Superoxide dynamics in irradiated seawater

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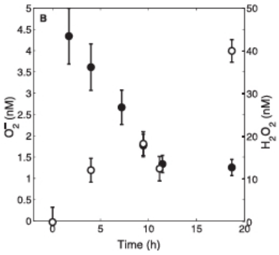
The cycling of reactive oxygen species (ROS) in the ocean can play a pivital role in controlling the chemical form and reactivity of redox sensitive elements critical for biological function. Photochemistry dominates production of ROS in the photic zone with superoxide (O_2^-) identified as a ubiguitous product produced in the photooxidation of colored dissolved organic material (CDOM) in the photic zone. Only a few photochemical production rates of O_2^- in seawater have been reported, these being calculated by measuring steady state values with assumed matching production and decay in irradiated samples, and consequently quantifying decay rates when the light is turned off. If this assumption of identical seawater decay rates in the dark and light is not true, then O_2^- photoproduction, and the extent of control on redox sensitive trace elements (ex. FeII/III) may have been significantly underestimated.



Our previous work [1] shows that as irradiation of 0.2um filtered oligotrophic seawater proceeds, the O_2^- steady state declines (right), even though measured dark decay rates remained stable. While a possible loss of O_2^- source is likely, stoichiometric relationships with hydrogen peroxide production along with new open ocean measurements of increased antioxidant activity found only in the photic zone during daylight [2] suggest the possibility of transient photochemical sinks for O_2^- maintained by photochemistry. Here we present data from the evaluation of O_2^- dynamics in photochemcial experiments by taking advantage of chemiluminescent methods to quantify both O_2^- and antioxidant activity during light/dark cycling of coastal and open ocean seawater. Re-evaluation of O_2^- photoproduction estimates in seawater provide new details for surface ocean redox chemistry and consequent biogeochemical cycles.

[1] Powers et al. (2015) Mar. Chem. 177:306 [2] King et al. (2016) Front. Mar. Sci. **3**:217.