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Dissolved organic matter influences Fe-binding ligand availability for cyanobacteria in oligotrophic Ontario lakes

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Natural iron (Fe) binding ligands, such as dissolved organic matter (DOM) and microbial-produced siderophores, are ubiquitously found in terrestrial and aquatic environments. Siderophores are a group of Fe-binding ligands primarily secreted by bacteria and fungi during Fe-limited conditions as a Fe-scavenging strategy. DOM can have high Fe-binding capacity if it is relatively refractory (i.e. high humic acid concentration with high affinity for metal ions).

Cyanobacteria have been shown to utilize Fe bound to hydroxamate and catecholate siderophores when cells are Fe-limited. We assessed if the concentrations of DOM or the presence of siderophores, that increase when concentrations of ferric are low, in the water were correlated with the proportion of cyanobacteria in 25 oligotrophic lakes in Canada. We hypothesized that the highest siderophore concentration will be in lakes with modeled free ferric concentrations < 1x10-19 M; a level where cyanobacteria have shown to be competitive for Fe in laboratory experiments.

Proportion of cyanobacteria was measured with flow cytometry and DOM quality was assessed using excitation-emission matrices (EEMs) and PARAFAC modeling. Siderophore concentrations were measured using two traditional chemical analyses (Czaky and Arnow tests).

Cyanobacteria appeared to be regulated by the availability of ferric concentrations but the relationship was non-linear. The oligotrophic lakes had ferric concentrations that ranged from 1x10-25 M to 1x10-14 M. The highest % cyanobacteria occurred between ferric concentrations 1x10-23 M to 1x10-19 M. Hydroxamate siderophore concentrations showed the same pattern as % cyanobacteria across the modeled ferric gradient. In contrast, catecholate siderophore concentrations showed no relationship with % cyanobacteria or the modeled ferric gradient.

A positive relationship was found between DOM quantity and catecholate siderophore concentration (R^2 = 0.65, p<0.001). It was also found that as the protein (labile) content of DOM increased, catecholate siderophore concentration decreased (R^2 = 0.74, p<0.001). In contrast, as the humic (refractory) content of DOM increased, catecholate siderophore concentration increased (R^2 = 0.72, p<0.001). No relationship was found between DOM and hydroxamate siderophore concentration.

Cyanobacteria appear to produce catecholate siderophores (with relatively stronger Fe-binding capacity) when refractory DOM is high in concentration making Fe-scavenging from DOM complexes more challenging. In contrast, cyanobacteria appear to produce hydroxamate siderophores (with relatively weaker Fe-binding capacity) to scavenge Fe from labile DOM complexes. We believe this study presents the first report of hydroxamate and catecholate siderophores and changes in factors that result in greater siderophore concentrations may account for the increased incidence cyanobacteria bloom reports in Ontario, Canada.