



## Effects of copper, cadmium, and zinc on the production and exudation of thiols by *Emiliana huxleyi*

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Limnol. Oceanogr., 50(2), 2005, 508-515 | DOI: 10.4319/lo.2005.50.2.0508

**ABSTRACT:** Cultures of the ubiquitous coccolithophore *Emiliana huxleyi* grown at field-relevant fixed free ion concentrations of Cu, Cd, and Zn exude a broad array of thiols, some of which increase with increasing metal ion concentration. The primary thiols released are contingent on the particular metal or combination of metals added to the culture media. Exposure to Cu results in the release of arginine-cysteine, glutamine-cysteine, and cysteine; Cd causes these thiols and glutathione to be released; and high Zn results in the synthesis and exudation of predominantly  $\gamma$ -glutamate-cysteine ( $\gamma$ -Glu-Cys). Because the free ion concentrations of Cu and Cd used in these experiments are similar to those observed in the field, active exudation could be an important source of thiols to surface seawater and thus might affect trace metal speciation in the open ocean. Intracellular thiol concentrations were also clearly affected by metal concentrations, with  $\gamma$ -Glu-Cys being particularly dynamic. Additionally, the shift from exponential to stationary growth in batch cultures caused approximately two- to fourfold declines in the concentrations of nearly all intracellular thiols.

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