Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.23222

Clumped Isotopes of Methane: New Tools for Tracking Microbial Methane Production and Consumption in Tidal Wetlands

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With estimated emission about 25% of total emission from all sources together [Whalen, 2005], wetlands are the largest natural source of methane to the atmosphere [Saunois et al., 2016]. However, the role of wetlands in atmospheric methane is also associated with great uncertainty. Methane emissions from wetlands are determined by the balance between methanogenesis and methanotrophy. Constraining the role of each process can be difficult though.

In general, methanogens and methanotrophs significantly impact the global environment by playing an essential role in the global carbon cycle and the flux of methane emitted from wetlands. To better understand the balance of these two processes and their seasonal variation, we used methane isotopologues ($^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$, and $^{12}CH_2D_2$) in gas samples collected from a mesohaline tidal wetland; the Global Change Research Wetland (GCReW). This site is located on the western shore of the Chesapeake Bay, Maryland and dominated by the reed grass phragmites. Methane gas bubbles were collected weekly started from late April to late June and then from early September to late December (2023). Bubbles were collected from various zones along the tidal channel within the site using bubble traps. Overall, the observed oxidation signature of clumped isotopologues in all locations changed with temperature and other environmental factors known to impact microbial communities, such as root ventilation, during the growing season. For instance, methane samples collected from the narrow channel location at the interior of the marsh with high Phragmites abundance, show a higher oxidation signature in the warmer and greener season compared to the colder and drier time of the year.

In contrast, methane samples collected from the muddy, saline location along the main channel with no plant coverage indicate a shift from oxidation to production with increase in temperature during the warmer months.

This seasonal oxidation signature (particularly in $\Delta^{12}CH_2D_2$ values) can be observed and traced. Therefore, clumped isotopes of methane can provide a method for tracking microbial methane production and consumption and the seasonal variations in microbial activities. This could allow fingerprinting of microbial wetland contributions to atmospheric air.