



Iron and zinc enrichments in the northeastern subarctic Pacific: Ligand production and zinc availability in response to phytoplankton growth

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ABSTRACT: Iron- and zinc-enrichment experiments were carried out at Ocean Station Papa in the subarctic North Pacific. In iron-enriched treatments, phytoplankton chlorophyll *a* (Chl *a*) increased 20-fold ($9.7 \mu\text{g L}^{-1}$) above the concentration on day zero. No stimulation of Chl *a* production or nitrate drawdown was observed on addition of zinc alone compared to the control. In the iron-enriched treatment, bioavailable zinc concentration decreased to 0.2 pmol L^{-1} lower than that which is known in culture experiments to limit some phytoplankton growth. Theoretical analyses suggest that this zinc concentration would cause diffusion-limited growth of large diatom cells present at the end of the incubation. Direct measurements of zinc-binding ligands indicate that the natural microbial planktonic assemblages have the ability to respond rapidly to conditions of high dissolved zinc concentrations. Rapid ligand production may be a mechanism by which certain phytoplankton reduce zinc toxicity or for maintaining zinc concentrations in the upper water column. Zinc-binding ligands were observed to be both produced and removed on the timescale of 1 d. We suggest that these zinc-binding ligands are produced to assist assimilation, particularly under iron-enriched conditions when concentrations of bioavailable zinc were extremely low, thereby alleviating the effects of zinc limitation.

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