Geophysical Research Abstracts
Vol. 14, EGU2012-4490, 2012
EGU General Assembly 2012

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 restricted, shallow water body (average depth $\sim$ 2 m) that has been heavily impacted by human-induced, high riverine phosphate inputs. The high productivity in and restricted nature of the eutrophied estuary has led to the localised formation of organic-rich, sulfidic sediments. We investigated the interplay between physical sediment properties and the biogeochemical cycling of iron, phosphorus and sulfur at various sites (up to $\sim$ 1 m sediment depth) using a combination of grain size analyses, pore-water measurements and chemical fractionation methods. There was a large variability in grain size distribution between sites and within cores, ranging from coarse sand to mud. The occurrence of iron sulfide minerals was restricted to the more fine-grained sediments. Even thin buried layers of such fine-grained sediments were found to control pore-water chemistry throughout complete sediment cores, leading to high dissolved sulfide and nutrient concentrations in sediments that were predominantly coarse-grained. As such, the fine-grained sediments can be an important source of toxic sulfide and essential nutrients to the overlying water, which affects the water quality in the estuary. Our results further show that almost all reactive iron in the sediments was present in iron sulfide minerals, while the overlying water column is predominantly oxic. 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. This is important in light of the use of iron fractionation in palaeoenvironmental reconstructions. Furthermore, the iron and sulfur fractionation results suggest that pyrite (FeS2) formation in the fine-grained sediments occurs at least in part as direct precipitation from the pore-waters instead of via a precursor iron monosulfide (FeS) phase. Phosphorus concentrations in the sediment were low, occurring mainly in organic and iron-bound forms with little formation of authigenic calcium phosphate minerals, irrespective of sediment grain size. The presence of iron-bound phosphorus may reflect the formation of reduced iron phosphate minerals and/or the persistence of iron oxides with adsorbed phosphate, both of which are not commonly considered important in euxinic sediments. 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.