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Biogeochemical Processes Governing the Stable Carbon-Isotope Compositions of CH_4 and CO_2 in Freshwater Wetlands

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Differences in methanogenic pathways within the soils of freshwater wetlands result in two distinctive distributions of δ^{13}C-ΣCO_2 and δ^{13}C-CH_4 values across gradients of depth. The first distribution involves a systematic increase in α_C values with depth as a result of decreasing δ^{13}C-CH_4 and increasing δ^{13}C-ΣCO_2 values (type I). Such a distribution of α_C values corresponds with an early prevalence of aceticlastic methanogenesis followed by a progressive increase in the production of CH_4 via the CO_2-reduction pathway. Enhanced utilization of autotrophic acetate by methanogens will also cause an increase in α_C values. The type-II distribution occurs when both δ^{13}C-CH_4 and δ^{13}C-ΣCO_2 values decrease with depth, resulting in approximately constant α_C values. This condition results from a strong dependence of methanogens upon pore water ΣCO_2 as a carbon source via either the CO_2-reduction pathway or utilization of autotrophically formed acetate.

Freshwater wetlands possess both types of α_C-value distribution. Regression curves of δ^{13}C-CH_4 and δ^{13}C-ΣCO_2 values from four wetlands with the type-I distribution intersect at δ^{13}C-CH_4 = -40.7 ±6.1 permil (1σ) and δ^{13}C-ΣCO_2 = -23.9 ±4.8 per mil (1σ). These values are similar to δ^{13}C values for methyl and carboxyl moieties within acetate produced by anaerobic degradation of fresh C_3 plant matter. This similarity results from minimal expression of metabolic kinetic isotope effects associated with methanogenesis via acetate dissimilation because acetate abundance typically is low in freshwater wetlands during anaerobic decay. The slopes of linear regression curves determined from δ^{13}C-CH_4 and δ^{13}C-ΣCO_2 values for wetlands possessing a type-I distribution appear to vary as a function of the deposition and preservation of organic substrates. An abundance of labile substrates results in the steepening of α_C curves because aceticlastic methanogenesis is more prevalent and CH_4 and CO_2 formed are more ^{13}C-enriched. Diminished transfer of labile carbon to the methanogenic zone results in an increased prevalence of the CO_2-reduction pathway, yielding lower δ^{13}C-CH_4 and δ^{13}C-CO_2 values, and more shallowly sloping α_C curves. Very low rates of organic matter input or increased recalcitrance of detritus through enhanced aerobic exposure (e.g., through low water-table levels) leads to a predominance of methanogenesis via the CO_2-reduction pathway and the occurrence of the type-II distribution in freshwater wetlands.