A geochemical mechanism for Reactive Oxygen Species (ROS) activity in estuarine waters

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Here, we present the results of a kinetic study exploring a geochemical mechanism for H_2O_2 production mediated by the redox cycling of iron rather than photochemical input. The tidally-driven mixing of Fe(II) with dissolved oxygen at the groundwater-seawater interface creates a highly reactive zone conducive to the rapid cycling of iron and consequent ROS generation. To investigate the simultaneous production and consumption of H_2O_2 as a function of iron cycling, our experimental design consisted of spiking ambient creek water with either H_2O_2 or a deoxygenated Fe(II) solution and monitoring the production/decay. The measured rates were interpreted according to photochemical input, iron speciation, and groundwater composition; allowing for comparison of photochemical production against geochemical mechanisms of ROS production. Method optimization required the application of a two-instrument approach, whereby a continuous-flow instrument measuring time-resolved kinetics was externally-calibrated by a single-injection instrument using the method of standard additions. The heightened ROS production/consumption rates observed approximately six hours after sunset were in stark contrast to the low (almost negligible) rates characteristic of photochemical production, suggesting a significant geochemical contribution. Moreover, a simultaneous occurrence of micromolar levels of both Fe(II) and H_2O_2 was observed for approximately 2.5 hours (0200-0430 EST). Taken together, our results suggest that under these conditions, ROS activity is initiated by iron input with a negligible photochemical contribution, as well as provide preliminary evidence for the periodic occurrence of sustained Fenton chemistry in natural waters.