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Diel cycling of copper and zinc in the water column above a photosynthetic microbial mat

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The presence of a photosynthetic microbial mat (biomat) creates an environment for dynamic redox reactions and elemental cycling in the shallow (< 30 cm) overlying water column in unit process open water wetlands. The Prado Engineered Wetlands (Corona, CA), for example, exhibited diel cycles of pH from ~7.5 –9 (night/day) and dissolved oxygen (DO) concentrations from ~2-20 mg/L (night/day). Diel cycles of dissolved Zn, Cu, Fe, and Mn concentrations were also observed, all of which had a trend of increasing during the night and decreasing during the day except Cu. This inverse diel cycling of Cu is rarely observed in any other natural or lab-scale systems having neutral to basic pH ranges. To better understand these phenomena, we constructed lab-scale flow-through illuminated systems (81 by 8 by 6.5 cm each, with ~4cm deep biomat harvested from Prado) and observed diel cycles of dissolved Cu concentrations -decreasing during the night near the outlet and increasing during the day - mimicked Prado. Geochemical models from PHREEQC indicated that this diel cycle of Cu might be impacted by the inlet concentrations of Cu (natural low background Cu waters versus mining-impacted waters) and Cu sorption to Fe/Mn minerals in the biomat, which could also be further influenced by the diel cycles of Fe and Mn. Unlike Cu, the diel changes of dissolved Zn concentrations were negatively correlated with the diel changes of pH (R^2>0.6). The combination of controlled lab-scale systems with geochemical model predictions can help inform the relationships among the diel cycles of pH/DO, Fe/Mn, and metals such as Zn and Cu in the field. This can then be applied to assess the treatment capacity and system behavior of large-scale, open-water wetlands for mining and other impacted waters.