Atmospheric Greenhouse Gas Emissions from Wetlands: Dark Fenton-Hydroxyl Radical Production in a Peatland Bog and Prairie Potholes

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MOTIVATION

Significance & aim

Peatlands are sequesters of organic carbon whereas prairie pothole wetlands emit large quantities of greenhouse gases. This project seeks to understand how biogeochemical processes at oxic-anoxic interfaces in different wetland types modulate greenhouse gas fluxes.

Objectives

Quantify dark-Fenton generated reactive oxygen species (ROS) at the oxic-anoxic interface of SPRUCE peat samples.

Identify organic carbon, sulfur, and iron species within sediments that contribute to net hydroxyl radical production

Compare hydroxyl radical production across two wetland types: peatland versus prairie potholes

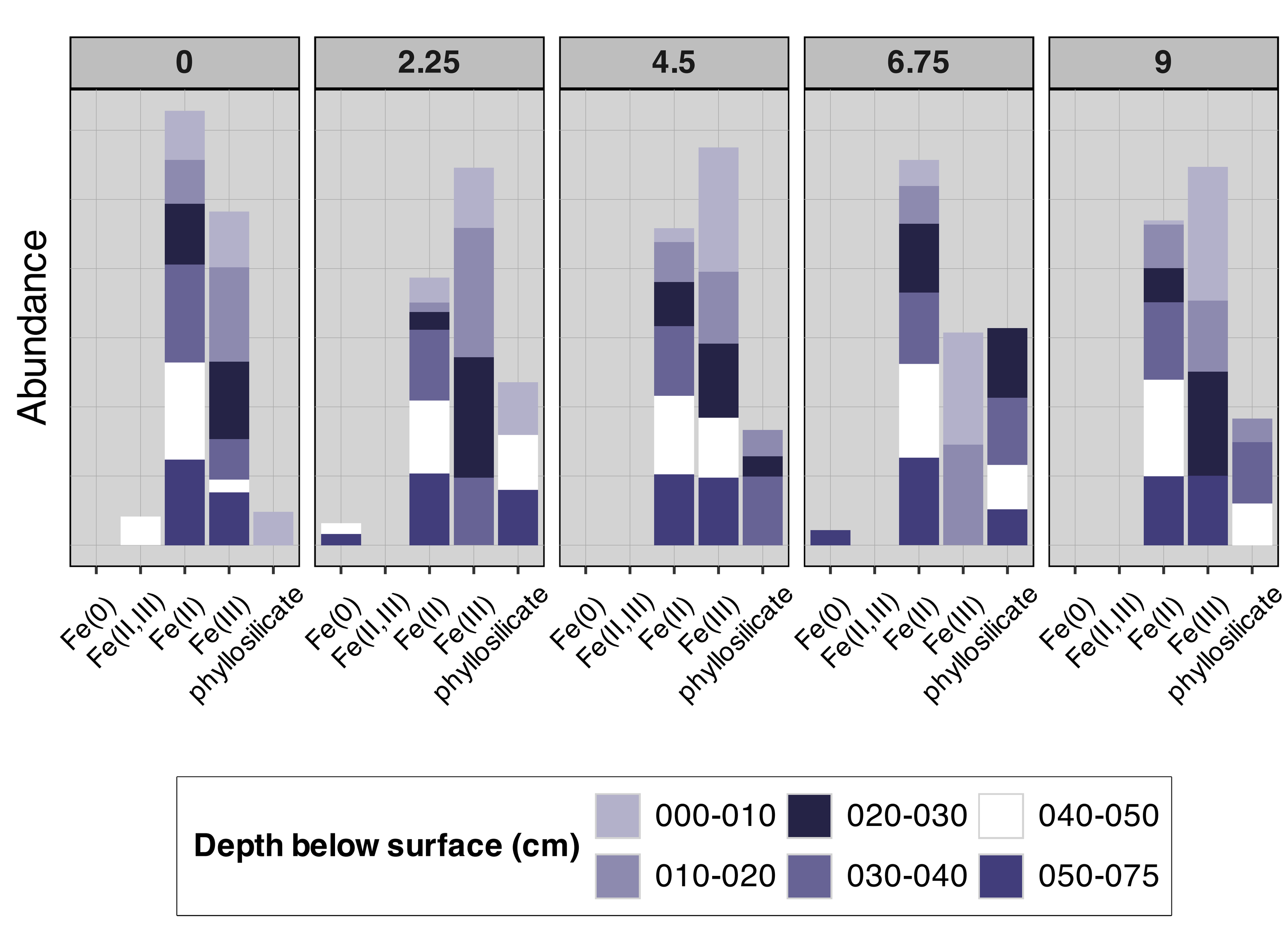
RESULTS: Sediment characterization

Bulk sediment composition

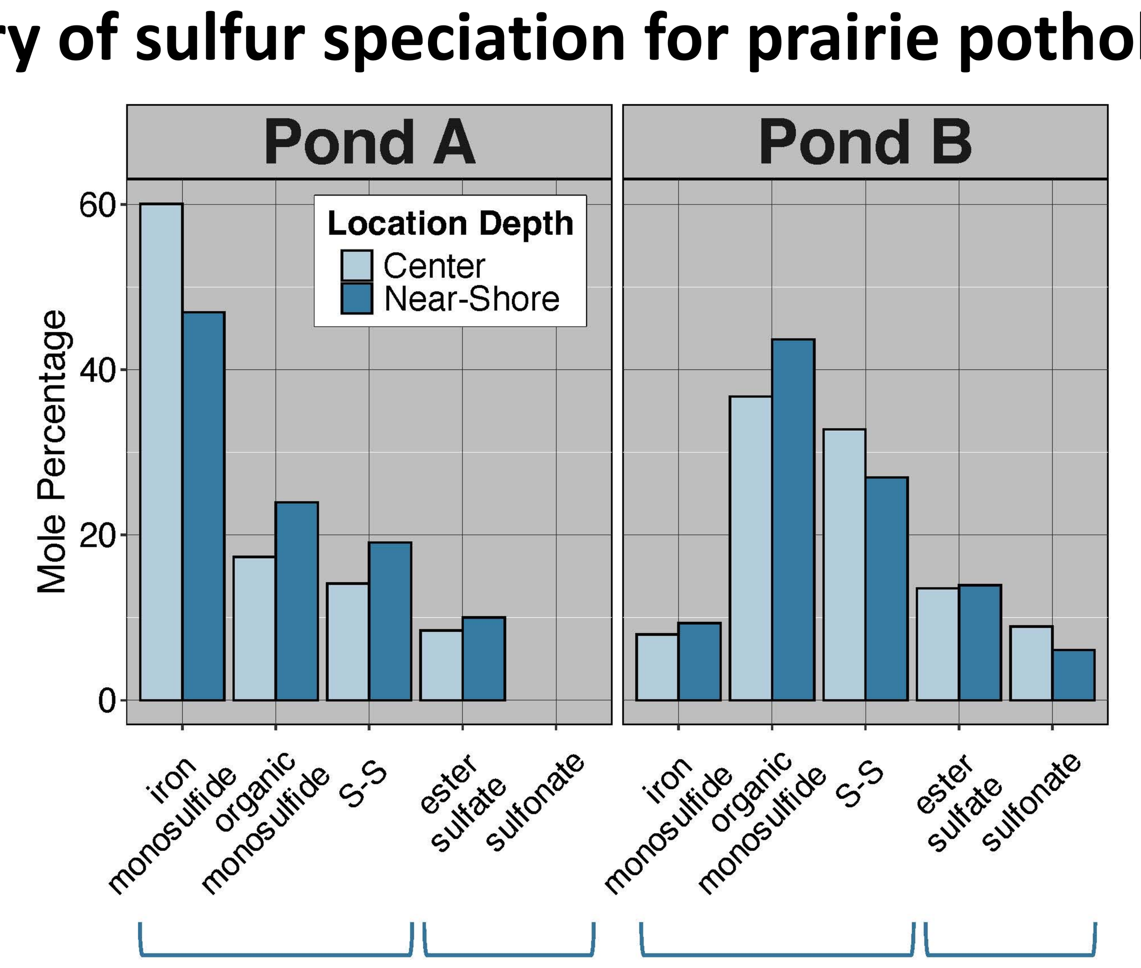
PPR measured at Research Analytical Laboratory, CFANS, UMN-TC

Sample ID	Total Iron mg/kg	Total Sulfur mg/kg	Total Carbon %	Total Organic Carbon %
PPR Pond A	30594	10420	7.80	5.849
PPR Pond B	20716	17213	16.53	5.901
SPRUCE[a]	293.6 – 21060	942.8 - 7768	10.6 – 55.3	-

Summary of iron speciation in SPRUCE samples



Summary of sulfur speciation for prairie potholes



APPROACH

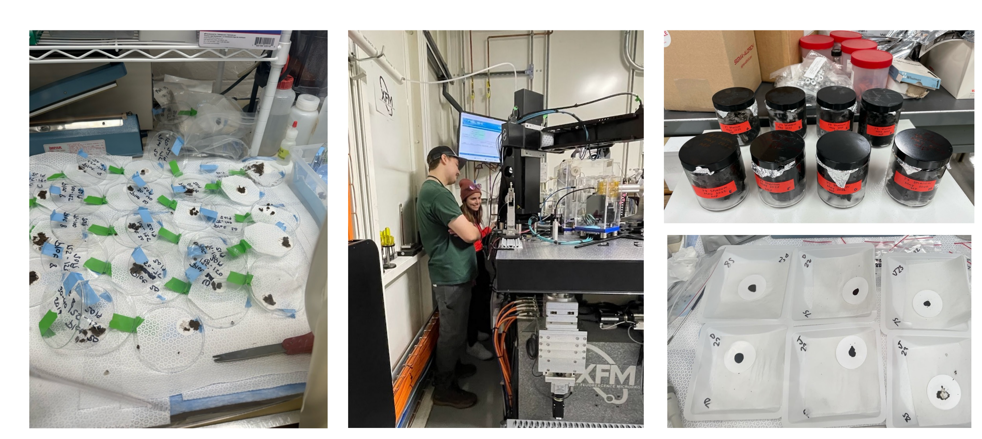
Field work

Peat samples were collected for two field seasons (2019 & 2021) at the USDA Forest Service operated Marcell Experimental Forest (MEF) in northern Minnesota, USA.

Prairie pothole samples were collected from two ponds in field seasons 2021-2023 at the United States Geological Survey (USGS) Cottonwood Lakes site near Jamestown, North Dakota, USA

Sediment sulfur & iron speciation

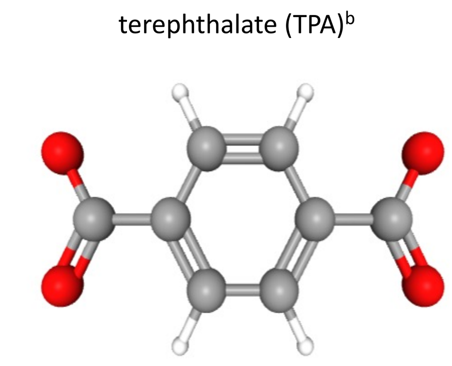
Synchrotron X-ray absorption near edge structure (XANES) spectroscopy was used to measure sulfur and iron speciation in sediments. Sulfur XANES was measured at the SXRMB beamline, Canadian Light Source (CLS), Canada. Iron XANES for SPRUCE samples was also measured at the SXRMB beamline. Iron XANES for prairie pothole samples was measured at the QAS beamline, National Synchrotron Light Source (NSLS II), Brookhaven National Laboratory, USA.



Hydroxyl radical production experiments

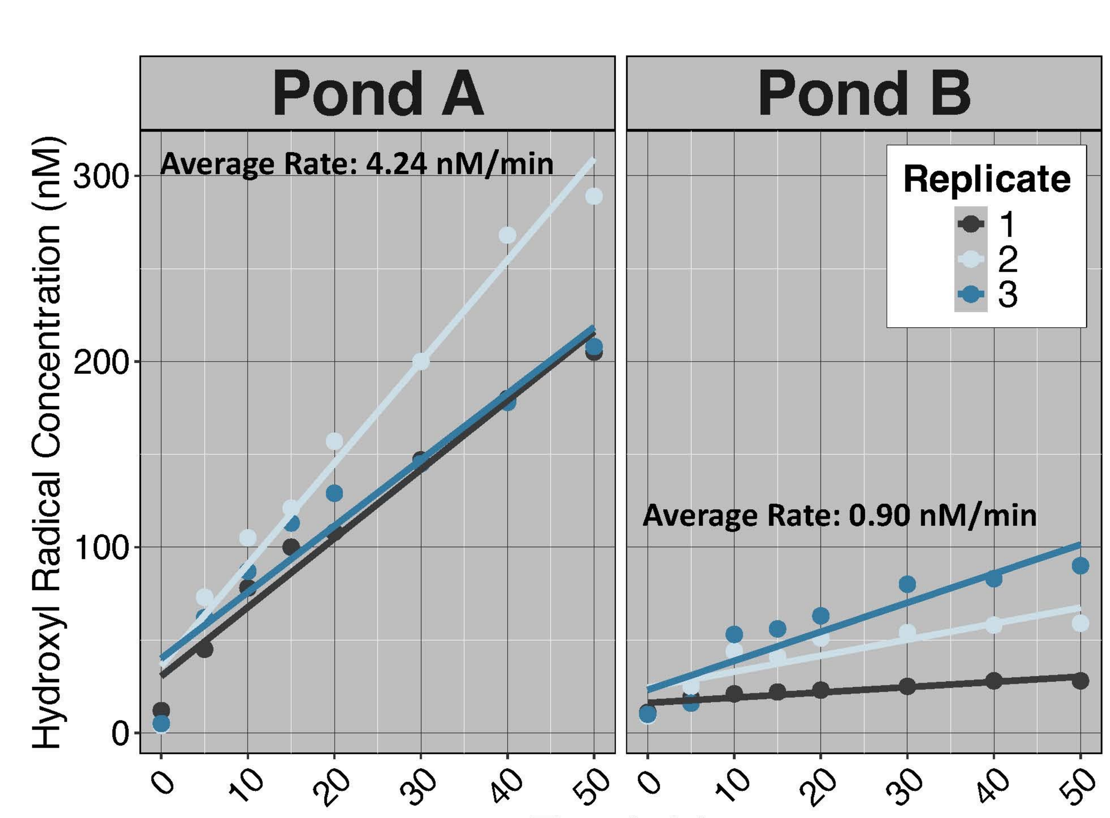
Sediment slurries were prepared in a Coy anaerobic chamber and spiked with a fluorogenic probe, terephthalate (TPA). Dissolved oxygen was introduced benchtop through stir bar mixing. As hydroxyl radical is produced (see reactions below) it is trapped in the form of hydroxy-TPA. Timed samples are quenched with methanol and the concentration of hydroxy-TPA is quantified using HPLC with fluorescence detection.

terephthalate (TPA)[b]



(1) $Fe(II)\ aq,s + O_2\ aq \rightarrow Fe(III)\ aq,s + HO_2\bullet / O_2^-\bullet\ aq$
(2) $Fe(II)\ aq,s + HO_2\bullet / O_2^- \rightarrow Fe(III)\ aq,s + H_2O_2\ aq$
(3) $Fe(II)\ aq,s + H_2O_2\ aq \rightarrow Fe(III) + HO\bullet\ aq + OH^-\ aq$

RESULTS: Hydroxyl radical production



SUMMARY: Rates of hydroxyl radical production are higher in Pond A. In comparison to Pond B, Pond A has higher total iron and iron monosulfide content (mackinawite, FeS), but lower sulfur and organic carbon content. Higher total iron and FeS mineral content likely fuels dark-Fenton reactions while the lower organic carbon results in less quenching of ROS by the sediment compared to Pond B. Experiments for PPR sediments were used for method development.

NEXT STEPS: Measure ROS production in 2019 and 2021 SPRUCE field samples.

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