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# Molecular characterization of porewater indicates hydrology is a major driver of dissolved organic matter composition in Prairie Pothole wetlands.

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Wetlands are global hotspots of carbon cycling, disproportionately storing a larger percentage of global soil organic matter than the percentage of global land mass they account for. Within wetlands, dissolved organic matter (DOM) acts as the major mediator of carbon, serving as both the substrate that fuels microbial respiration, as well as a precursor for the formation of stable mineral associated organic matter phases (i.e., potential $CO_2$/$CH_4$ sources or carbon sinks). However, hydrological variability within a single wetland may result in different dynamics and roles in carbon storage and gas emissions. To evaluate the major drivers of DOM variability across a wetland, we compared DOM concentrations and molecular composition across spatial, depth, and seasonal scales in a pristine wetland located in the Prairie Pothole region of North Dakota, USA. Molecular characterization was performed using reverse phase liquid chromatography coupled to ultrahigh resolution orbitrap mass spectrometry. We found that permanently inundated sediment porewaters were consistently euxinic and contained significantly more DOM than the suboxic porewaters in the transiently inundated transition zone. Molecular analysis revealed that the DOM accumulating in the permanently inundated porewaters was significantly enriched in aromatic, high molecular weight species that had a higher nominal oxidation state of carbon. The depletion of these species in the transition zone sediments suggests increased microbial consumption of aromatic, oxidized, and heavy DOM in the suboxic zone, and/or the partitioning of these species into the mineral associated organic matter phase uniquely in the suboxic zone. Aromatic, oxidized, and high molecular weight DOM adsorbs preferentially to iron oxide minerals through ligand exchange, suggesting that adsorption to iron minerals may play a central role in governing the accumulation and composition of DOM in transiently inundated wetlands. Furthermore, depletion of higher energy terminal electron acceptors in the euxinic zone suggests that selective microbial anaerobic respiration may additionally be a key driver of wetland DOM composition and concentration. Our results provide insight into the mechanism by which DOM affects long-term carbon storage and contributes to defining the role of wetlands in larger-scale models.