A TIME-INTEGRATED SAMPLER FOR RADIOCARBON ANALYSIS OF AQUATIC METHANE

M H Garnett[1]*⦿ • J F Dean[2]

[1]Scottish Universities Environmental Research Centre, NEIF Radiocarbon Laboratory, Rankine Avenue, East Kilbride, G75 0QF, UK
[2]University of Bristol, School of Geographical Sciences, Bristol, UK

ABSTRACT. Freshwater ecosystems are responsible for a large proportion of global methane emissions to the atmosphere. The radiocarbon (^{14}C) content of this aquatic methane is useful for determining the age and source of this important greenhouse gas. Several methods already exist for the collection of aquatic methane for radiocarbon analysis, but they tend to only sample over short periods of time, which can make them unsuitable for characterizing aquatic methane over longer timespans, and vulnerable to missing short-term events. Here, we describe a new time-integrated method for the collection of aquatic methane that provides samples suitable for radiocarbon analysis, that are representative for periods of up to at least 16 days. We report the results of a suite of tests undertaken to verify the reliability of the method, and the ^{14}C age of aquatic methane from field trials undertaken at sites within Scotland, UK. We believe that this new method provides researchers with a simple approach that is easily deployable and can be used to collect representative time-integrated samples of methane for radiocarbon analysis from a wide range of aquatic environments.

KEYWORDS: aquatic, carbon, freshwater, methane, radiocarbon.

INTRODUCTION

Methane (CH_4) is a powerful greenhouse gas and its concentration in the atmosphere is increasing (Rosentreter et al. 2021). It is released to the atmosphere from many different sources, some natural (e.g. via anaerobic decomposition of organic matter) and some a consequence of anthropogenic activities (e.g. exploitation of fossil fuel reserves; Skeie et al. 2023). Freshwater ecosystems, such as rivers, lakes and streams are responsible for almost half of global CH_4 emissions to the atmosphere (Rosentreter et al. 2021; Rocher-Ros et al. 2023). Thus, predicting future atmospheric CH_4 concentration requires an understanding of the role of aquatic environments in the production and transport of CH_4, especially given the sensitivity of its production to climatic warming (e.g. Jansen et al. 2022).

The radiocarbon (^{14}C) concentration of CH_4 can provide unique information on its age and source (Garnett et al. 2019). For example, CH_4 from geological stores is considerably depleted in ^{14}C because of its great age (all of the ^{14}C having been radioactively decayed; Zazzeri et al. 2023). In contrast, CH_4 from the anaerobic decomposition of fresh organic matter is relatively ^{14}C-enriched and has a similar ^{14}C content to contemporary atmospheric CO_2 (Wahlen et al. 1989). Both of these CH_4 sources contrast considerably in ^{14}C content compared to contemporary atmospheric CH_4 which, due to radio-CH_4 emissions from nuclear power plants, is even more ^{14}C-enriched (Graven et al. 2019). The differences in the ^{14}C content of these CH_4 sources can be used to partition their contributions to the atmosphere, thus enabling a greater understanding of CH_4 dynamics (Zazzeri et al. 2023).

In freshwater environments, a focus has been on the use of CH_4 radiocarbon measurements to investigate carbon cycling in peatlands, and ecosystems in the high northern latitudes, particularly to investigate whether climatic warming is leading to increased aquatic CH_4

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*Corresponding author. Email: MARK.GARNETT@GLASGOW.AC.UK

emissions of ancient carbon (e.g. Zimov et al. 1997; Walter Anthony et al. 2016). In these environments, CH_4 occurs as both ebullitive (bubble) emissions and as dissolved gas in the water which is subsequently evaded to the atmosphere (Rocher-Ros et al. 2023). Most $^{14}CH_4$ studies have considered only ebullitive emissions of CH_4, as shown in a review by Estop-Aragonés et al. (2020) who found that of 9 studies investigating aquatic $^{14}CH_4$ in the northern permafrost region, only 2 had considered dissolved $^{14}CH_4$. This may be due to the relative ease of collecting ebullitive emissions, the bubbles of which can often be visually located and have high CH_4 concentration. Given studies have found that in many environments dissolved CH_4 emissions can exceed ebullitive emissions (e.g. DelSontro et al. 2016), there is a pressing need for more studies to consider the ^{14}C dating of dissolved CH_4 emissions.

Dissolved CH_4 ^{14}C studies typically rely on the collection of water samples from which the CH_4 is subsequently extracted for analysis (e.g. Garnett et al. 2016; Elder et al. 2018). Usually, these water samples are collected over a short period of time, often referred to as "grab" sampling (Turnbull et al. 2017), which can usually only be considered to be representative for the period of sample collection. This is a concern because other studies have shown high temporal variability in aquatic CH_4 concentration (Podgrajsek et al. 2014; Sieczko et al. 2020; Stanley et al. 2023) and because we have very little information on the temporal variability of ^{14}C in aquatic CH_4. Moreover, the propensity to undertake sample collection during convenient, daylight hours, can lead to significant bias, as illustrated by Sieczko et al. (2020) who found that aquatic CH_4 emissions were 2.4 times greater during the day compared to night. Without due care, sampling methods for the collection of CH_4 for radiocarbon analysis that rely on a single collection event could lead to similar misrepresentation.

The relatively high expense for the collection and analysis of radiocarbon samples has meant that it is usually not possible to overcome the potential bias of grab samples simply by increasing the frequency of sample collection and analysis. However, by collecting "time-integrated" samples, researchers can overcome the bias of grab samples, without increasing resource requirements. For example, Levin et al. (2008) have been collecting time-integrated samples of atmospheric carbon dioxide (CO_2) for decades in their long-term atmospheric $^{14}CO_2$ monitoring program. Passive samplers, using cartridges of CO_2-adsorbing zeolite molecular sieve, that simply rely on diffusion, have been developed for collection of ^{14}C time-integrated samples of CO_2 from the atmosphere and soil respiration (Garnett et al. 2009; Garnett and Hartley 2010; Walker et al. 2015; Pedron et al. 2021), and have also been adapted for collection of aquatic CO_2 (Garnett et al. 2012). Indeed, plant material can also be used as passive $^{14}CO_2$ samplers, however, the requirements of photosynthetic fixation mean that it can potentially bias towards daylight hours (Turnbull et al. 2017). The lack of a need for infrastructure mean that these passive samplers are easily deployed and, therefore, are particularly suitable for CO_2 sample collection in remote locations. Unfortunately, to our knowledge, a CH_4-adsorbent with the necessary trapping properties at ambient temperatures is not available, which has prohibited the development of an equivalent time-integrated passive CH_4 sampler for radiocarbon analysis.

An alternative to the passive sampling time-integrated approach is to use devices that actively accumulate sample material from repeated collections over the period of time of interest. Here, we describe such a system for the collection of time-integrated samples of dissolved aquatic CH_4 for subsequent analysis of ^{14}C content. Separation of the CH_4 from water is achieved using a gas-permeable hydrophobic filter, and aliquots of the isolated sample gas are collected using a simple programmable microcontroller-driven pump unit attached to a foil gas bag. We
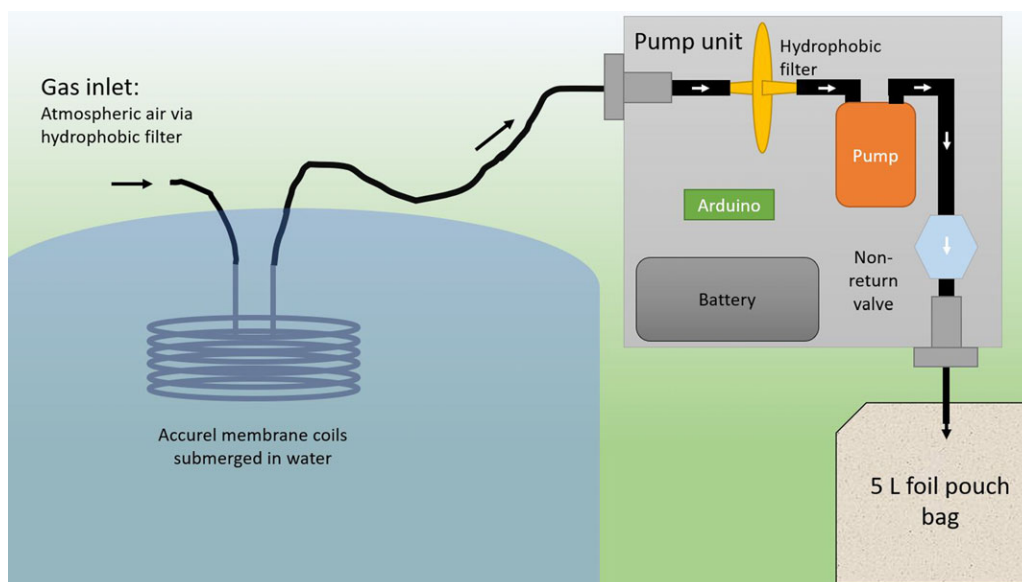
Figure 1   Schematic diagram of the time integrated aquatic methane sampler.

present the results of tests used to verify the collection and storage of radiocarbon CH_4 samples in the foil bags and to optimize the collection of CH_4 samples. We also present the first results from field trialling of the method.

METHODS

Description of the Time-Integrated Aquatic Methane Sampler

The CH_4 sampler consists of three main components (Figure 1 and Supplementary). First, a hydrophobic, gas-permeable membrane which acts as an equilibration volume into which aquatic gases diffuse from the water body under investigation. Second, a battery-powered air-pump used to transfer gases from the hydrophobic membrane into the third component, a foil pouch gas storage bag. Collection of time-integrated samples, over several days or weeks, is achieved using a programmable microcontroller to briefly switch on the pump and transfer a small volume of gas from the equilibration coils to the bag, repeatedly, at designated time intervals.

We used 6 m of a polypropylene hydrophobic tube membrane (i/d 4 mm, o/d 6 mm, Accurel PP V8/2 HF, Membrana GmbH, Germany) as the equilibration volume. The tubing was mounted in coils (ca. 40 cm diameter) on a cross-shaped steel frame with plastic supports which held and separated the coils of the tubing about 1–10 cm above the steel frame. Rigid nylon tubing (6 mm o/d general pneumatic hose) was connected to either end of the hydrophobic membrane and sealed in place using a rubber paint (Plasti-dip, USA). The nylon tubing at one end (the air inlet) was 2 m in length and open to atmosphere via a hydrophobic syringe filter (0.2 μm PTFE-Membrane, Fisher Scientific, UK) to prevent entry of liquid water and particulates. The other length of nylon tubing (outlet or pump end) was also 2 m long and was connected to the pump unit.

The pump unit, housed in a water-tight 1 L storage box, contained a second hydrophobic filter (to further guard against particulates and liquid water) and a small air-pump (TCS Micropumps, UK) powered by 6 C-type rechargeable batteries (Amazon Basics, Amazon UK) via an Arduino Nano microcontroller (www.arduino.cc). The pump transferred gases from the hydrophobic tubing into a foil bag, via a non-return (check) valve (TCS Micropumps, UK) which prevented back-flow of sample gas from the storage bag. Flexible tubing (Isoversinic, Saint Gobain, France and C-Flex, Cole Palmer, UK) was used to connect the different components of the pump unit, and Quick couplings (Colder Products Co., USA) which automatically seal when disconnected were used to connect the pump unit to the pneumatic hose and the foil gas bag. A pouch of activated silica gel was placed inside the box to guard against humidity and condensation.

The gas storage bag has previously been described (Garnett et al. 2023) and consisted of an aluminium foil pouch bag ("5 L Spouted pouch bag"; https://www.pouchshop.co.uk/) plugged with a one-holed rubber bung (Fisher Scientific, UK) containing a 5 cm length of stainless-steel tube (6 mm o/d, Swagelok, USA). A 5 cm length of Isoversinic tubing was attached to the end of the steel tube into which a Quick coupling was inserted, facilitating easy connection to the pump unit. A WeLoc clip (Scandinavia Direct, UK) placed across the Isoversinic tubing provided an additional seal when the bag was not being used for sampling. Prior to use, the foil bags were cleaned by repeatedly (at least three times) filling and emptying with 1–2 L of high purity nitrogen gas (Research Grade, BOC, UK) over several days.

During deployment, the hydrophobic coils of the equilibration volume were continuously submerged in the water body under investigation, with the steel frame supporting the coils resting on the pond or stream bed. As the pump unit transferred the equilibrated air from inside the hydrophobic coils into the foil bag replacement atmospheric air was drawn in via the hydrophobic filter. Thus, in this configuration we accepted that the CH_4 samples would be contaminated with ca. 2 ppm of atmospheric CH_4, which we discuss later.

We initially programmed the Arduino microcontroller to activate the pump for 1 minute every hour, with the microcontroller going into a low power mode to conserve battery energy when the pump was inactive. After it was established that average pump speed was about 120 mL/minute, pumping time for each cycle was halved to 30 seconds (i.e. ca. 60 mL pumped volume) to avoid the pumped volume exceeding that of the hydrophobic coils (75 mL). Thus the standard procedure is for the pump to operate for a fixed 30 seconds, while the time between pump events (equilibration time) can be varied depending on the length of the overall sample collection period to ensure recovery of a 5 L sample. Given each 30 second pump event transfers ca. 60 mL of gas, the 5 L storage bag can accept gas from approximately 80–90 pump events. Thus, programming the microcontroller to operate the pump every 0.5, 1, 2, or 4 hours can be used for time-integrated sample collection over approximately 2, 4, 8, and 16 days respectively.

Testing the Reliability of the Pump Unit

We deployed the sampler at a garden pond to test whether the pump unit reliably collected time-integrated samples. We chose to use a garden pond for these tests partly out of convenience since frequent attendance to take measurements was required. However, apart from site access, we consider these test conditions to be not dissimilar to the target field sampling locations of the method (i.e. any inland water body, including rivers, streams, and ponds).

The time integrated sampler was assessed with the microcontroller set to collect samples with an overall sampling period of 2, 4, 8 and 16 days (i.e. the total time to collect a gas volume of 5 L), testing each configuration in duplicate. These tests were used to verify that the sampling equipment performed as intended in real-world conditions, with a particular focus on battery longevity and potential problems associated with sampling in humid conditions. Moreover, we considered that representative time-integrated sample collection could only be achieved if we observed a constant linear increase in the volume of collected sample gas over time. Thus, for each of the sampling tests we measured the progressive increase in the volume of gas collected in the foil bags on four different occasions throughout the overall sampling period (e.g. daily measurements were performed when the overall sampling period was 4 days). This was done by using a 500 mL syringe (Amazon, UK) to transfer measured aliquots of collected gas from the foil bag into a second bag, which was subsequently replaced on the sampler.

Assessing the Equilibration Time

Our sampler relies on diffusive transfer of CH_4 gas across the hydrophobic membrane for isolating the CH_4 from the surrounding water. We therefore performed an experiment to assess the time for the CH_4 inside the Accurel coils to reach a concentration equilibrium with the surrounding water. We considered such information to be valuable for optimizing the collection of samples from water bodies with low CH_4 concentrations, since ensuring that the sampled gas was fully equilibrated would maximize CH_4 recovery.

The experiments were performed under controlled laboratory conditions using a sealed barrel (30 L Open Top Keg, Ampulla, UK) containing CH_4-rich water because we wished to maintain an approximately constant CH_4 concentration in the water during equilibration tests. The barrel contained four ports on the upper surface which could be sealed to ensure air-tightness. Two of the ports were used to add water to the barrel, and during tests, to connect a water pump (Flojet RLF122202, Flojet, China) to simulate a slow movement of water that would be expected in a natural water body. The other two ports were connected to each other via a 6 m length of the same hydrophobic tubing as used in the field tests of the time-integrated sampler, which was submerged in the barrel water.

Methane-rich water was produced by mixing tap water and CH_4 gas in a sealed 5 L foil pouch bag, leaving the bag overnight to allow for CH_4 invasion into the water. A proportion of this CH_4-rich water was transferred to the 30 L barrel which had been prefilled with tap water; we did not measure the amount of CH_4-rich water added, but simply added as much as necessary to achieve the desired CH_4 concentrations in the barrel water. We ensured that the barrel did not contain a significant headspace by allowing the water to overflow when filling, and prior to the equilibration tests the water pump was used to ensure that the added CH_4-rich water had thoroughly mixed inside the barrel.

To perform an equilibration measurement we first flushed the hydrophobic coils inside the barrel with lab air using the air pump of an EGM5 infrared gas analyser (PPsystems, USA; flushed for 2 minutes with a flow rate of 470 mL/minute). The air pump was then removed, and the gas ports of the hydrophobic membrane sealed for a set amount of time (the "equilibration" time). Immediately after the equilibration time had been reached, 150 mL of gas was removed from the hydrophobic coils with a gas-tight syringe and injected into an empty 500 mL foil gas bag sealed with a Quick connect coupling (Colder Products Co., USA). The bag was immediately connected to a DetectoPak Infrared (DP-IR) CH_4 analyser (Heath Consultants

Inc, USA) to measure the CH_4 concentration of the gas. We note that the volume of gas extracted was greater than the internal volume of the hydrophobic coils and therefore would be diluted with lab air, however, this volume of gas was necessary for the DP-IR measurement and would not affect the interpretation of the results because all samples were treated alike. We performed the above tests for 7 different equilibration times from 0 to 240 minutes, on waters of 3 different CH_4 concentrations.

Tests on Foil Pouch Bags for Storage of Methane Samples

Our time-integrated CH_4 sampling method is designed for collection of samples for up to at least 2 weeks, and therefore, it is necessary to determine whether the foil bags we use are reliable for storage over at least this period. To do this, we performed three tests. First, we set up 10 identical foil pouch bags containing ca. 1 L of high purity oxygen (Research grade, BOC, UK), 1 L high purity nitrogen gas (Research grade, BOC, UK) and 2 mL of a ^{14}C-dead laboratory background CH_4 standard (BOC, UK). One bag was processed immediately (T0) and recovered as CO_2 in a sealed glass tube using the methods described below. Subsequently, sets of 3 bags were processed after 2, 7, and 35 days of storage using the same processing methods. We considered that the bags would demonstrate reliability if there was no significant increase in methane ^{14}C content (from contamination with atmospheric CH_4; 130 percent Modern carbon (pMC); Lassey et al. 2007; Zazzeri et al. 2023) or reduction in CH_4 volume (reflecting leakage) over time.

Secondly, we performed repeat measurements of the CH_4 concentration in three foil pouch bags that contained different levels of CH_4. The samples were all collected using the time-integrated sampler from a garden pond, and thus were representative of field-collected samples. Methane measurements were performed using a DP-IR (Heath Consultants Inc, USA) on multiple occasions up to a maximum storage time of 50 days, and we considered that reliability of the storage bags would be supported if there was no significant change in CH_4 concentration over this time.

Third, we analysed the radiocarbon concentration in CH_4 of a sample collected using the time-integrated sampler from a garden pond immediately after collection, and again after 35 days storage in the foil bag, considering that reliability of the foil bag would be demonstrated if there was no significant difference in ^{14}C content between the two measurements.

Field Trials of the Time-Integrated Methane Sampler

We deployed the time-integrated sampler in field trials to recover samples for ^{14}C analysis of the collected CH_4. One sample was collected on 21–24 October 2022 from the aforementioned garden pond in central south-west Scotland, and subsequently divided into two and used for the storage test described above. Two other samples were collected from streams draining blanket peatland in northern and north-western Scotland and analysed within 3 weeks of the collection date. The peatland streams were in the Flow country (Lat: 58.521338°, Long: –4.007995°) where the sampler was deployed between 8–11 September 2022, and the Isle of Lewis (Lat: 58.219915°, Long: –6.550161°) where a sample was collected from 13–17 September 2022. All samples were collected using atmospheric air as the headspace gas into which the aquatic CH_4 evaded, and therefore required correcting for the presence of atmospheric CH_4. We used values of 1.9 ppm concentration and 130 pMC ^{14}C content (Lassey et al. 2007; Zazzeri et al. 2023) for atmospheric CH_4, and corrected the results using:

$$^{14}C_{sample} = (^{14}C_{meas} \times Vol_{meas} - ^{14}C_{atmosCH4} \times Vol_{atmosCH4})/(Vol_{meas} - Vol_{atmosCH4}) \qquad (1)$$

Where ^{14}C represents radiocarbon concentration (in pMC), and Vol the volume of CH_4, in the measured sample ($_{meas}$) and atmospheric CH_4 component ($_{atmosCH4}$) of the sample, the latter calculated using:

$$Vol_{atmosCH4} = (1.9/1 \times 10^6) \times Vol_{tot} \qquad (2)$$

Where Vol_{tot} represents the volume of atmospheric air collected in a single foil bag sample.

Processing of Methane Samples for ^{14}C Measurement

All CH_4 samples were processed using the method described by Garnett et al. (2019) which involves passing the sample gas through traps containing soda lime and a zeolite molecular sieve to remove impurities (e.g. carbon dioxide), followed by combustion of the CH_4 to CO_2 using a catalyst (platinum-alumina beads, Johnson Mathey Chemicals, UK) at 950ºC. Subsequently the CH_4-derived CO_2 was dried by passing through a slush trap (–78ºC; mix of dry-ice and methylated spirits) and recovered as pure CO_2 using liquid nitrogen-cooled traps (–196ºC) and high vacuum. The volume of the recovered CO_2 was measured using a pressure transducer in a calibrated volume and the sample split into aliquots. One aliquot was measured for $\delta^{13}C$ using isotope ratio mass spectrometry on a Delta V (Thermos-Fisher, Germany). A second aliquot was converted to graphite using Fe:Zn reduction (Slota et al. 1987) and analysed for ^{14}C using accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre AMS Facility and Keck Carbon Cycle AMS Laboratory, University of California. Following convention (Stuiver and Polach 1977), radiocarbon results were normalized to a delta ^{13}C of –25‰ and expressed as pMC.

Statistical Tests

Minitab 19 was used to perform Analysis of variance with Tukey *post-hoc* tests. Correlation coefficients were determined using Microsoft Excel.

RESULTS

Assessing the Reliability of the Pump Unit

We observed very constant accumulation of gas in the foil bags when deployed at a garden pond (Figure 2), with correlation coefficients >0.999 for all 4 of the sampling protocols which ranged from 2 to 16 days total sample collection time. Linear accumulation rate was maintained despite some of the sample collections substantially exceeding the nominal 5 L capacity of the pouch bag, with total volumes of up to 5.8 L.

Assessing the Equilibration Time

As expected, the CH_4 concentration of the air inside the hydrophobic coils was greater when left to equilibrate for a longer time (Figure 3). However, the rate of increase in CH_4 concentration was not linear with equilibration time, with only a small increase in CH_4 concentration after 4 hours, compared to 1 hour (an increase that was not significant if the uncertainty on the DP-IR measurements is considered). Thus, after 1 hour equilibration time the CH_4 concentration in the hydrophobic tubing was between 85–95% of the value achieved
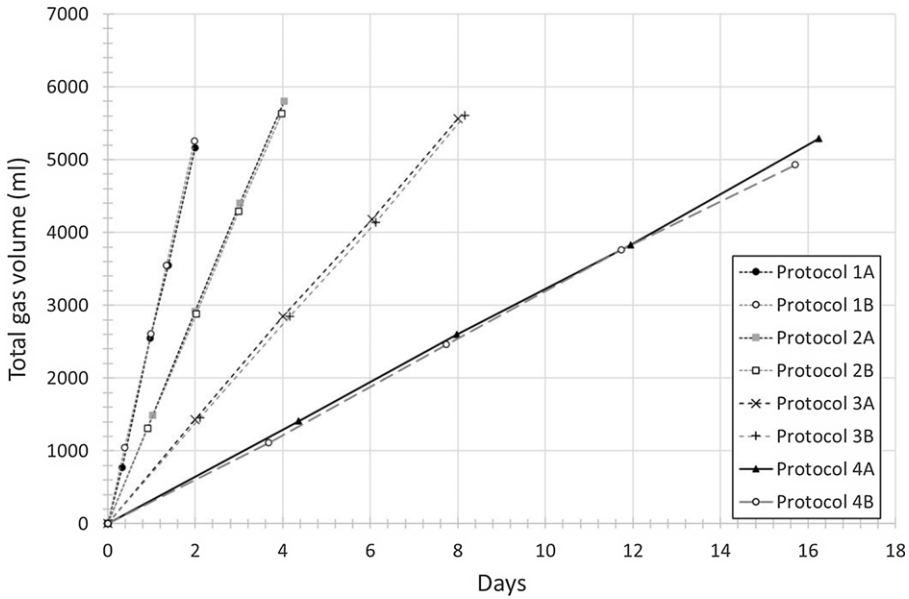
Figure 2   Collection of equilibrated gas samples using the time integrated sampler. Equilibrated air from inside the hydrophobic tubing that was submerged in a pond was pumped into foil storage bags using 4 different sample collection protocols: 1 = gas pumped for 1 minute every hour; 2 = gas pumped for 0.5 minutes every hour; 3 = gas pumped for 0.5 minutes every 2 hours; 4 = gas pumped for 0.5 minutes every 4 hours. Protocols were performed in duplicate (A and B). Dashed lines are presented to aid interpretation of the results.
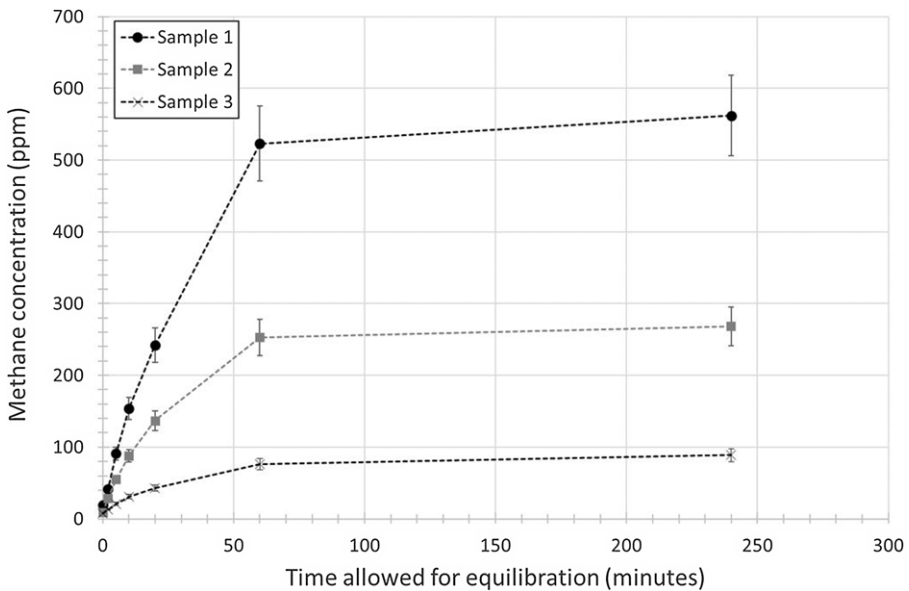

Figure 3   Equilibration of methane gas across the coils of hydrophobic tubing. The graph shows the concentration of CH_4 inside the hydrophobic tubing when sampling three methane-rich waters when allowed to equilibrate for different lengths of time. Dashed lines are presented to aid interpretation of the results.

Table 1 Radiocarbon concentration of ^{14}C-dead CH_4 background standards stored in foil pouch bags for different lengths of time. Each bag was established with ca. 2 L of high purity oxygen and nitrogen plus approximately 2 mL of the background CH_4 standard. After storage, the CH_4 was combusted and cryogenically recovered as purified CO_2 using routine techniques and dated. Error terms represent the instrument uncertainty only, and ^{14}C values have not been background corrected.

Publication code	Storage time (days)	CH_4 volume (mL)	$\delta^{13}C \pm 0.1‰$	pMC $\pm 1\sigma$
SUERC-103988	0	2.85	–42.6	0.20 ± 0.01
SUERC-105012	0	2.38	–40.9	0.23 ± 0.01
SUERC-103982	2	2.13	–47.8	0.12 ± 0.01
SUERC-103983	2	2.09	–43.2	0.11 ± 0.01
SUERC-103984	2	2.12	–42.3	0.15 ± 0.01
SUERC-103985	7	2.14	–42.8	0.13 ± 0.01
SUERC-103986	7	2.15	–42.4	0.13 ± 0.01
SUERC-103987	7	1.94	–45.6	0.12 ± 0.01
SUERC-105004	35	2.09	–42.0	0.18 ± 0.01
SUERC-105005	35	2.06	–41.8	0.25 ± 0.01
SUERC-105006	35	1.89	–42.0	0.21 ± 0.01

after 4 hours, whereas after just 10 minutes equilibration time only approximately 30% of the maximum CH_4 concentration had been achieved.

Storage of Methane Samples for Radiocarbon Analysis in Foil Pouch Bags

Radiocarbon concentration of the background CH_4 standard when stored in foil pouch bags for 2-, 7- and 35-days was 0.13 ± 0.02, 0.13 ± 0.01, and 0.21 ± 0.04 pMC, respectively (Table 1). Analysis of variance with Tukey post-hoc test indicated a significant difference (p = 0.006), with the 35-day storage results being significantly higher in ^{14}C compared to the others. However, all ^{14}C results (including the 35-day values) were easily within 1 σ of the long-term laboratory background for CH_4 samples, and indeed the 35-day storage samples were not significantly different to the 2 laboratory CH_4 process standards processed alongside the samples (0.20 ± 0.01 and 0.23 ± 0.01 pMC). No significant differences were found between storage time and either $\delta^{13}C$ or total sample volume recovered.

We found no significant decline in the CH_4 concentration of pond gas samples stored in foil bags for up to 50 days, which would be indicative of leakage/permeation of CH_4 (Figure 4). Conversely, one sample appeared to increase in CH_4 concentration from ca. 1220 ppm to 1250 ppm after about 40 days ($r^2 = 0.602$, p<0.05). However, the increase in CH_4 concentration was much smaller than the instrument measurement uncertainty (+/–10% of reading), and indeed, for each of the 3 sample bags, all DP-IR CH_4 concentration measurements overlapped at less than 1 σ.

The sample collected using the time-integrated sampler and then split into two gave radiocarbon concentrations that agreed within 1.1 σ, when measured after storage in a foil bag for 0 and 35 days (Table 2). The agreement was the same for the samples before and after correction for atmospheric CH_4, and indeed, the atmospheric correction only changed the results by 0.08 pMC.
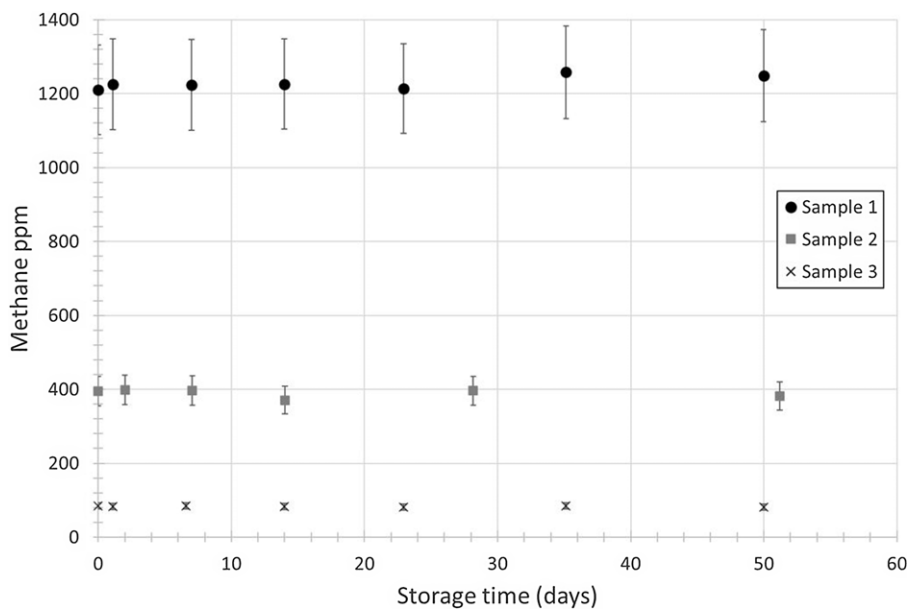
Figure 4   Concentration of methane gas over time for samples stored in foil pouch bags. Three bags were set up with differing CH_4 concentrations in air and measured on multiple occasions over the next ca. 50 days. Error bars represent instrument error.

Field Trials of the Time-Integrated Methane Sampler

Radiocarbon concentration of the two samples of pond CH_4 collected using the time-integrated sampler in 2022 was 99.69 ± 0.46 and 98.72 ± 0.45 pMC (25 ± 37 and 103 ± 37 BP) after correction for atmospheric CH_4 (Table 2). The total volume of CH_4 recovered from the peatland sites was smaller than expected, partly because of the lower concentration of CH_4 in the recovered samples, but also due to incomplete sealing of the non-return valve failing to fully prevent back-flow of sample gas from the bag (an issue that was subsequently fixed by changing to non-return valves from TCS Micropumps, UK). The atmosphere-corrected CH_4 samples from the peatland streams were found to be older than the pond samples, with ^{14}C contents of 96.43 ± 0.43 and 92.50 ± 0.43 pMC (292 ± 36 and 626 ± 37 BP) for the Flow country and Isle of Lewis samples, respectively (Table 2).

DISCUSSION

Radiocarbon measurements of dissolved CH_4 are usually undertaken on samples collected at a single point in time ("grab" samples), which may be desirable when investigating specific events (e.g. freshet or floods) or processes (e.g. paired/multi-site studies). However, such samples may not be appropriate in cases where a measurement that is representative of a longer period of time, or more general processes, is required. A time-integrated method for the collection of aquatic CH_4 samples for ^{14}C measurement should be more representative of the multiple processes/carbon sources that contribute to aquatic CH_4 fluxes, and therefore a potentially more practical and cost-effective approach to characterizing aquatic CH_4 at a given site.

Existing aquatic CH_4 sampling methods often involve collection over just a few minutes (e.g. Garnett et al. 2016), however, there are also methods that accumulate samples over hours,

Table 2 Results for field samples collected using the time integrated aquatic gas sampler. Samples were collected over a period of 4 days using the methods described in the text, during September and October 2022. Upon collection, the Garden Pond sample was divided into two with one fraction (A) being recovered to CO_2 immediately, and the second (B) being processed after 35 days stored in the foil pouch bag. #Radiocarbon results have been corrected for laboratory background and atmospheric CH_4 contamination (see Methods).*Insufficient sample for IRMS $\delta^{13}C$ and ^{14}C results normalized using on-line AMS $\delta^{13}C$ values.

Publication code	Site	Total gas (mL)	CH_4 mL (STP)	CH_4 concentration (ppm)	$\delta^{13}C \pm 0.1‰$	Measured CH_4 pMC $\pm 1\sigma$	Air-corrected# CH_4 pMC $\pm 1\sigma$	CH_4 CRA# (BP $\pm 1\sigma$)
UCIAMS-272918	Flow country	3300	0.13	39	n/a*	98.05 ± 0.43	96.43 ± 0.43	292 ± 36
UCIAMS-272919	Isle of Lewis	2000	0.12	60	n/a*	93.69 ± 0.43	92.50 ± 0.43	626 ± 37
SUERC-105007	Garden Pond A	1675	1.23	734	−33.8	99.77 ± 0.46	99.69 ± 0.46	25 ± 37
SUERC-105008	Garden Pond B	1675	1.30	776	−33.2	98.80 ± 0.45	98.72 ± 0.45	103 ± 37

which could be considered to have some time-integration. For example, the method described by Elder et al. (2018) involves sample collection over up to 1 hour, whereas Dean et al. (2017) describe a method for sample collection that can take many hours. But in at least the case of the latter, it can be questioned how representative of the total sampling period the recovered sample will actually be since it involves a single equilibration stage into a nitrogen-filled gas collection vessel. Thus we could expect bias with proportionally more CH_4 collected at the start of the sampling period when the diffusion gradient is greatest. Although individual equilibration stages using our new method could also be biased in the same way, we substantially reduced this issue in the final integrated sample because this final sample is the product of potentially ∼80–90 individual sample collection events.

The evidence that we present supports the assertion that our new sampling approach should provide a representative time-integrated sample that is reliable for ^{14}C measurement of aquatic CH_4. Firstly, we found a constant linear increase in the volume of collected sample gas over time, indicating that gas samples are recovered at a constant rate over up to at least 16 days (depending on the chosen sampling protocol; Figure 2). Secondly, our tests confirm the reliability of the foil bags for storage of methane ^{14}C samples for many weeks, with for example, analysis of stored ^{14}C-dead CH_4 standards indicating no significant ingress of atmospheric CH_4. Doubtless this is aided by the fact that atmospheric CH_4 occurs at very low concentrations compared to a routine-sized $^{14}CH_4$ sample (atmospheric $CH_4 = 2$ ppm; 1 mL CH_4 sample in 5 L of air = 200 ppm). However, repeated measurements of CH_4 concentration in test bags did not show any change over time that would indicate significant loss from leaks or permeation (Figure 4), and indeed, a pond CH_4 sample split into two and processed 35 days apart gave radiocarbon results that were within measurement uncertainty. More recently, the same bags have been shown to be reliable for storage of $^{14}CO_2$ samples (Garnett et al. 2023).

There are, however, a number of areas where we could foresee potential limitations with this sampling approach, which may require further investigation. Firstly, we did not investigate whether isotopic fractionation occurs across the hydrophobic membrane. Our equilibration tests suggest that concentration equilibration had occurred, or was close to occurring, when the equilibration time was greater than 1 hour (Figure 3), however, over shorter time periods the lower recovered CH_4 concentration implies incomplete equilibration, and therefore, it is possible that some isotopic fractionation of the samples had occurred. Following radiocarbon convention (Stuiver and Polach 1977), all ^{14}C results were normalized to a $\delta^{13}C$ of –25‰, and therefore are corrected for this fractionation. We note that $\delta^{13}C$ measurements on CH_4 can also be very enlightening, for example, to identify methanogenic pathways (Whiticar et al. 1986) and so further tests to establish the amount of isotopic fractionation that occurs, if any, are required. It should be noted that other types of gas-permeable hydrophobic tubing are available (e.g. expanded polytetrafluoroethylene; ePTFE), in different densities and dimensions, and therefore there might be opportunities to improve the equilibration of samples using alternative products.

We observed discoloration of the Accurel hydrophobic tubing over time. We attribute this to either bio-fouling or staining from dissolved organic carbon and/or small organic particles. While we have no evidence that indicates that this affected the gas permeability of the hydrophobic tubing, and indeed, can confirm that even when heavily stained we recovered high CH_4 concentrations in samples, replacement of heavily stained tubing might be advisable until this issue has been investigated. That said, we encountered no physical damage to the hydrophobic tubing from over several months of testing, although clearly in some aquatic

environments there may be a need to protect the hydrophobic tubing. On a couple of occasions we also observed that after many weeks of continuous use a small amount of water had condensed inside the sample tubing and on the hydrophobic filter of the pump unit potentially causing a blockage. Thus it is recommended to routinely check for the buildup of water inside the sampling tubing and to remove it if necessary, and to consider including a moisture trap before the hydrophobic filter.

Finally, during sample collection we chose to equilibrate the aquatic CH_4 into atmospheric air even though the latter would have ca. 2 ppm CH_4. Thus we used a mathematical approach to correct for this contamination, which we believe to be reliable because the variables involved are well defined (i.e. atmospheric CH_4 concentration and ^{14}C content, recovered sample volume). Moreover, the contamination from the low CH_4 concentration of atmospheric air in a routine-sized radiocarbon sample (ca. 1 mL CH_4 or more) using this new approach should never exceed 1% of the total sample, and therefore is unlikely to significantly alter the ^{14}C result for routine-sized samples unless they are close to the radiocarbon detection limit (e.g. samples >1 mL changed < 0.1 pMC following air-correction in Table 2). For a detailed assessment of the effect of atmospheric CH_4 contamination of radiocarbon samples we direct the reader to Dean et al. (2017). An alternative sampling approach could be to equilibrate into high purity nitrogen gas using a 5 L foil gas bag attached to the inlet before the coils of Accurel tubing. However, we caution that even research grade gases (99.9995% purity) can contain up to 5 ppm impurities that are potentially carbon-containing and of undetermined ^{14}C content, and therefore this approach may not actually provide an advantage.

Future Development

Our future development will focus on the aforementioned issues, but we will also investigate whether the time-integrated sampling method that we have developed for ^{14}C analysis of CH_4 can also be used to ^{14}C date aquatic CO_2. While time-integrated passive samplers already exist for $^{14}CO_2$ (e.g. Garnett et al. 2012) our new approach provides greater control of the sample collection period, since this can be determined on the frequency of the pump events. In addition, we are currently testing a version of the method that enables collection of multiple samples, enabling automated collection of aquatic CH_4 samples over 1–2 days.

DATA ACCESS

All data supporting this study are provided in the "Results" section of this paper.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.31

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