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The iron “redox battery” in coastal sandy sediments and its effect on the cycling and turnover of phosphorus and organic matter

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Coastal sandy sediments cover 50-60% of the continental shelves and are important filters and bioreactors that regulate terrestrial input of nutrients into the ocean. In permeable sandy sediments, the dynamic advective flow of porewater can lead to frequent redox oscillation, which significantly affects the turnover of organic matter (OM) and nutrients in the sands. In this study, we used natural North Sea sands and seawater filled in closed flow-through reactors (FTRs) to investigate the biogeochemical processes in sands under progressively reducing conditions. During the recirculating, closed-system incubation, we found the rapid depletion of O_2 and NO_3^-, and the successive release of dissolved inorganic carbon, NH_4^+, P, Mn, Ba, Fe, Si, and As into the circulating porewater. Fe(III) oxyhydroxides were quantitatively found as the dominant electron acceptors for anaerobic OM remineralization. However, the release of reduced Fe was significantly delayed, with most Fe(II) (~96%) remaining in the solid phase either through adsorption or formation of authigenic Fe(II)-bearing minerals. Under frequent redox oscillation as typically observed in natural coastal sands, Fe(II) in the solid phase can be re-oxidized and repetitively used as electron acceptor for anaerobic OM remineralization (“redox battery”). We also found the net release of Fe(III)-associated P started before the build-up of Fe(II) in the porewater. This early released P could have a better chance to escape from the sediments with dynamic advection of porewater, as P re-immobilization during Fe(II) re-oxidation in the redox interface could not occur yet. After increased Fe(II) release was detected, P release was also accelerated with a constant elemental P/Fe(II) ratio of 0.26 in the porewater. Further Fe(III) reduction by sulfide prevented Fe(II) release with the formation of blackish FeS_x coprecipitate, while P liberation continued. Our study suggests that Fe(III) oxyhydroxides in sands can serve as a “redox battery”. Its importance for anaerobic OM remineralization and P turnover can be intensified under frequent oscillation of redox conditions as observed in sandy deposits. The role of Fe in the molecular fractionation and preservation of dissolved OM in coastal sandy sediments will also be discussed.