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Ancient dissolved methane in inland waters revealed by a new collection method at low field concentrations for radiocarbon (^{14}C) analysis

Joshua F. Dean [a], [b], [*], Michael F. Billett [c], Callum Murray [a], Mark H. Garnett [a]

[a] NERC Radiocarbon Facility, East Kilbride, G75 0QF, UK
[b] Department of Earth Sciences, Vrije Universiteit Amsterdam, 1081 HV, Amsterdam, The Netherlands
[c] Biological and Environment Sciences, University of Stirling, Stirling, FK9 4LA, UK

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ABSTRACT

Methane (CH_4) is a powerful greenhouse gas that plays a prominent role in the terrestrial carbon (C) cycle, and is released to the atmosphere from freshwater systems in numerous biomes globally. Radiocarbon (^{14}C) analysis can indicate both the age and source of CH_4 in natural environments. In contrast to CH_4 present in bubbles released from aquatic sediments (ebullition), dissolved CH_4 in lakes and streams can be present in low concentrations compared to carbon dioxide (CO_2), and therefore obtaining sufficient aquatic CH_4 for radiocarbon (^{14}C) analysis remains a major technical challenge. Previous studies have shown that freshwater CH_4, in both dissolved and ebullitive form, can be significantly older than other forms of aquatic C, and it is therefore important to characterise this part of the terrestrial C balance. This study presents a novel method to capture sufficient amounts of dissolved CH_4 for ^{14}C analysis in freshwater environments by circulating water across a hydrophobic, gas-permeable membrane and collecting the CH_4 in a large headspace volume. The results of laboratory and field tests show that reliable dissolved $\delta^{13}CH_4$ and $^{14}CH_4$ samples can be readily collected over short time periods (~4–24 h), at relatively low cost and from a variety of surface water types. The initial results further support previous findings that dissolved CH_4 may be significantly older than other forms of aquatic C, and is currently unaccounted for in many terrestrial C balances and models. This method is suitable for use in remote locations, and could potentially be used to detect the leakage of unique $^{14}CH_4$ signatures from point sources into waterways, e.g. coal seam gas and landfill gas.

1. Introduction

Methane (CH_4) is a powerful greenhouse gas (GHG), second only to carbon dioxide (CO_2) in importance to global climate through radiative forcing (O'Connor et al., 2010). The influence of CH_4 on climate means it is vital to understand how this GHG is produced, cycled and released within the terrestrial carbon (C) cycle (Schaefer et al., 2016). Inland waters – lakes, rivers, streams and ponds – although occupying only a small percentage of land cover are estimated to release 0.65 Pg C (CO_2 equivalents) yr^{-1} of CH_4, equivalent to one quarter of the global terrestrial C sink (Bastviken et al., 2011). Inland waters therefore have the potential to play a significant role in future climate warming scenarios by releasing CH_4 as part of positive feedback loops under current warming conditions (Vonk et al., 2015).

Radiocarbon (^{14}C) is a key tool in identifying both the source and age of aquatic CH_4 (e.g. Leith et al., 2014), and its significance to terrestrial C balances and climate feedback loops. Previous work has indicated that CH_4 released from freshwater systems can be significantly older than dissolved CO_2 and dissolved organic C in the same system (Garnett et al., 2013; Leith et al., 2014), suggesting the source and fate of dissolved CH_4 can differ significantly from other forms of freshwater C.

Previous $^{14}CH_4$ studies have focused primarily on CH_4 ebullition (e.g. Negandhi et al., 2013; Walter Anthony et al., 2016), as CH_4 is generally present in high concentrations in ebullition bubbles (4–100% CH_4; Walter Anthony et al., 2010) making it easier to obtain sufficient material for ^{14}C analysis. Dissolved (or diffuse)

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[*] Corresponding author. Department of Earth Sciences, Vrije Universiteit Amsterdam, 1081 HV, Amsterdam, The Netherlands.
E-mail address: j.f.dean@vu.nl (J.F. Dean).

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CH_4, however, is often only present in low concentrations in freshwater streams (0.13–7.57 μmol l^{-1}; Holgerson and Raymon, 2016; Dean et al., 2016), making it difficult to obtain sufficient material for ^{14}C analysis without degassing large volumes of water (Garnett et al., 2016a). Further, the need for $^{14}CH_4$ analysis in remote regions, such as in Arctic inland waters where potentially significant CH_4 climate feedbacks have been identified (Vonk et al., 2015), means that this technical challenge is heightened by the need for a method that allows the degassing of large volumes of water with relatively low power demand, and captures the sample in a form that can be safely transported to a laboratory and readily processed (e.g. Garnett et al., 2016b).

Despite often low concentrations in inland waters, dissolved CH_4 can be a significant conduit of vertical and lateral C fluxes in wetlands (Billett and Moore, 2008; Poindexter et al., 2016), making it important to understand its production and fate across ecosystems. Ebullitive CH_4 is predominantly generated in sediments, and can pass relatively unchanged through the water column before outgassing at the air-water interface (Barros et al., 2011). Dissolved CH_4 can more readily move laterally through soils via transport in the saturated zone (Paytan et al., 2015; Poindexter et al., 2016), as well as vertically via plant aerenchyma (open, conductive plant tissue; Cooper et al., 2014), and may be subjected to a wider range of biogeochemical transformations prior to reaching an open water body and (potentially) degassing. This means that the isotopic signatures of dissolved CH_4, particularly ^{14}C and $\delta^{13}C$, may be different from ebullition CH_4, representing different sources and pathways and/or its potential to be oxidised to CO_2 in the water column – the latter alleviating the warming potential of CH_4 production. $^{14}CH_4$ and $\delta^{13}C$ can further be used alongside δ^2H-CH_4 to elucidate methanogenic pathways (e.g. Negandhi et al., 2013).

^{14}C analysis is also a particularly useful indicator of thermogenic CH_4, such as in coal seam gas, since it is radiocarbon-dead (i.e. 0% modern C [pmC]). Coal seam gas is liberated by hydraulic fracturing, and fugitive emissions to the atmosphere from these projects can be enormous (e.g. Caulton et al., 2014). It is not yet fully known how the development of coal seam gas projects and fugitive CH_4 emissions may impact local inland water CH_4 concentrations (Currell et al., 2016; Li et al., 2016), but groundwater CH_4 can be rapidly transported into surface water systems if they are well connected (e.g. Paytan et al., 2015). ^{14}C has also been applied as a tracer in wastewater studies (Law et al., 2013), in which CH_4 can be a significant component. It can also be a useful tracer for landfill gas migration (Palstra and Meijer, 2014).

Here we present a new method to collect sufficient dissolved CH_4 for ^{14}C analysis using a coiled degassing membrane, a large headspace in a collapsible vessel, and a 12-V self-priming water pump. The method, which isolates dissolved CH_4 and excludes ebullition CH_4, is shown to (1) accumulate sufficient CH_4 for ^{14}C analysis, even in water with low dissolved CH_4 concentrations, (2) provide reproducible $^{14}CH_4$ ages and (3) non-fractionated $\delta^{13}CH_4$ values. We demonstrate the application of the method across two different inland water types at peatland sites with a range of CH_4 concentrations and isotopic signatures, as well as its potential application to detecting localised CH_4 inputs to fluvial systems.

2. Methods

2.1. Description of the new method

The degassing vessel is constructed with 6 m of hydrophobic, gas-permeable membrane tubing (Accurel® PP V8/2 HF, Membrana GmbH, Germany) coiled inside a 15 L collapsible water carrier (Highlander, Livingston, UK). The collapsible water carrier is filled with 8 L of ambient headspace, and sample water is pumped through the membrane tubing allowing gas to pass from solution into the headspace of the collapsible water carrier. The collapsible water carrier is sealed with a rubber stopper, the membrane tubing is attached to outlets drilled into the stopper and sealed with auto-shutoff couplings (Colder Products Company, USA). Two other outlets, also sealed with auto-shutoff couplings, are drilled into the stopper to allow sampling of the headspace in the collapsible water carrier (Fig. 1). The complete system is herein referred to as a "Coiled Membrane Vessel" (CMV).

The 8 L headspace was selected based on the size of readily available gas sample bags (10 L foil gas bags, SKC Ltd, UK – these are filled to 8 L to allow for expansion and reduce the risk of leakage and/or puncture) used in the Natural Environment Research Council (NERC) Radiocarbon Facility (East Kilbride, UK; Garnett et al., 2016a). The length of tubing was selected after preliminary tests showed that increasing tubing length increased the CH_4 degassed per unit water pumped through the CMV (see section 3.1), but at a rate of diminishing returns, and with the consideration of cost. 6 m of membrane tubing allows ample opportunity for the water pumped through it to equilibrate with the headspace, and also fits comfortably within the collapsible water carrier; longer lengths of tubing decreased the membrane:headspace surface contact area as the coils of tubing bunched up.

Following collection, the 10 L foil gas bags were processed as soon as possible (within a few days) at the NERC Radiocarbon Facility (the bags are not recommended for long-term storage). First, CO_2 was removed by passing the sample gas through a cartridge containing soda lime. If required, high purity oxygen was added to ensure enough was present for the oxidation of the entire CH_4 sample, and then the sample was pumped through a cartridge containing a platinum catalyst heated to 950 °C to oxidize the CH_4 (Garnett et al., 2016a). The CH_4-derived CO_2 was cryogenically purified and the volume determined. If > ~1 ml CO_2 was recovered it was split into separate aliquots for IRMS (Thermo Fisher Delta V) and graphitisation followed by Accelerator Mass Spectrometry (SUERC AMS Facility, East Kilbride, UK). For these samples ^{14}C results were normalised to a $\delta^{13}C$ of −25‰ using the IRMS $\delta^{13}C$ values (normalisation of ^{14}C results is done by convention, and corrects the results for isotopic fractionation; Stuiver and Polach, 1977; Garnett et al., 2016a). Samples that provided < ~1 ml CO_2 were graphitized and then analysed for both $\delta^{13}C$ and ^{14}C content using AMS (UC Irvine, California, USA), and the on-line $\delta^{13}C$ values used to normalize the ^{14}C results. All $\delta^{13}C$ values are presented in ‰ relative to the VPDB standard, while ^{14}C values are expressed as either pmC or as conventional radiocarbon ages (y B.P., where 0 y B.P. = 1950 CE; Stuiver and Polach, 1977).

The $^{14}CH_4$ and $\delta^{13}CH_4$ values were corrected for the ambient atmospheric CH_4 component in the headspace where appropriate, following Garnett et al. (2016a), using equation (1):

$$Ci_{corr} = \frac{Ci_{meas} - F_{atmos} \cdot Ci_{atmos}}{1 - F_{atmos}} \quad (1)$$

where Ci represents the isotopic content (^{14}C as pmC or $\delta^{13}C$ as ‰) of the corrected CH_4 sample ($_{corr}$), measured sample ($_{meas}$), and ambient atmosphere ($_{atmos}$). $^{14}CH_{4\ -\ atmos}$ was assumed to be 130 ± 5 pmC (Lassey et al., 2007), and $\delta^{13}C$ assumed to be −47.2 ± 0.2‰ (Lassey et al., 2007; Schaefer et al., 2016). F_{atmos} is the fraction of atmospheric CH_4 (the concentration of which is assumed to be 2 ± 0.2 ppm; Kirsche et al., 2013) in the sample CH_4; headspace CH_4 concentration was measured after sampling using a Detecto Pak-Infrared (DP-IR; Gas Measurement Instruments Ltd, UK; accuracy ± 10%) gas analyser, and was also back calculated from the CH_4 recovered as CO_2 during processing (Supplementary Table S3). We estimate that the additional uncertainty introduced by this correction was ±0.56 pmC and ±0.2‰ for ^{14}C and $\delta^{13}C$, respectively, and this is incorporated into our results (see section 3); the uncertainty propagation was calculated as:

$$\delta Q = \sqrt{\delta a^2 + \delta b^2} \tag{2}$$

where δQ is the propagated uncertainty of δa, the analytical uncertainty, and δb, the uncertainty introduced by the atmospheric correction.

2.2. Laboratory trials

We first tested the reliability of the CMV headspace to contamination in free-standing "static" mode by filling three CMV headspaces with a dilute CH_4 gas sample (~550 ppm), and allowing them to stand for 72 h. The CH_4 concentrations in the headspaces at the beginning and end of this period were measured with the DP-IR. All CMVs were leak tested prior to the field and lab tests. CMVs were not sterilized between the collection of samples, but were flushed thoroughly with clean water to remove excess residue from previous samples. Lab experiments were conducted at room temperature (~21 °C).

The effect of pumping rate and membrane tubing length on the isotopic composition of the degassed CH_4 were tested with a single experiment, using an in-house CH_4-rich water standard that we created. The water standard was generated by circulating a headspace filled with commercially available cylinder CH_4 through tap water in a large 120 L barrel; this created 120 L of water supersaturated in CH_4 with respect to the atmosphere. The water standard was created using ^{14}C-dead fossil CH_4 as this would be most sensitive to contamination by modern ambient CH_4; however, the standard was primarily used to test for $\delta^{13}C$ fractionation and ^{14}C replicability, as ^{14}C values were corrected relative to a $\delta^{13}C$ value of −25‰ by convention (see section 2.1; Stuiver and Polach, 1977). This water was then pumped via Tygon tubing (E3603 diameter 8 mm, wall 1.6 mm, Fisher, UK), using a 12-V self-priming water pump (non-branded aquarium pump, made in China), through three CMVs connected in series (i.e. the outflow of the first CMV flowed directly into the second and so on), at a rate of 14 L h^{-1}, simulating a membrane length of 18 m, three times that of a single vessel. The water standard was also pumped through a fourth CMV at a rate of 3 L h^{-1}, representing a lower pumping rate with 6 m of membrane tubing. The headspace CH_4 concentrations in all four CMVs were monitored using the DP-IR every ~50 min during the 360 min experiment (Fig. 2a).

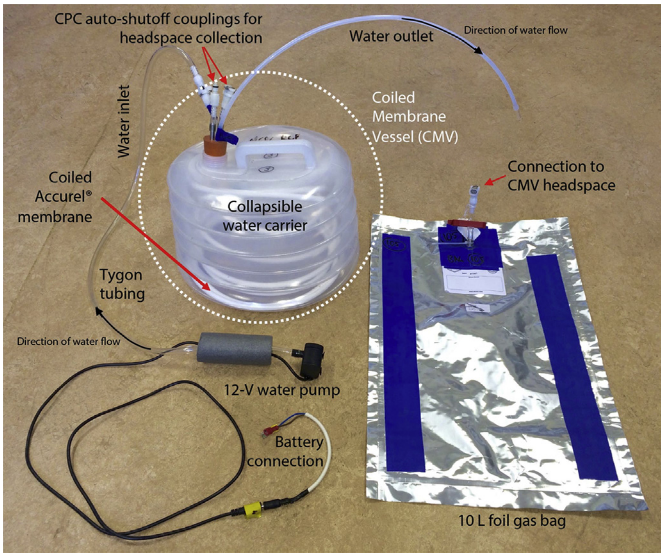

Fig. 1. A complete Coiled Membrane Vessel (CMV), with a 12-V water pump and 10 L foil gas bag for collection of the headspace sample for $^{14}CH_4$ analysis.

Concurrent samples were collected from the same water standard using the established accordion water carrier (AWC) shaking method for rapid extraction of dissolved CH_4 from water (Garnett et al., 2016a), at 18 min (using an N_2 headspace to test the impact of using ambient headspace), 45 min (ambient headspace) and 155 min (ambient headspace) into the experiment, all using a 3:1 water to headspace ratio.

2.3. Field trials

A replicated field trial was first carried out on 22 July 2015 in a stream at Langlands Moss (55°44′3.9″N 04°10′36.6″W), which drains an ombrotrophic raised bog in central southwest Scotland. The site has previously been used for methodological development of $^{14}CH_4$ and $^{14}CO_2$ sampling methods (Garnett et al., 2013, 2016a, 2016b). Three dissolved $^{14}CH_4$ samples were collected from the midpoint of the stream using the new CMV method, with a fourth CMV sample collected as backup. The build-up of CH_4 in the headspace of each of the CMVs was monitored every 20 min over the 260 min collection period using a DP-IR (Fig. 2b). The 12-V water pump intakes were positioned within 5 cm of each other in the stream, 5–10 cm beneath the stream surface. Pumping rates, which were very similar for each CMV (420–500 ml min^{-1}), are controlled by a variety of factors including ambient temperature and battery voltage (air and water temperatures of the field studies are included in Supplementary Table S2). The water pumps were powered by individual 12-V 3.2-Ah rechargeable batteries (Yuasa Battery, Inc.). An aggregated $^{14}CH_4$ sample was concurrently collected using the AWC method (Garnett et al., 2016a). This involved the equilibration of 33 L of stream water at a 3:1 water to headspace ratio and five 6:1 ratio equilibrations to maximise the volume of CH_4 collected; the resulting 6 L of sample headspace was combined into a single gas bag for processing.

We also performed a replicated overnight test of the method from 22 July to 23 July 2016 in a transect. This tested the ability of the method to detect small-scale downstream spatial changes in CH_4 isotopic composition. One CMV was set up collecting stream water in the same place as the first set of replicates (see above), another collected water 8 m upstream in a small tributary (running from a neighbouring golf course) to the stream draining Langlands Moss peatland, and a third collected stream water 4 m downstream. A mass balance (assuming no small-scale loss or gain of water within the stream reach) was used to estimate the ^{14}C signature of the input CH_4 from the stream draining Langlands Moss peatland (comparing the mid-point of the transect with the small tributary at the upstream point of the transect), as a proxy for a CH_4 point source, calculated from:

$$Ci_{input} = \frac{(Ci_{down} \cdot M_{down}) - (Ci_{down} \cdot (M_{down} - M_{up}))}{(M_{down} - M_{up})} \tag{3}$$

where Ci is the isotopic content (in pmC) and M is the concentration (in any concentration unit) of the input or point source ($_{input}$) CH_4, upstream ($_{up}$) CH_4, and downstream ($_{down}$) CH_4, respectively.

In the final experiments, we tested the lower limits (in terms of CH_4 concentration) of the new method by performing replicated field sampling at sites with lower dissolved CH_4 concentrations (relative CH_4 concentrations were measured by shaking ~500 ml water with a 1:1 headspace-water ratio in a bottle for 1 min, and

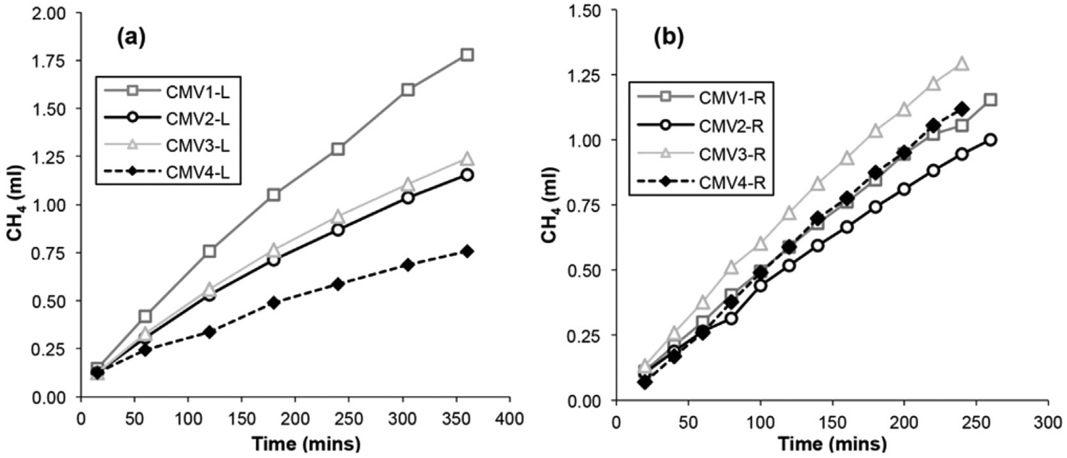

Fig. 2. Degassing rates of CH_4 into the headspaces of the four CMVs in (a) the lab experiment using commercially available bottled CH_4 dissolved in tap water, and in (b) the field experiment at the stream draining the Langlands Moss peatland.

measuring the headspace concentrations using the DP-IR – results not reported). The samples from the lowest CH_4 concentration water were collected from a blocked drain along the southeast edge of the peatland (Supplementary Fig. S1) on 28 July 2015, with the degassed CH_4 collected on the morning of 29 July. Samples were also collected from a natural pool downstream of the blocked drain on 29 July to 30 July 2015, which had a higher dissolved CH_4 concentration. For both replicate measurements, three CMV samples were collected into ambient headspace, while a fourth sample was collected in a CMV with a pure N_2 gas headspace to verify the atmospheric correction (see section 2.1).

A single CMV $^{14}CH_4$ sample was also collected on 05 November 2014 from a natural peatland pool in the Flow Country of N Scotland (Loch Leir - 58° 23′ N 03° 46′ W; Turner et al., 2016). This sample was collected at an early stage in the development of this method to verify its viability in the field prior to initiating the full-scale testing presented here.

3. Results and discussion

3.1. Coiled membrane vessel leak testing

The CMV is designed to be left pumping for several hours, even overnight. In our tests (see section 3.3), the CMVs were often left to pump overnight, but usually ran out of power before we collected them the next day. This could be avoided by using larger batteries for the water pumps (we used 3.2-Ah batteries); regardless, we tested the stability of the headspace after sample collection over several days. CMV headspace leakage was tested over a 72-h period, with the measured headspace CH_4 values dropping by 7–14% over this time period (Supplementary Table S1). We recommend collecting the headspace samples within 24 h of initiating the water pumping, as during this time CH_4 losses from the headspace would be minimal based on these results. Given that the CH_4 concentration gradient would be from the headspace to the atmosphere in almost all cases, and could never be more than the ambient atmosphere (~2 ppm), further atmospheric contamination will be negligible.

3.2. Flow rate and hydrophobic tubing length effects on ^{14}C- and $\delta^{13}C$-CH_4

The impacts of water flow rate through the membrane and the membrane length on the rate of equilibration of CH_4 in the CMV headspace and its measured isotopic composition were tested in the lab experiment. The bottled CH_4 used in the water standard in this test had a ^{14}C signature of 0.24 ± 0.01 pmC and $\delta^{13}C$ of −43.6‰ (Table 1). The AWC samples taken during the lab experiment had $\delta^{13}CH_4$ signatures of −40.1, −41.3 and −42.0‰ at 18, 45 and 355 min, respectively.

CH_4 concentrations were higher (1.48 ml-CH_4, CMV1; Fig. 2) at the faster pumping rate compared to the slower rate (0.63 ml-CH_4, CMV4), but the slower water-pumping rate allowed more CH_4 to degas per volume water pumped through the membrane (0.03 ml-CH_4 $[L\text{-}H_2O]^{-1}$ compared to 0.02 ml-CH_4 $[L\text{-}H_2O]^{-1}$; Table 1). The CH_4 equilibration rate was approximately equal in the two CMVs connected in series after CMV1 (CMV2-3; Fig. 2), and the amount of CH_4 degassed per volume water pumped was the lowest at 0.01 ml-CH_4 $(L\text{-}H_2O)^{-1}$ (Table 1).

The $\delta^{13}CH_4$ signatures of the fast and slow pumping rates were −42.4‰ and −42.2‰, respectively (Table 1), within the range of analytical uncertainty (±0.2‰), but slightly heavier than the pure bottled CH_4, and slightly lighter than the AWC generated samples. CMVs 2 and 3 had similar $\delta^{13}CH_4$ values (−42.1 and −41.9‰, respectively) to CMVs 1 and 4, and these also fell within the range of values generated by the AWC method. This shows good agreement between the different $\delta^{13}CH_4$ signatures measured (all within ±0.9‰), which is reasonable given that the CMV samples are aggregate samples over the 6-h experiment (during which the standard water was exposed to the ambient lab atmosphere), while the AWC samples are spot samples from specific time points (±5 min).

$^{14}CH_4$ was only measured in the CMVs connected in series, as there was insufficient CH_4 in the other samples – the primary aim of the lab experiment was to test for fractionation of $\delta^{13}C$, while ^{14}C replication was tested in more detail in the field. The lab test $^{14}CH_4$ values generated by the CMV method all agreed with the bottled CH_4, ranging from 0.59 ± 0.58 to 1.42 ± 0.56, which is reasonable given that even slight ingress of ambient modern-CH_4 will have a strong effect on a sample very close to radiocarbon-dead (~0 pmC; see section 3.4).

The CH_4 equilibration rate was then examined in a stream with relatively high CH_4 concentrations draining the Langlands Moss peatland (Garnett et al., 2016a). Here, four CMVs pumped water from the same point in the stream, at faster pumping rates than in the lab (25–30 L h^{-1} versus 14 L h^{-1}), due to the different environmental conditions. The equilibration rates were relatively similar for all sampling vessels (Fig. 2b), with the efficiency of CH_4

Table 1
Lab test comparison between different degassing tube lengths (CMV1-3) and pumping rates (CMV1-3 vs. CMV4), and the AWC method (Garnett et al., 2016a); all values are corrected for atmospheric CH_4 contamination except where noted.

Sample ID	Treatment	Experiment time (min)	Water volume (L)	Recovered CH_4 volume (ml)	Headspace CH_4 concentration (ml-CH_4 [L-H_2O]$^{-1}$)	$\delta^{13}CH_4$ (±0.2‰)	$^{14}CH_4$ (pmC)
CH_4 bottle	–	–	–	2.32	–	−43.6[a]	0.24 ± 0.01
CMV1-L	In series, high flow	360	84.3	1.49	0.02	−42.4	0.91 ± 0.56[b]
CMV2-L	In series, high flow	360	84.3	1.05	0.01	−42.1	1.42 ± 0.56[b]
CMV3-L	In series, high flow	360	84.3	0.97	0.01	−41.9	0.59 ± 0.58[b]
CMV4-L	Single, low flow	360	18.9	0.63	0.03	−42.2	n.d.
AWC1-L	–	18	3.3	0.16	0.05	−40.7	n.d.
AWC2-L	–	45	3.0	0.13	0.04	−41.3	n.d.
AWC3-L	–	355	3.0	0.21	0.07	−42.0[a]	n.d.

n.d. = not determined.
[a] No atmospheric correction required – accuracy is ±0.1‰.
[b] Includes error introduced by the atmospheric correction.

equilibration in each vessel 0.01 ml-CH_4 (L-H_2O)$^{-1}$ (Table 2).

Despite the slight variation in CH_4 equilibration efficiency between the CMV and AWC samples (Table 2), the $\delta^{13}CH_4$ values from each sample were in excellent agreement, within ±0.3‰, with the exception of CMV2 where, due to the low sample volume, $\delta^{13}CH_4$ was determined online with the AMS, rather than by IRMS (AMS measurement of $\delta^{13}C$ is often less reliable than IRMS). $^{14}CH_4$ was also consistent, ranging from 67.61 ± 0.65 to 68.91 ± 0.58 pmC in the CMV samples, very similar to the AWC sample of 69.64 ± 0.64 (Table 2).

These results show that despite different pumping rates and lengths of membrane tubing, there was no evidence of isotopic fractionation of CH_4 equilibrated into the CMV headspace. Hence the method provided reliable $\delta^{13}CH_4$ values. The results also demonstrate the replicability of the $^{14}CH_4$ values across multiple CMV vessels, corroborated by the results from the established AWC degassing method.

3.3. *Significance of dissolved CH_4 radiocarbon ages*

Replicate samples were collected from two contrasting sites in the Langland's Moss peatland, one a naturally occurring pool and the other a man-made artificial pool created behind a blocked drain (see Table 3 for the relative CH_4 volumes yielded from the different sampling points). Artificial pool formation due to drain blocking is a widespread practice in UK peatlands, and globally, as a result of efforts to stabilise peatland C stores by raising the water table to prevent organic matter oxidation, and to limit C loss via erosion (Parry et al., 2014; Turner et al., 2016).

The replicate dissolved $^{14}CH_4$ samples from the natural pool at the study site were in very good agreement, and fell within the error range (66.19 ± 0.63 to 66.62 ± 0.64 pmC; Table 3). $\delta^{13}CH_4$ ranged from −63.7 to −64.1‰, overlapping at 2σ uncertainty (±0.04‰); the sample for which $\delta^{13}CH_4$ was determined online with the AMS – which is often not as reliable for $\delta^{13}CH_4$ measurement as IRMS – was slightly lighter at −64.4‰. In the artificial pool, replicated $^{14}CH_4$ values were significantly ^{14}C-enriched (younger) and ranged from 94.13 ± 0.59 to 95.03 ± 0.60 pmC, again with overlapping error ranges (Table 3). The $\delta^{13}CH_4$ values were more variable than in the natural pool (−58.5 to −61.4‰), but this was likely due to three of these being measured online with the AMS.

The isotopic agreement between the replicates is excellent, including for the samples that were equilibrated into a N_2 headspace rather than ambient air (Table 3). This supports the reliability of the method for both $^{14}CH_4$ and $\delta^{13}CH_4$ in field applications, and the robustness of the atmospheric contamination correction (Supplementary Table S3).

The radiocarbon ages of the dissolved CH_4 in the two pool types were dramatically different (Table 3). While the average age of the dissolved CH_4 in the natural pool was 3262–3315 y B.P., the artificial pool CH_4 was much younger (410–486 y B.P.; Table 3). The $^{14}CH_4$ in the natural pool was similar to that seen in the stream outlet of the peatland (Table 2; Garnett et al., 2016a) and older than that observed in peat surface emissions at the same site (Garnett et al., 2012) and up to 2 m depth in the peat (Garnett et al., 2011). This suggests that the dissolved CH_4 in the natural pool and at the stream outlet are likely derived from considerable depth in the

Table 2
Field tests comparing replicate CMV samples (CMV1-4) and AWC samples in this study and Garnett et al. (2016a), collected from the stream draining Langlands Moss peatland, UK; all values are corrected for atmospheric methane contamination except where noted otherwise.

Sample ID	Sampling date	Experiment time (min)	Water volume (L)	Recovered CH_4 volume (ml)	Headspace CH_4 concentration [ml-CH_4 (L-H_2O)$^{-1}$]	$\delta^{13}CH_4$ (±0.2‰)	$^{14}CH_4$ (pmC ± 1σ[a])	$^{14}CH_4$ (yBP ± 1σ[a])
CMV1-R	22/07/2015	260	109	1.16	0.01	−63.0	67.61 ± 0.65	3144 ± 76
CMV2-R	22/07/2015	260	130	1.03	0.01	−65.6[b]	68.91 ± 0.58	2992 ± 67
CMV3-R	22/07/2015	260	118	1.36	0.01	−63.1	67.72 ± 0.64	3131 ± 76
CMV4-R	22/07/2015	260	113	1.31	0.01	−63.3	n.d.	n.d.
AWC-R	22/07/2015	aggregate	35	1.23	0.04	−62.7	69.64 ± 0.64	2907 ± 74
Garnett et al. (2016a)	22/02/2013	–	5.3	1.45	0.27	−64.2[c]	67.61 ± 0.38	3144 ± 45
	22/02/2013	–	13.2	2.78	0.21	−64.1	67.88 ± 0.35	3112 ± 41
	04/04/2013	–	7.0	1.64	0.23	−64.6	66.60 ± 0.32	3265 ± 38
	04/04/2013	–	8.5	1.94	0.23	−64.4	68.43 ± 0.32	3047 ± 37

n.d. = not determined.
[a] Includes additional uncertainty introduced by the atmospheric correction.
[b] $\delta^{13}C$ determined online with the AMS.
[c] Accuracy is ±0.2‰ (Garnett et al., 2016a).

Table 3
Application of the CMV method in natural and artificial pools, and a stream transect at peatland sites in the UK.

Sample ID	Location	Sampling date	Initial pump rate (L min^{-1})	Recovered CH_4 volume (ml)	$\delta^{13}CH_4$ (±0.2‰)	$^{14}CH_4$ (pmC ± $1\sigma^{a}$)	$^{14}CH_4$ (yBP ± $1\sigma^{a}$)
CMV1-LL	Loch Leir – natural pool	05/11/2014	n.d.	0.78	−66.9	104.75 ± 0.62	modern
Replicates							
CMV1-N	LM – natural pool	30/07/2015	0.38	0.78	−64.4[c]	66.48 ± 0.58	3279 ± 70
CMV2-N	LM – natural pool	30/07/2015	0.41	1.21	−63.7	66.62 ± 0.64	3262 ± 77
CMV3-N	LM – natural pool	30/07/2015	0.44	1.80	−64.1[b]	66.47 ± 0.31[b]	3281 ± 37[b]
CMV4-N	LM – natural pool	30/07/2015	0.48	1.26	−63.8	66.19 ± 0.63	3315 ± 76
Replicates							
CMV1-A	LM – blocked drain	29/07/2015	0.57	0.53	−60.6[b]	94.54 ± 0.22[b]	450 ± 20[b]
CMV2-A	LM – blocked drain	29/07/2015	0.52	0.44	−58.6[c]	94.13 ± 0.59	486 ± 50
CMV3-A	LM – blocked drain	29/07/2015	0.53	0.54	−61.4[c]	95.03 ± 0.60	410 ± 50
CMV4-A	LM – blocked drain	29/07/2015	0.54	0.55	−58.5[c]	94.64 ± 0.59	443 ± 50
Transect							
CMV1-T	LM stream – upstream	23/07/2015	n.d.	0.69	−54.6[c]	76.30 ± 0.58	2173 ± 61
CMV3-T	LM stream – middle	23/07/2015	n.d.	3.20	−63.2	68.05 ± 0.63	3092 ± 75
CMV4-T	LM stream – downstream	23/07/2015	n.d.	3.12	−61.4	70.14 ± 0.65	2849 ± 74

n.d. = not determined.
LM = Langlands Moss.
[a] Includes additional uncertainty introduced by the atmospheric correction.
[b] N_2 headspace used – no atmospheric correction required ($\delta^{13}C$ accuracy is ±0.1‰).
[c] $\delta^{13}C$ determined online with the AMS.

peatland, possibly via peatland pipes that provide a potential pathway along which aged gaseous C can be transported rapidly to the surface from depth (e.g. Billett et al., 2012). This C loss is not observed at the surface of the peatland (Garnett et al., 2012), only in the aquatic-export phase, which is possibly due to oxidation of deeper CH_4 in the soil profile during vertical transport or the dominance of shallower layers for the source of surface CH_4 emissions. The CH_4 in the artificial pool, however, more closely matched the isotopic signature of that released from the surface of the peatland (~200–1400 y B.P.; Garnett et al., 2012), suggesting that the CH_4 in this artificial pool created by the drain blocking process is not dramatically altering the age of the CH_4 lost to the atmosphere. This is an important finding for peatland management where drain blockage is common in peatland restoration globally (Cooper et al., 2014; Parry et al., 2014).

At a natural pool (Loch Leir) in the Flow Country peatlands of northern Scotland, dissolved CH_4 was found to be modern (104.75 ± 0.62 pmC), with a lighter $\delta^{13}CH_4$ (−66.9‰) than observed at Langlands Moss (Table 3). This suggests that the age and source of dissolved aquatic CH_4 can vary substantially from site to site, and further research in a range of areas where natural and artificial pools occur is needed to confirm these observations.

A transect was set up along a short reach of the stream draining Langlands Moss peatland to assess the ability of the method to detect small-scale changes in CH_4 sources along a stream or river section, or at a confluence. A CMV sample was collected at the same point as the replicates in the stream for the field degassing test (the middle transect point; Table 3), whilst two other samples were collected upstream on a tributary, and downstream of the middle transect point. The middle and downstream samples were similar in both ^{14}C- and $\delta^{13}CH_4$ content, whilst the upstream site was significantly different (Table 3). The upstream sample was 600–900 years younger than the downstream and middle samples (2849 and 3092 y B.P., respectively; Table 3), and the $\delta^{13}CH_4$ was also much heavier in the upstream sample (−54.6‰, compared to −62.4 and −63.2‰); the latter value being exacerbated by being analysed online with the AMS, so it is not known how different this was from the other transect samples in absolute terms. This highlights that ideally enough sample should be collected to allow for both IRMS and AMS isotopic analysis where the AMS is not tuned for $\delta^{13}CH_4$. At the NERC Radiocarbon Facility, in order to split the sample for both analyses, this requires at least 1.0 ml CH_4, equivalent to 125 ppm CH_4 in an 8 L headspace; $^{14}CH_4$ analysis is still possible at much lower concentrations with this method, however (Fig. 3).

A mass balance (equation (3)) between the upstream and middle point in the transect estimated that the $^{14}CH_4$ content of the stream CH_4 sourced directly from the Langlands Moss peatland was 3561 ± 107 y B.P (Table 4). This is based on stream CH_4 concentrations of 0.029 and 0.091 ml-CH_4 (L-H_2O)$^{-1}$ at the upstream and middle points, respectively (relative CH_4 concentrations were measured by shaking ~500 ml water with a 1:1 headspace-water ratio in a bottle for 1 min, and measuring the headspace concentrations using the DP-IR). The age of the CH_4 derived from the mass balance calculation overlaps at 2σ uncertainty with the values from the natural pool at the peatland outlet (3262 ± 77 to 3315 ± 76; Table 3), indicating that the CH_4 in the Langlands Moss stream is mostly sourced directly from the peatland, as would be expected. Although not surprising, this result demonstrates the ability of such transects, using the new CMV method, to detect the isotopic signature of CH_4 from point sources (this can also be repeated for $\delta^{13}C$, but was not carried out here due to the upstream sample $\delta^{13}CH_4$ value being measured online on the AMS).

The ancient (>1000 years) CH_4 observed at the Langlands Moss stream site is likely directly sourced from methanogenesis utilising the deep peat substrate in the peatland itself. This may vary depending on the time of year due to variations in precipitation and water table height influencing the source zone of water contributions from the peatland. Variability in dissolved CH_4 contributions to the stream could also be driven by hydrodynamic transport, whereby temperature gradients (primarily at night time) drive thermal convection, causing relatively rapid upwelling of CH_4 from deeper layers by both diffusion and advection (Poindexter et al., 2016). This process varies on a seasonal basis, lending weight to the possibility that the age and source of CH_4 would vary seasonally at the study site if hydrodynamic diffusion is a significant process. Garnett et al. (2011) measured evasion CH_4 from the same stream, observing CH_4 ages which ranged from 1500 to 2000 y B.P. These are substantially younger than the values presented in this study and those of Garnett et al. (2016a; Table 2); however, all of these studies were collected at different times of the year. The results of our new study support those of Garnett et al. (2016a), but this does not rule out the possibility that dissolved and evaded CH_4 may be of different age – a comparison of concurrent measurements of evaded and dissolved $^{14}CH_4$ at the same site(s) are required to test this.

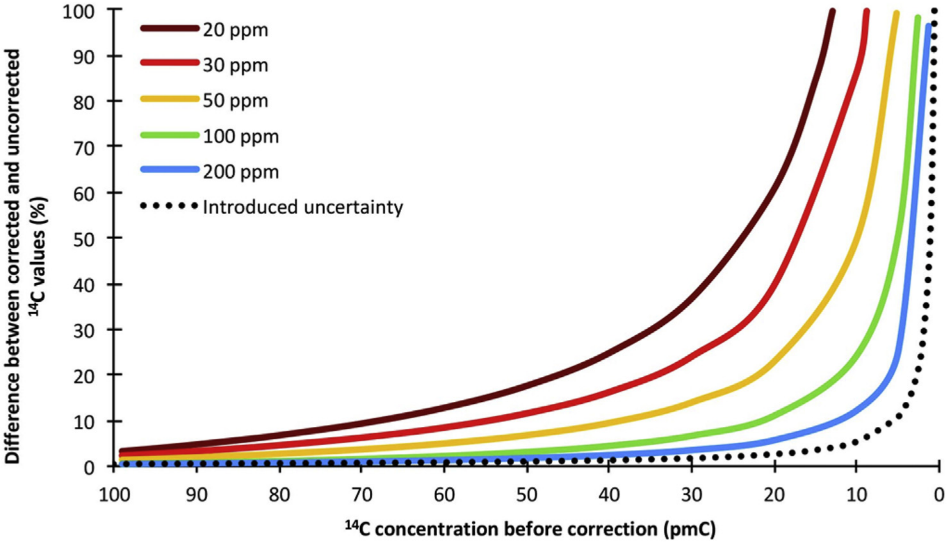

Fig. 3. The shift in ^{14}C age introduced to CH_4 samples collected using the CMV method, based on CMV headspace CH_4 concentrations and the atmospheric contamination introduced when using an ambient headspace; also included is the additional uncertainty introduced by the atmospheric correction itself.

Table 4
Transect mass balance inputs and results.

Transect location	Isotopic content (pmC ± 1σ[a])	CH_4 concentration [ml-CH_4 (L-H_2O)$^{-1}$]
Upstream (CMV1-T)	76.30 ± 0.58[b]	0.029
Middle (CMV3-T)	68.05 ± 0.63[b]	0.091
Input from stream directly draining Langlands Moss peatland	64.19 ± 0.86 (3561 ± 107 y B.P.)	–

[a] Includes additional uncertainty introduced by the atmospheric correction.
[b] From Table 3.

3.4. Method limitations and future application

This method is specifically designed to be able to collect dissolved $^{14}CH_4$ samples from inland waters where CH_4 concentrations are low. However, this can mean that only low concentrations will build up in the CMV headspace. For low CH_4 concentration samples using an ambient headspace in a CMV, we calculated the age shift introduced by atmospheric contamination using eq. (1) (Fig. 3). For more ^{14}C enriched samples (>70 pmC), correction for atmospheric contamination shifts the age by less than 10%, with the greatest shift seen in the lowest headspace concentrations due to the higher fraction of atmospheric CH_4 present. In a headspace with only 20 ppm CH_4, the age shift introduced by atmospheric contamination increases dramatically when the age of the sample is below 70 pmC; for sample headspaces of 30 ppm CH_4 and above, this increase in age shift isn't seen until the sample ^{14}C content is closer to 40 pmC. Natural CH_4 ages in inland water systems have not generally been observed older than ~3000 y B.P. (~70 pmC; e.g. Bouchard et al., 2015), although some notable exceptions exist (e.g. Walter Anthony et al., 2016), suggesting that headspace concentrations of 20 ppm using an ambient headspace should not introduce too much of an age shift. However, in samples where significantly more depleted $^{14}CH_4$ signature may be expected it is better to only analyse samples with headspace concentrations above 100 ppm; this headspace concentration should be achievable with even low CH_4 concentration waters, as seen in the blocked drain pool samples in this study (Table 3). The error introduced by the atmospheric correction increases dramatically when dealing with very depleted $^{14}CH_4$ samples (Fig. 3), so in these cases it would be best to use a headspace containing no atmospheric CH_4 (e.g. pure N_2), as demonstrated in this study.

During the field trials presented here, the CMV headspace was measured using a DP-IR CH_4 analyser in the field to determine whether the CH_4 concentration build-up was high enough to provide sufficient CH_4 for ^{14}C analysis. A comparison between atmospheric correction based on the DP-IR values and those based on the CH_4 recovered in the lab (assuming an 8 L headspace was used at all times), shows less than 1% difference in the field samples in this study (Supplementary Table S3). A DP-IR, or similar portable CH_4 measuring instrument, represents considerable financial investment, and it is possible to collect samples without these measurements in the field, basing the atmospheric correction on the recovered CH_4 values.

In order to ensure enough sample was collected for ^{14}C analysis in waters with very low CH_4 concentrations using this method, two or three CMVs could be connected in series, such as in the lab trial (see section 2.2), allowing more CH_4 to be collected without affecting the isotopic values of the sample. For samples with significantly higher CH_4 concentrations, it may be simpler to use the more rapid AWC degassing method, although atmospheric correction is still required if an ambient headspace is used with this method (see section 2.3; Garnett et al., 2016a). The CMV method is designed to collect sufficient CH_4 for ^{14}C analysis when CH_4 is only present at low concentrations in freshwaters. There is no clear cutoff as to when it should be employed over the AWC method. The AWC can be a rapid collection method if the CH_4 concentrations are high (i.e. > 0.2 ml CH_4 [L-H_2O]$^{-1}$, or *c.* 1000 ppm CH_4 in a 1 L headspace; see Garnett et al., 2016a). However, the lower the concentration, the more headspaces will need to be collected using the AWC method, and thus more time spent on site. Further, based on the analysis in Supplementary Table S3 (see previous paragraph), knowledge of the headspace CH_4 concentration on site is not necessary for the CMV method. Both aquatic CH_4 concentrations and field practicalities should be considered when choosing between these methods.

The transect study (Table 3) presented here demonstrates the utility of this new CH_4 equilibration method for point source pollution studies, particularly the use of mass balances for detecting the isotopic content of point source CH_4 (Table 4). For example, the failure of coal seam gas infrastructure has the potential to release large quantities of thermogenic CH_4 from coal beds into aquifers and surface waters. This CH_4 will have a unique isotopic C signature, and where the determination of ^{13}C may be insufficient to identify a methanogenic origin, ^{14}C can clearly indicate the presence of coal seam derived CH_4, which will be radiocarbon-dead (pmC ≈ 0; Table 1). This method can be deployed at field sites relatively rapidly (within 5 min per site), and could provide multiple measurements along a reach to identify point sources or areas of unique isotopic CH_4 contributions along a fluvial system.

Where mixed ^{14}C- and $\delta^{13}CH_4$ signals may be present, potentially masking thermogenic and biogenic CH_4 isotope signals, isotopic end-member (e.g. Vihermaa et al., 2014) and/or age distribution analysis (e.g. Evans et al., 2014) can be used to partition the sources in a mixed signal. Where very fine differences in ^{14}C at very low pmC enrichments are needed to distinguish between CH_4 sources (e.g. Pohlman et al., 2009), we recommend the use of other source indicators alongside ^{14}C- and $\delta^{13}CH_4$, and the use of a CH_4-free headspace.

The CMV method has significant potential for deployment in a range of wetland and peatland systems, from tropical to polar regions, as it is a simple, robust design and can be readily deployed in remote areas. This is particularly important as these are the types of organic-rich landscapes where climate feedbacks from GHGs produced from recently liberated ancient organic matter are of greatest concern (Evans et al., 2014; Vonk et al., 2015). Furthermore, Butman et al. (2015), argue for "… additional research that begins to quantify the proportion of aged carbon 'leaking' from the landscape and identify where along river reaches this carbon is potentially processed to better constrain its impact on the carbon cycle and river biogeochemistry." The simple and cost-effective method presented here provides a real opportunity to explore these issues with regards to the age and source of CH_4 in fluvial systems draining vulnerable and disturbed catchments.

4. Conclusions

In this study we present a new field method which extracts sufficient dissolved aquatic CH_4 for ^{14}C analysis from inland waters, where naturally low CH_4 concentrations precluded the use of existing methods. We tested the method in both laboratory and field conditions showing that:

- the method provides reliable and reproducible $^{14}CH_4$ and $\delta^{13}CH_4$ measurements in a range of conditions, both at low and high aquatic CH_4 concentrations;
- the method provides a cost-effective and simple technique for investigating the source of localised CH_4 contributions to surface waters, and may be particularly useful in detecting ancient C leakage from disturbed landscapes as well as CH_4 pollution sources such as coal seam gas and landfill gas;
- the CH_4 exported in the stream draining Langlands Moss peatland in SW Scotland was 2900–3100 y B.P in age and much older than CH_4 released at the peat surface, supporting previous findings, but also suggesting that fluvial $^{14}CH_4$ may be seasonally dynamic;
- the observed aquatic CH_4 age in an artificial pool at Langlands Moss peatland was much younger than in a natural pool, suggesting that artificial pools formed by drain blocking may not alter the CH_4 age and source dynamics of peatlands, though further investigation is clearly needed.

Whereas previous methods can require a lengthy sampling period at a single site to collect a sample with sufficient CH_4 for radiocarbon analysis, this new method allows the collection of multiple samples that can be initiated in a relatively short space of time, and then readily collected less than 24 h later with no user input required during sampling. We suggest that this method will be particularly useful for observing the aquatic leakage of ancient C from organic-rich landscapes disturbed by anthropogenic activity and climate change, in ecosystems ranging from the tropics to the polar regions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.03.009.

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