Fluorescence Spectroscopy Suggests that Extracellular Electron Shuttling is a Dominant Metabolic Pathway in Temperate Peatlands

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The Peatland Paradox:

Peatlands:
- Cover ~10% of the Earth’s surface
- Harbor ~30% of terrestrial carbon
- Are net sinks of atmospheric CO2
- With carbon residence times of thousands of years
- Provide critical organic matter inputs that feed streams and lakes

Yet…

Metabolic pathways leading to peatland C stabilization or mineralization are not well understood; it is impossible to predict the fate of these carbon stores in the face of climate change

Hypotheses:

H1: Oxidized and reduced quinone-like DOM exhibits control over oxidation-reduction potential in peat porewater
H2: Low water table and aerenchymous plants drive DOM redox

Methods

Sampled porewater from 40 cm in bog mesocosms blocked by water table (high and low) and vegetation (Carex spp, Ericoid shrub, unmanipulated). Measured phenolic content and oxidation-reduction potential.

Results

- Low water table and Carex treatments showed higher Eh and more humified DOM
  Water table p = 0.03
  Water table x Vegetation p = 0.04
- Humic/fulvic content correlated with Eh and phenolics suggesting a reduced pool of DOM
- Tannin-like content correlated negatively with phenolics, suggesting quinone-like DOM

Discussion and Conclusions

The mechanism for extracellular reduction here may be attributable to a single reduction of tannin-like material, followed by a condensation reaction involving radical products, ultimately producing humics and fulvics.

- Subset of samples from 70 cm showed similar trend (HP explained abberently high Eh)
- 13C NMR will inform whether condensation is occurring
- FT-ICR-MS will inform whether DOM pools are different between treatments—possible vegetation feedback to DOM redox activity.
- Anaerobic incubation will track CO2 production during DOM reduction.
- Investigation of metal-DOM interactions will identify metal-binding fluorophores and ascertain abiotic carbon destabilization pathways (Fenton-like chemistry)

Figure 1: Oxidation-reduction potential ranges of common electron acceptors.

Figure 2: Redox of phenolic-quinone pairs is a feasible pathway for heterotrophic metabolism in anoxic or hypoxic environments but has not yet been evaluated in the context of community-level biogeochemical processes.

Figure 3: Treatments simulate outcomes of climate change: lowered water table and shift in dominant vascular vegetation. Dashed line represents sample depth.

Humification Index2 = Intensity (Humic+Fulvic) / Intensity (Tannin+Protein)