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

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Methane (CH_4) is a powerful greenhouse gas and is released to the atmosphere from freshwater systems in numerous biomes globally. Radiocarbon (^{14}C) analysis of methane can provide unique information about its age, source and rate of cycling in natural environments. Methane is often released from aquatic sediments in bubbles (ebullition), but dissolved methane is also present in lakes and streams at lower concentrations, and may not be of the same age or source. Obtaining sufficient non-ebullitive aquatic methane for ^{14}C analysis remains a major technical challenge. Previous studies have shown that freshwater methane, in both dissolved and ebullitive form, can be significantly older than other forms of aquatic carbon (C), and it is therefore important to characterise this part of the terrestrial C balance.

We present a novel method to capture sufficient amounts of dissolved methane from freshwater environments for ^{14}C analysis by circulating water across a hydrophobic, gas-permeable membrane and collecting the methane in a large collapsible vessel. 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 ($\sim$4 to 24 hours), at relatively low cost and from a variety of surface water types.

The initial results further support previous findings that dissolved methane can be significantly older than other forms of aquatic C, especially in organic-rich catchments, 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.