

# **Dynamics of Metal-Limited Phosphorus Cycling in the North Pacific Ocean**

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Phosphorus (P) is an essential nutrient required by all forms of life. In the ocean, dissolved organic phosphorus (DOP) supports the health and productivity of marine microbes across different ecosystems. To assimilate DOP, marine microorganisms express an array of hydrolytic enzymes which often require metal cofactors and may be subject to environmental trace metal availability, as seen in the limitation of DOP hydrolysis by iron or zinc in the North Atlantic. However, the regulation of DOP utilization by different trace metals across the global ocean and the linkages between microbial P physiology and trace metal cycling remain poorly understood. Here, we report the first study of metal-dependent DOP turnover in the North Pacific. Comprehensive shipboard incubations were conducted during a research cruise in the California Current ecosystem (CCE) spanning from inshore upwelling zones to the edge of the North Pacific oligotrophic gyre (NPG). Natural mixed microbial communities from these biomes were amended with potential metal cofactors for DOP hydrolases (iron, zinc, cobalt, manganese), in combination with different P sources and nitrogen. DOP hydrolysis rates reflected the high ecosystem variability in the CCE by exhibiting a mosaic of trace metal and nitrogen effects on enzymatic activity. In the offshore zone bordering the NPG, metal-stimulation of DOP remineralization indicates that microbial P acquisition is potentially limited by trace metals. We complement these field studies with the molecular characterization of two hitherto unknown inorganic pyrophosphatases detected in the exoproteomes of diatoms able to grow on polyphosphate, a form of DOP for which no metabolizing exoenzymes are currently described. Recombinant expression and screening for activity toward different DOP substrates confirmed that these metalloenzymes are capable of polyphosphate degradation. In addition, the presence of alternative metal cofactors (manganese, cobalt) to the native cofactor (magnesium) expanded the substrate scope and accelerated the reaction rates toward different classes of DOP. These new findings point to a more widespread dependence of P cycling on trace metals than previously recognized and advance our understanding of compound-specific DOP transformations, which is especially important given the trajectory of increasing P limitation across large areas of the modern global ocean.