

**An acid sulfate soil precursor. Iron, phosphorus and sulfur dynamics in sediments from the Peel-Harvey Estuary, WA.**

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**Abstract**

The Peel-Harvey Estuary in south-western Australia is faced with a dire combination of man-made challenges. Agricultural activity in the adjacent area has for decades caused the influx of large quantities of nutrients (most notably phosphorus) into the estuary, fuelling algal blooms and the formation of organic-rich, sulfidic sediments. The abundance of sulfide in this restricted system has had detrimental effects on both the water quality and marine biology. Free sulfide in the water column is highly toxic to marine life and the disturbance and oxidation of sulfidic sediments can cause severe deoxygenation in the water column. At the same time, sulfide-rich sediments on the edges of the estuary are being drained for urban development, causing problems associated with sulfide oxidation and soil acidification. As such, the sulfidic sediments that form in the estuary today are tomorrow's acid sulfate soils.

Besides management challenges, the reducing sediments in the estuary also provide opportunities to study geochemical processes under extreme conditions. These investigations may not only help to combat the environmental threats to the Peel-Harvey estuary, but also to better understand the links between geochemical signatures in ancient sediments and the palaeo-environmental conditions during deposition. The present as key to understanding the past, however ugly both may be.

In this study, we investigate in detail the dynamics of iron (Fe), phosphorus (P) and sulfur (S) in sediments from different sites in the Peel-Harvey Estuary. At several sites, there is an abundance of iron monosulfide minerals (FeS) up to ~ 40 cm sediment depth. These minerals are commonly highly reactive and rapidly transform into more stable pyrite (FeS<sub>2</sub>). Grain-size distribution seems to play an important role in sedimentary FeS preservation: the oxygen required for partial oxidation of FeS and subsequent formation of FeS<sub>2</sub> diffuses relatively slowly into fine-grained sediments, extending the lifetime of labile FeS. The fine-grained, FeS-rich sediments are easily disturbed and oxidised, which may negatively affect water oxygenation and ecosystem health. The abundant pore-water sulfide effectively scavenges dissolved Fe to form FeS, resulting in low pore-water Fe concentrations and a very high fraction of total Fe in reduced reactive minerals. The sulfide-rich pore-waters also record very high concentrations of nutrient N and P. The sequestration of P through calcium phosphate

mineral formation in these reducing sediments is strongly limited. The sediments thus act as a source of nutrients back to the water column, adding to any fluvial input. As such, the rapid internal recycling of nutrients in the estuary may drive the system into a eutrophied state which is more or less independent of external inputs. The coupled Fe, P and S biogeochemical cycles can create an environment which is optimal for the continued formation of organic-rich, sulfidic sediments that may be the precursors of acid sulfate soils in this heavily anthropogenically altered ecosystem.