# Dark Production Of Reactive Oxygen Species (ROS) At Groundwater Mixing Fronts In Coastal Waters

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Submarine groundwater discharge (SGD) is a major source of dissolved iron to coastal waters with inputs primarily as reduced Fe(II) [1]. Model studies have shown that discharge of Fe(II) and/or solid phase Fe sulphides into oxygenated seawater can initiate dark production of Reactive Oxygen Species (ROS) [2, 3]. Fe(II) concentrations > 5 μM can initiate ROS production, yet subsequent Fe cycling can maintain ROS production at much lower Fe(II) levels [2].

Time series experiments were conducted in a salt marsh creek system near Charleston SC to validate model results. Short-lived Ra isotopes were used as tracers of groundwater contributions to the system as a function of tidal forcing. A redox front characterized by an increase in Fe(II) to levels near 100 μM and a decrease in dissolved $O_2$ developed prior to the dark period low tide. A sharp increase in the inventory of ROS (as $H_2O_2$) was measured coincident with the Fe(II) rich redox front. ROS production remained high for several hours following the Fe(II) maximum. The activity of $^{224}$Ra was highly correlated to Fe(II) ($R^2 > 0.90$) and $H_2O_2$ concentrations ($R^2 > 0.85$). Results confirm a geochemical mechanism for ROS production coupled to SGD. Evidence suggests that SGD supports sustained hydroxyl radical production by the Fenton mechanism (i.e. co-ocurrence of Fe(II) and $H_2O_2$). SGD initiated hydroxyl radical production may promote NOM transformation in estuarine systems.

[1] Windom *et al* (2006) *Mar. Chem* **102**, 252-266. [2] Burns *et al* (2010) *ES&T* **44**, 7226–7231. [3] Murphy *et al* (2014) *ES&T* in press.