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Reassessing the stable isotope composition assigned to methane flux from natural wetlands in isotope-constrained budgets

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Stable isotope ratios in CH_4 preserve information about its origin and history, and are commonly used to constrain global CH_4 budgets. Wetlands are key contributors to the atmospheric burden of CH_4 and typically are assigned a stable carbon isotope composition of ~-60 permil in isotope-weighted stable isotope models despite the considerable range of $\delta^{13}C(CH_4)$ values (~ -100 to -40 permil) known to occur in these diverse ecosystems. Kinetic isotope effects (KIEs) associated with the metabolism of CH_4-producing microorganisms generate much of the natural variation but highly negative and positive $\delta^{13}C(CH_4)$ values generally result from secondary processes (e.g., diffusive transport or oxidation by soil methanotrophs). Despite these complexities, consistent patterns exist in the isotope composition of wetland CH_4 that can be linked conclusively to trophic status and consequently, natural succession or human perturbations that impact nutrient levels.

Another challenge for accurate representation of wetlands in carbon cycle models is parameterisation of sporadic CH_4 emission events. Abrupt release of large volumes of CH_4-rich bubbles in short periods of time can account for a significant proportion of the annual CH_4 flux from a wetland but such events are difficult to detect using conventional methods. New infrared spectroscopy techniques capable of high temporal resolution measurements of CH_4 concentration and stable isotope composition can readily quantify short-lived CH_4 pulses. Moreover, the isotope data can be used conclusively to determine shifts in the mode of CH_4 transport and provide the potential to link initiation of abrupt emission events to forcing by internal or external factors.