increased with depth, and highest values were reached at deepest sampling points. On the other hand, SR samples from DAM showed atmospheric or sub-atmospheric CH_4 concentrations at all times (Fig. 1). In all SR samples O_2 concentrations were between 98 and 100 % of ambient air (not shown).

Clearly, elevated CH_4 concentrations at GRF could not be explained by sample handling or analytical procedures, as for both sampling instruments the actual extraction of soil gas, storage and CH_4 measurement were identical. Sub-atmospheric CH_4 concentrations from siliceous sites showed that the SR did not "generate" CH_4 by an unknown mechanism. Furthermore, we are confident that sampling with the MLS reflected steady-state situations, as suggested by various tests with the instrument (Nauer et al., 2013). Using the MLS the soil is not disturbed during sampling through access

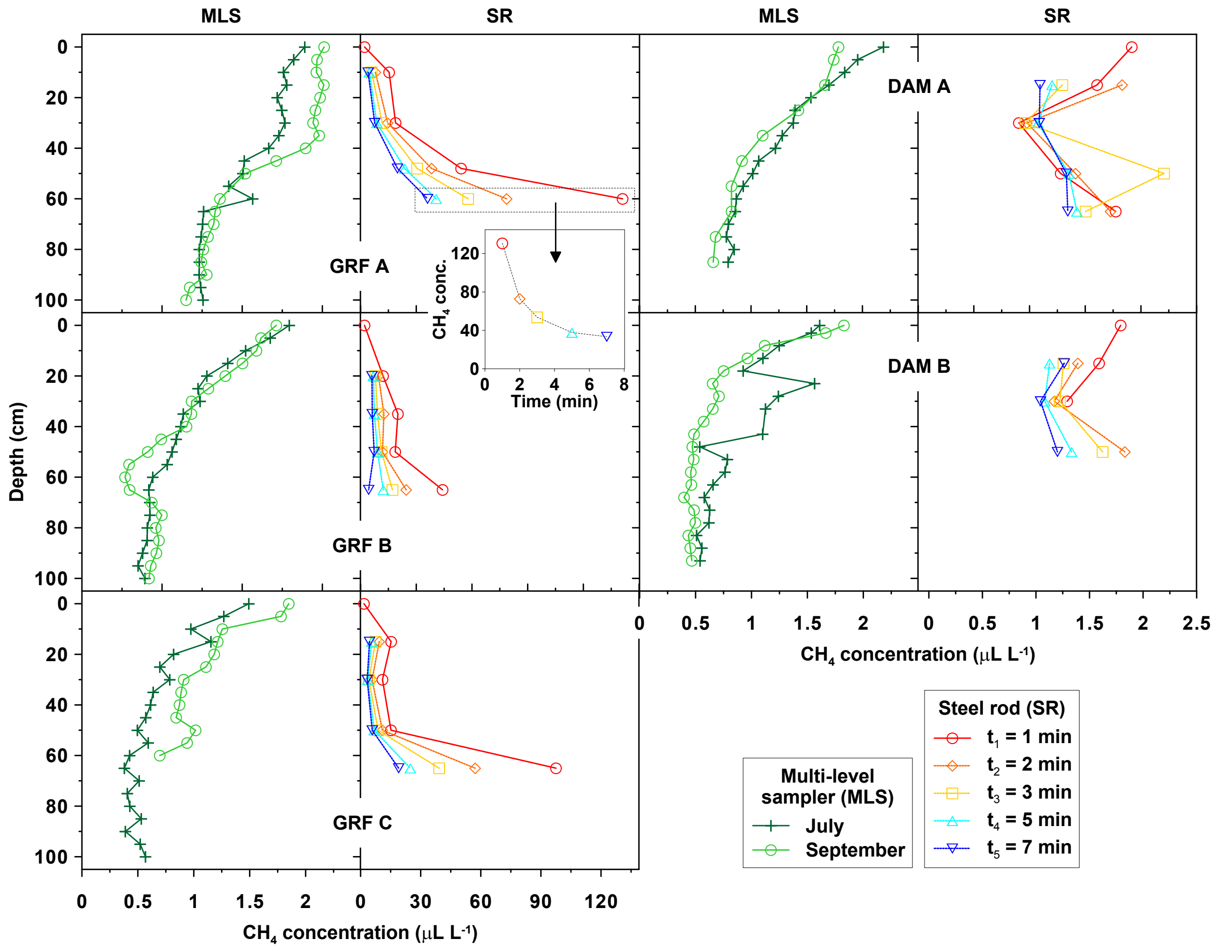

Fig. 1. Soil-CH_4 profiles obtained from the MLS and the SR time-series soil-gas samples. The red SR samples (t_1) can be directly compared to profiles for which each depth is sampled only once. Note the different scales of the x axis for the SR profiles in GRF and DAM graphs.

tubes; disturbance occurs only once when the access tubes are installed (weeks earlier). Hence, the most probable explanation for the elevated CH_4 concentrations in GRF soil is the momentary release of entrapped CH_4 when hammering the SR into the soil.

3.2 Time-series sampling with the SR

At all GRF locations, elevated CH_4 concentrations were decreasing exponentially within minutes when sampling several times at the same depth before hammering the SR to the next sampling depth (Fig. 1). This is likely a consequence of the incremental dilution due to sampling, as well as diffusive gas transport away from the release source (depicted in the insert of Fig. 1 with samples from GRF A at 60 cm depth). Possibly, concentrations immediately after hammering were even higher. This clearly shows that the elevated CH_4 concentrations were transient and released by the act of sampling with the SR.

Time-series samples from DAM remained subatmospheric, with one exception at DAM A, t_3 (Fig. 1). However, CH_4 concentrations tended to slightly increase with depth and decrease with time in the deepest samples. The variability of soil-CH_4 concentrations between samples from the same depth was likely caused by soil heterogeneity and the increasing volume of soil gas extracted during repeated sampling. In GRF samples, potential variability was likely masked by the released CH_4. However, it cannot be excluded that even in siliceous soils, small amounts of CH_4 could be released by sampling with the SR.

With no additional information, the shape of the SR profiles t_1 from GRF might suggest a deep-soil CH_4 source (Nauer et al., 2012), similar to what has been observed in landfills or peat bogs (Fechner and Hemond, 1992; Urmann et al., 2007; Schroth et al., 2012). However, given the transient nature of the elevated CH_4 concentrations in samples from the SR, a steady-state interpretation of such soil-gas profiles involving a continuous source has to be rejected. More likely, as suggested by results from the MLS, glacier

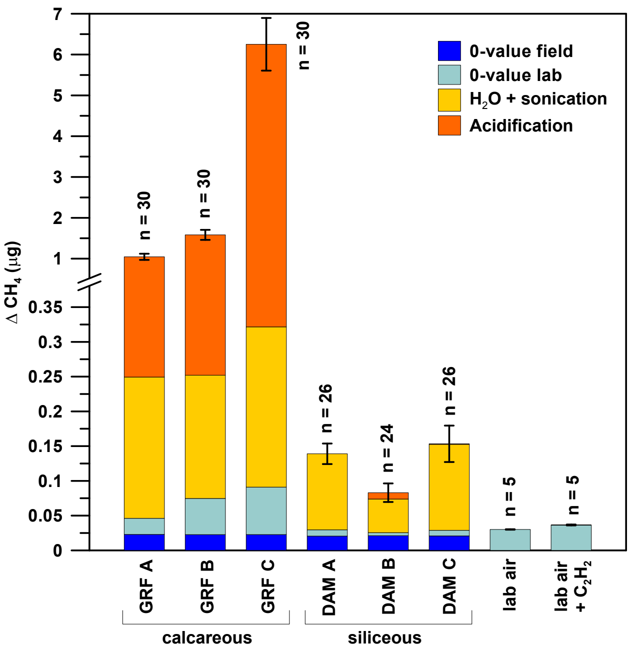

Fig. 2. Cumulative, average amount of CH_4 released from miniature soil cores after treatments to disturb the soil structure. Note the break and variable scaling of the *y* axis. Zero-values in the field represent the estimated amount of CH_4 contained in enclosed ambient air; 0-values in the lab represent the (additional) amount of CH_4 released during transport and storage. Error bars denote standard deviation of the mean of the total amount of CH_4 in the vials.

forefield soils on both bedrock types appear to be stable sinks for atmospheric CH_4. Nonetheless, the performed time-series sampling provided strong indications that additional CH_4 from sources other than the atmosphere are retained in these fully oxic soils, whereby the amount present appears to be orders of magnitude larger in GRF compared with DAM soils. Considering the clear pattern reported in Nauer et al. (2012), where all SR samples from five calcareous glacier forefields showed elevated CH_4 concentrations (10–1000 μL L^{-1}), the phenomenon of entrapped CH_4 might be more widespread in these environments.

3.3 Miniature-soil-core experiments

For a first quantitative assessment of entrapped CH_4, miniature soil cores enclosed in vials in the field were disturbed by different treatments in the laboratory, and the released CH_4 was measured (Fig. 2). The average amount of CH_4 released from cores of each location increased significantly during the course of the experiment, while in the control vials containing laboratory air or air + C_2H_2 it remained constant and even decreased marginally after acidification (decrease not visible in Fig. 2). Hence, cores from all locations contained some CH_4 that was released with either sonication or both sonication and acidification.

However, the average amounts of CH_4 released from calcareous soil cores were much higher than from siliceous cores (Fig. 2). Some of the GRF cores already released CH_4 during transport from the field to the laboratory. It is unlikely that methanogenesis was ongoing in these cores as they were closed under oxic conditions. Rather we believe that CH_4 was released when part of the core structure was disturbed. The addition of water itself had only a negligible effect (preliminary experiments, not shown), but sonication of the suspended cores released significant amounts of CH_4 from DAM and GRF cores (2–5 times more from the latter; Fig. 2). This is a first indication that at least part of the CH_4 could be entrapped in soil colloids or cemented particles that can be suspended by ultrasound. Acidification almost exclusively affected calcareous cores, for which the average amount of CH_4 in the vials increased again by an order of magnitude or more (Fig. 2). Similar CH_4 concentrations in the headspace of the vial containing the soil core and in the vials containing the excess gas volume showed that CH_4 release from the core ceased once the added acid was buffered. As the acid affects all calcareous minerals, it is unclear from which particle fraction this massive CH_4 increase originated. Likely, the acid foremost affected the smaller particle fractions in suspension, and only the surface of larger particles, before it was completely buffered. Although calcareous gravel (2–5 mm fraction) from another glacier forefield (Griessen glacier; Nauer et al., 2012) and a quarry showed CH_4 release during acidification, total release was in the range of DAM cores (data not shown). This indicates that the bulk mass of CH_4 in GRF samples may be entrapped in the finer soil fractions, e.g. in cemented particles. Clarification of this issue will require further investigation, which was beyond the scope of this study.

On a mass basis, CH_4 in the vials from GRF increased on average by a factor of 45–270 compared to the originally enclosed air. This is roughly the same order of magnitude as the increase in soil-gas concentrations when sampling with the SR in the field. For DAM, the mass increase in the vials was in the range of 4–7, although no substantial increase in CH_4 concentrations was observed with the SR in the field. Reasons for this are unclear; it might be attributed to the 1 min delay between disturbance (hammering) and sampling with the SR, which could be sufficient to dilute potentially released CH_4 to ambient levels. However, it may also point towards a different nature of entrapment in siliceous versus calcareous soils.

When considering individual cores, cumulative amounts of released CH_4 showed considerable variability (Fig. 3). Amounts released from GRF cores ranged from 0.12 to 7.5 μg CH_4 (g d.w.)$^{-1}$, which was 1–2 orders of magnitude higher than the 0.002–0.16 μg CH_4 (g d.w.)$^{-1}$ from DAM cores. For the latter, the increase of CH_4 in some vials was smaller than the estimated CH_4 originating from the enclosed air. In contrast, all GRF cores released substantial amounts of CH_4, but some “hotspots” were responsible for the most

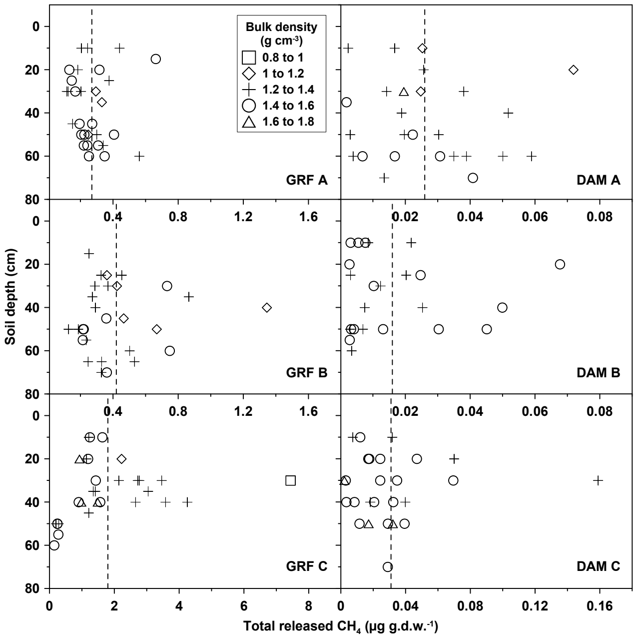

Fig. 3. Depth distribution and cumulative CH_4 released from individual miniature soil cores. The different symbols denote bulk-density classes of individual cores. Vertical dashed lines indicate the average cumulative CH_4 release for each location.

pronounced increase. However, we could not observe a clear pattern of the released CH_4 with respect to the sampling depth of the cores, with the exception of GRF B and C, where highest amounts of CH_4 were released from samples collected around 30–40 cm depth (Fig. 3). Furthermore, there was no obvious correspondence with bulk-density classes. However, it is remarkable that the only sample with an exceptionally low bulk density released the highest amount of CH_4 from all cores (Fig. 3, GRF C). At present, we lack a conclusive explanation for this observation.

4 Implications for further studies

In summary, we can state that there is CH_4 entrapped in both the GRF and DAM soils, but the former retains orders of magnitude more CH_4. In light of previous results (Nauer et al., 2012) our findings suggest that CH_4 entrapment might be a common feature of glacier forefield soils, in particular on calcareous bedrock. At present, we can only speculate about the origin of released CH_4 and the nature of entrapment. The observation that the bulk mass of CH_4 appears to be entrapped in the finer soil fraction or aggregates could hint towards a potential role of secondary carbonate precipitates of glacial origin (Ford et al., 1970; Fairchild et al., 1993; Lacelle, 2007). Water films existing at the base of temperate glaciers can refreeze due to pressure changes while calcite precipitates and cements particles together (Fairchild et al., 1993; Carter et al., 2003). Methane produced by subglacial methanogenesis may get entrapped in closed-off pores or fissures. Such a mechanism would partially prevent or delay the outgassing of any subglacially produced CH_4 after glacial meltdown. Secondary carbonate precipitates have also been reported from environments on siliceous bedrock (Carter et al., 2003; Lacelle et al., 2007). However, it is unlikely that such precipitates would be preserved in the DAM soil with pH of 4–5 (Bernasconi et al., 2011). Here, other types of aggregates might be responsible for CH_4 entrapment. In both glacier forefields, CH_4 might also originate from recent methanogenesis in sealed microsites.

For calcareous glacier forefields we cannot exclude the possibility that the CH_4 is entrapped in the bedrock itself. In this case the likely origin of the CH_4 would be thermogenic. Sampled calcareous glacier forefields in Nauer et al. (2012) lie on late jurassic or early cretaceous limestones as part of the Helvetic nappes (Geological Atlas 1 :500 000, Federal Office of Topography swisstopo, Wabern, Switzerland). The occurrence of these limestones partially overlaps with a zone where fluid inclusions in quartz-filled fissures are dominated by thermogenic CH_4 (Mullis et al., 1994; Tarantola et al., 2007). In some adjacent marls in the Helvetic nappes, CH_4-dominated fluid inclusions in calcite-filled fissures have also been documented (Gautschi et al., 1990).

Further insights in the nature of these CH_4 entrapments require additional experiments with fresh samples, including initial separation of grain-size classes, and complete dissolution of calcareous minerals to establish a total mass balance. Radiocarbon age determination and auxiliary stable isotope measurements may shed light on the origin of entrapped CH_4. Furthermore, given the relative ease of how entrapped CH_4 was released, its potential bioavailability should be addressed. Particularly in glacier forefields, CH_4 diffusing from such entrapments could represent an additional source of carbon in an otherwise oligotrophic environment.

Supplementary material related to this article is available online at http://www.biogeosciences.net/11/613/2014/bg-11-613-2014-supplement.pdf.

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