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Abstract:

Physical and chemical drivers of iron, phosphorus and sulfur cycling in a eutrophied shallow estuary

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The Peel-Harvey Estuary in Western Australia is a strongly restricted, shallow marine water body (average depth ~ 2 m) that has been strongly impacted by human-induced, high riverine phosphate inputs. The high productivity in and restricted nature of the eutrophied estuary has led to the localized formation of organic-rich, sulfidic sediments. We investigated the interplay between physical properties and the biogeochemical cycling of iron, phosphorus and sulfur at various sites in the estuary with a combination of grain size and pore-water analyses and chemical fractionation methods of core samples up to ~ 1 m sediment depth. There is a large variability in grain size distribution from site to site and within cores, ranging from coarse sand to clay-rich silt. There is a strong physical control over the geochemical conditions in the sediment; iron sulfides are only formed in the more fine-grained sediments. However, even thin buried layers of such fine-grained sediments strongly affect overall pore-water chemistry, resulting in high concentrations of dissolved sulfide and nutrients in sediments that contain predominantly coarse-grained sediments. This has important implications for water quality and biology in the estuary, as the sediments may act as an important source of toxic sulfide and essential nutrients to the overlying water. Our results further show that almost all reactive iron in the sediments is present in iron sulfide minerals, despite the overlying shallow, wind-mixed water column. This indicates that the fractionation of iron is controlled by the physical and chemical properties of the sediment rather than redox conditions in the water column, as is often assumed in paleoenvironmental reconstructions. In addition, the iron and sulfur fractionation results suggest that pyrite (FeS₂) formation occurs at least in part as direct precipitation from the pore-waters instead of via a precursor iron monosulfide (FeS) phase. Phosphorus burial is limited, occurring mainly in organic and iron-bound form with very little formation of authigenic calcium phosphate minerals, irrespective of sediment grain size. The presence of iron-bound phosphorus in the sulfidic sediments is surprising, and may indicate the formation of reduced iron phosphate minerals or the persistence of iron oxides with adsorbed phosphate. Such mechanisms are commonly neglected in sulfidic sediments but could be important for an accurate understanding of redox-dependent phosphorus burial. Overall, our results signify the strong dependence of sediment geochemistry on the physical properties (i.e. grain size) of the sediment. Furthermore, internal (re)cycling of sulfur and phosphorus likely plays an important role in the water quality and nutrient status of this restricted estuary.