

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

MOJHGAN A. HAGHNEGAHDAR<sup>1\*</sup>, EDWIN A. SCHAUBLE<sup>1</sup>,  
ISSAKU KOHL<sup>1</sup>, JABRANE LABIDI<sup>1</sup>, KATEY WALTER  
ANTHONY<sup>2</sup>, EDWARD D. YOUNG<sup>1</sup>

<sup>1</sup>Earth, Planetary, and Space Sciences, UCLA, CA, USA

(\*Correspondence: mojhganhagh@ucla.edu)

<sup>2</sup>Water and Environmental Research Center, UAF, AK, USA

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 2007<sup>1</sup>. Annual emissions of methane from boreal lakes are predicted to increase by up to 54% by the end of this century<sup>2</sup>. 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 literature<sup>2</sup>, we modeled the likely impacts of boreal lakes on the future atmospheric  $\text{CH}_4$  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  $\Delta^{13}\text{CH}_3\text{D}$ .  $\delta\text{D}$  also increases  $\sim 10\text{‰}$  in this model, reaching a pseudo-steady state in  $\sim 50$  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