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Atmospheric Greenhouse Gas Emissions from Wetlands: Dark Fenton-Hydroxyl Radical Production in Prairie Pothole Wetlands

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Chemical reactions in aquatic-terrestrial landscapes may promote or inhibit the microbial production of greenhouse gases (GHG). This study focuses on the abiotic interactions between carbon and reactive elements like iron and sulfur found in Prairie Pothole wetlands. In dark Fenton and Fenton-like reactions, iron and sulfur donate electrons to dissolved oxygen in water to produce hydroxyl radicals in the absence of light. Hydroxyl radicals decompose organic matter that becomes available for microbial decomposition, leading to GHG emission. The objective of this research was to identify whether hydroxyl radicals were generated through dark Fenton reactions in Prairie Pothole samples. Sediment was collected from the USGS operated Cottonwood Lakes site located northeast of Jamestown, North Dakota. Two wetland ponds across a three-year time series (2021-2023) were analyzed to address spatial and temporal variations. Prairie Pothole wetlands have high concentrations of total iron (20,760 mg/kg) and sulfur (12,432 mg/kg), therefore, we hypothesized that iron sulfide minerals would be a source of hydroxyl radicals. X-ray absorption near edge structure spectroscopy (XANES) and X-ray fluorescence mapping was used for iron and sulfur chemical speciation. Samples were analyzed at the Canadian Light Source and National Synchrotron Light Source II. Sulfur analysis revealed that iron monosulfide (FeS) and iron disulfide (FeS2) were present in samples, as well as organic monosulfide and ester sulfates. Iron analysis showed much higher concentrations than sulfur, and thus, contrary to our hypothesis, iron was primarily found in iron silicate and phyllosilicate minerals. We hypothesize that iron XANES was unable to detect the smaller fraction of iron in iron sulfide minerals due to the abundance of phyllosilicates and silicates present. Hydroxyl radical production for natural samples was measured using a probe molecule that was measured via high performance liquid chromatography (HPLC). Preliminary results indicate that hydroxyl radicals are produced and suggest that there are spatial differences in production rates between ponds. The rate of hydroxyl radical production for pond A and B were measured to be 36.7 nM/min and 10.2 nM/min respectively for 2023 field samples.