Biological factors regulating the chemical speciation of Cu, Zn, and Mn under different nutrient regimes in a marine mesocosm experiment

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ABSTRACT: Previous mesocosm experiments and field studies have indicated a central role of major nutrients (e.g., N, P, and Si) in regulating phytoplankton abundance and species composition and influencing the rate of uptake of bioactive metals by phytoplankton. We monitored the changes in bioactive metals (Cu, Zn, and Mn) concentration and speciation that occurred over the course of a bloom of the coccolithophore *Emiliana huxleyi* under three different nutrient treatments. In each treatment, the electrochemically labile fraction of Cu decreased from 1.1 to 0.3 nmol L^{-1} during the formation of the *E. huxleyi* bloom. This decrease was likely due to the active release of organic ligands by phytoplankton, which shut off as soon as the level of labile Cu reached 0.3 nmol L^{-1} ($[Cu^{2+}]$ = 0.02 nmol L^{-1}). Organic Zn-binding ligands showed elevated concentrations in bag 1 (the N- and P-replete bag) only. The release of these ligands coincided with a 15-fold increase in the concentration of dead *E. huxleyi* cells in bag 1 but only a threefold increase in the P- or N-depleted bags. This suggests that the Zn-binding ligands may have originated from dead or decaying *E. huxleyi* cells. In both the P- and N-limited bags, labile Mn concentrations showed a succession of two peaks and troughs over the 2-week period; these were synchronized but inversely correlated with bacterial abundance. Labile Mn showed weaker fluctuations and no clear synchronization with bacterial abundance in the N- and P-replete bag. We hypothesize that the passive release of organic Zn-binding ligands under the nutrient-replete conditions may have helped restrict the detrimental effect of Zn^{2+} on Mn uptake by phytoplankton cells, thus diverting part of the dissolved Mn away from sequestration or oxidation by bacteria.