

## Photo-microbial reduction and extracellular dark oxidation of mercury in marine surface waters

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Redox transformations of mercury in marine surface waters affect the exchange of mercury between the ocean and atmosphere<sup>1</sup> and the accumulation and isotopic fractionation of mercury in marine food webs.<sup>2,3</sup> Previous studies in marine systems showed simultaneous photochemically-driven reduction of Hg(II) and oxidation of Hg(0)<sup>4</sup> but the role of planktonic organisms in these processes is unclear. The roles of microbes and light in the net redox balance of inorganic mercury was examined in shipboard incubation experiments within a coastal marine system of the western North Atlantic and in laboratory experiments with cultured phytoplankton. In unfiltered estuarine and coastal marine surface waters exposed to ambient visible plus UV light, the net redox balance was toward the reduction of Hg(II). In continental shelf surface waters, far from the influence of coastal runoff, however, the reduction and oxidation of inorganic Hg were approximately balanced. Upon removal of planktonic microbes and other particles (>0.2  $\mu\text{m}$ ) or light from unfiltered water, net reduction of Hg(II) decreased or the redox balance shifted to net oxidation of Hg(0). Removal of UVB radiation from unfiltered water had a much smaller effect than removal of all light indicated that photoreduction was at least partially driven by UVA or visible light. The oxidation of Hg(0) occurred in the dark and was largely independent of the presence of planktonic microbes or other suspended particles. Together with laboratory experiments showing the reduction of intracellular Hg(II) in cultured phytoplankton, these results indicate that the net reduction of Hg(II) in coastal marine surface waters depends on the presence of both planktonic microbes or other suspended particles as well as light. The intracellular environment of planktonic microbes living in the photic zone, which has high intracellular concentrations of Hg(II) and reactive oxygen species, may therefore be an important site of mercury reduction in the marine environment.

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