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Seasonal Terrestrial and Oceanic Dissolved Organic Matter Controls on Copper (Cu) Speciation and Bioavailability Under High Anthropogenic Pressure

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Cu is a trace metal playing a dual role in oceans. At low concentrations (nM – pM), it serves as a micronutrient for phytoplankton, while toxic at elevated levels. A major portion (> 90%) of dissolved Cu (Cu_{TD}) in seawater is found to be present in organically complexed form, which is non-bioavailable for phytoplankton. However, anthropogenic Cu inputs could elevate the [Cu_{TD}] that potentially exceeds the Cu buffering capacity of Dissolved Organic Matter (DOM), increasing the bioavailable (Cu^{2+}_{f}) Cu pool. This could eventually lead to toxicity in phytoplankton. The Singapore Strait is one of the busiest shipping hubs on the planet, with potentially high Cu inputs through shipping and other industrial activities. Also, it experiences seasonal shifts in DOM inputs, where in the Southwest Monsoon (SWM), large terrestrial DOM inputs dominate, and in the Northeast Monsoon, it is mostly oceanic. Hence, the Singapore Strait provides an ideal site to study how these two sources of DOM aid in buffering Cu bioavailability under high anthropogenic pressure. We investigated this by conducting three-year time series sampling at a monthly resolution. We measured [Cu_{TD}], Cu binding organic ligand (L) concentrations, modelled their binding strengths (log $K_{Cond\ Cu}^{2+}$), and [Cu^{2+}_{f}]. $\delta^{13}C_{DOC}$ and DOM spectral properties (CDOM $S_{275-295}$, $SUVA_{254}$ & $SUVA_{350}$) were used for tracing DOM sources. Results to date show that [Cu_{TD}] varies seasonally (5-9 nM) with strong correlations with salinity and DOC. [Cu_{TD}] was relatively high during SWM and NEM. A similar trend was observed for [L]. Strong correlations of [L] with DOM spectral properties and $\delta^{13}C_{DOC}$ provide evidence of L being terrestrially originated. Increasing [L] with freshwater inputs (SWM and NEM) effectively buffers the extra Cu inputs, while keeping the [Cu^{2+}_{f}] relatively stable through the seasons, which was evident by the lack of significant correlations between [Cu^{2+}_{f}] with salinity, and [DOC]. Average pCu^{2+}_{f} was 13.02 ± 0.23, ≤ 1% of [Cu_{TD}]. Average log $K_{Cond\ Cu}^{2+}$ was 13.49 ± 0.3. We will present time series speciation data to test the hypothesis that tDOM inputs from tropical peatlands contain strong Cu-binding ligands, thereby controlling the bioavailability of Cu across the region.