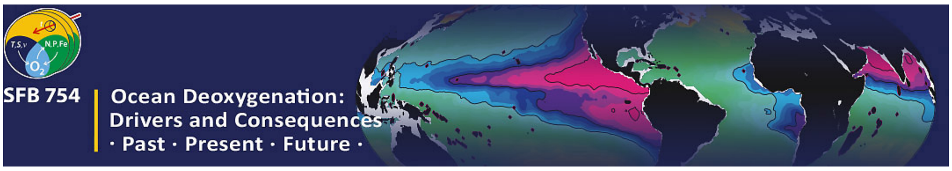

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How the oxygen concentration can impact the redox processes of trace elements and reactive oxygen species

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Iron (Fe), Manganese (Mn) and Copper (Cu) are three redox active trace metals required for a range of critical biological processes in marine organisms. Iron is known as the essential in photosystem I, for its dust input and it being the limiting element in about 30% of the surface of the Ocean. Manganese is the active metal centre in several redox enzymes, most notably in photosystem II where it converts water (H2O) to oxygen (O2), and in the Mn family of Superoxide dismutases (SODs), which are used as an intracellular defence against reactive oxygen species (ROS). Copper is widely known to be toxic to most species of phytoplankton, in part because it competitively inhibits Mn uptake and once inside the cells is implicated in the production of ROS. However, recent studies have suggested that Cu, in the form of multi-copper oxidases, is essential for the uptake of Fe by phytoplankton. .
All three micronutrients have a redox pair (Cu(II)/Cu(I), Fe(II)/Fe(III) and Mn(II)/Mn(III)) that can react with reactive oxygen species like superoxide (O2-) and its daughter hydrogen peroxide (H2O2). The distribution and speciation of Fe, Cu and Mn, contrast markedly in the surface ocean due to organic complexation vs free ions and their solubilities contrast starkly. However, these metals are strongly linked through the competition for metal binding sites in phytoplankton uptake systems and through common redox processes involving ROS. The partitioning of these redox sensitive trace elements are controlled by the dissolved oxygen concentration and therefore under low O2 conditions (< 10 µM) the more soluble lower oxidation states are stabilized leading to longer residence times for these elements in the water column with implications for the distribution of these elements in these waters. Potential feedbacks may also occur whereby enhanced Fe concentrations, fuel surface water productivity resulting in higher fluxes of sinking organic matter which when respired further decreases O2 in the OMZ.
In this presentation we will examine a series of datasets collected during 3 cruises in the oligotrophic Eastern Tropical North Atlantic (M80/1, M83/1 and MSM17/4) and 2 cruises in the Eastern South Pacific (M77/4 and M90). Here we use the collected data to identify the respective contributions of Mn and Cu to ROS cycling in the upper ocean and oxygen minimum zone and the implications this has to the residence time for Fe, Cu and Mn in these regions.

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