

## The methane paradox in peat systems is linked to redox transitions

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Peatlands store a significant portion of terrestrial organic C (OC) that is anaerobically converted to CH<sub>4</sub> on a global scale. Natural wetting and drying cycles in peat, including periodic shifts in precipitation and water-table depth, cause dynamic redox oscillations. Recently, significant CH<sub>4</sub> emissions have been identified that originate from frequently oxygenated environments, leading to a methane paradox in which O<sub>2</sub> may be important for facilitating CH<sub>4</sub> production. Conceptually, methanogenesis in peat may be promoted by O<sub>2</sub> via formation of free radicals and changes in microbial activity, respectively, which could aid in the transformation of OC to methanogenic substrates. We hypothesized that oxygenation stimulates methanogenesis in peat exposed to a redox transition. To test this hypothesis, we incubated peat suspensions for 98 d under 0%, 5% and 10% headspace O<sub>2</sub>, after which anoxic conditions were maintained for an additional 134 d. Peat suspensions exposed to either O<sub>2</sub>-addition treatment displayed significantly higher headspace CH<sub>4</sub> on average (4526 ±770 ppm; p <0.001) following a redox transition compared to strictly anoxic controls (3.06 ±0.64 ppm) by the end of the incubation. Characterizations of OC in the peat will include ion cyclotron resonance (FT-ICR-MS) studies. X-ray absorption near edge structure (XANES) and Mössbauer spectroscopies are being used to identify heterogeneous Fenton-like Fe phases likely involved in OC oxidation. Microbial diversity and activity are being assessed with DNA and RNAseq analyses. We are integrating this data into a climate model. Our findings suggest that CH<sub>4</sub> emissions are strongly coupled to redox transitions in peat systems depending on both abiotic and biotic OC transformations involving O<sub>2</sub>. This work will provide a better understanding of the global C cycle based on redox oscillations in peatlands.