Persistence of iron(II) in surface waters of the western subarctic Pacific

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ABSTRACT: The distribution of dissolved iron(II) [Fe(II)] was studied in surface waters of the western subarctic Pacific during the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study-II (SEEDS II) iron enrichment experiment using highly sensitive flow injection-based luminol chemiluminescence. Vertical profiles of Fe(II) and total dissolved iron were measured outside of the fertilized patch to investigate the chemical speciation of iron in this high-nitrate low-chlorophyll (HNLC) region. Ambient total dissolved iron concentrations ranged from 50 pmol L^{-1} to 150 pmol L^{-1} depending on depth and sampling times. Unexpectedly, Fe(II) accounted for up to half of total dissolved iron, with concentrations up to ~50 pmol L^{-1}. Fe(II) concentrations decreased exponentially with depth and were undetectable at depths below 50 m. There was no evidence of increased Fe(II) concentrations associated with the subsurface chlorophyll maximum, indicating that photolysis, rather than biological reduction of Fe(III), was the primary source of Fe (II). Because Fe(II) concentrations in the fertilized patch remained elevated for more than a week after enrichment, Fe(II) oxidation rates at near-ambient concentrations were measured. Indeed, the temperature-dependent Fe(II) oxidation rates were significantly slower than predicted by Fe (II) oxidation models and rates measured in ligand-free seawater. These findings suggest that Fe(II) binding ligands may exist in these HNLC waters, with conditional stability constants on the order of 10^{8}- 10^{9} with respect to Fe^{2+}. The accumulation of Fe(II) during daylight hours did not alleviate iron limitation of eukaryotic phytoplankton in these waters, contrary to expectations from recent iron uptake models.