

Dark Production of Hydrogen Peroxide in Groundwater at Rifle, Colorado

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The dominant source of H₂O₂ in natural waters has long been thought to be photo-dependent processes, yet recent studies have indicated that dark production of H₂O₂ in deep seawater, principally biological production, is potentially on par with photochemical generation. Here, we present evidence for the unrecognized and light-independent generation of H₂O₂ in groundwater in an alluvial aquifer adjacent to the Colorado River near Rifle, CO. In situ H₂O₂ concentrations were determined using a sensitive chemiluminescence-based method. Our results suggest H₂O₂ concentrations ranged from lower than the detection limit (< 1 nM) to 54 nM along the depth profile of several groundwater wells across the Rifle site, which were comparable to the concentrations presented in sunlit waters. Such detected H₂O₂ patterns in Rifle groundwater suggest the existence of a balance between H₂O₂ sources and sinks, which potentially involves a cascade of biogeochemically significant processes, including the generation of highly reactive species (such as hydroxyl radical), the interconversions between ferrous and ferric species, significant biological production and decomposition, and further transformation of natural organic matter and other chemical pollutants. More importantly, our results also suggest that reactive oxygen species (ROS) production is not only widespread in oceanic and atmospheric systems, but also in the subsurface domain, the large but probably the least-understood component of the biogeochemical cycles. Occurrence of ROS in the subsurface system could potentially have high impact on metal/nutrition cycling on groundwater-dependent ecosystems, such as wetlands and springs.

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