

$^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ Measurements of Methane from Boreal Lakes

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In order to begin building a realistic budget of atmospheric sources and sinks of methane that includes the abundances of multiply-substituted isotopologues, we analyzed $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ in methane emitted from nine boreal lakes located in Alaska, Canada, and Siberia. Wetlands are one of the most important sources of atmospheric methane. Methane emissions from Arctic wetlands ($>67^\circ\text{N}$) appear to have increased by $30.6 \pm 0.9\%$ during 2003 to 2007¹. Annual emissions of methane from boreal lakes are predicted to increase by up to 54% by the end of this century². Our measurements show boreal lake methane $\Delta^{12}\text{CH}_2\text{D}_2$ and $\Delta^{13}\text{CH}_3\text{D}$ ranging from -41.6 to $+18.7\text{‰}$, and -1.2 to $+5.4\text{‰}$, respectively. Most of the samples (six of nine lakes) resemble methane from laboratory cultures of microbial methanogens, with isotopic signatures that depart markedly from the equilibrium composition of $\Delta^{12}\text{CH}_2\text{D}_2 \approx +20$ and $\Delta^{13}\text{CH}_3\text{D} \approx +6$ at plausible environmental temperatures. Using these data, and taking predicted emissions growth models from the literature², we modeled the likely impacts of boreal lakes on the future atmospheric CH_4 isotopologue budget (up to year 2100). Our model predicts that a gradual rise of 17 Tg/yr in boreal wetland methane emission by 2100 will result an increase of $\sim 16\text{‰}$ in atmospheric $\Delta^{12}\text{CH}_2\text{D}_2$ but less than 0.2‰ change in $\Delta^{13}\text{CH}_3\text{D}$. δD also increases $\sim 10\text{‰}$ in this model, reaching a pseudo-steady state in ~ 50 years. The sensitivity of $\Delta^{12}\text{CH}_2\text{D}_2$ suggests a potential use for tracking changes in the atmospheric methane budget.

1-Bloom et al., 2010, *Science*, 327:5963,322-325

2- Wik et al., 2016, *Nature Geo.*, 9,99-106